Investigation of Kinetic Isotopic Fractionation of Water during Bare Soil Evaporation

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Key Points:

- Kinetic fractionation during soil evaporation was determined during three experiments differing in soil water and aerodynamic conditions
- Soil and atmospheric water stable isotopic compositions were monitored non-destructively
- Daily values of the kinetic fractionation factor were obtained by inversing a well-known isotopic linear resistance model

ABSTRACT

The kinetic fractionation factor (α_{K}) controls to a large extent the isotopic enrichment of surface waters during evaporation (*E*). In contrast to the well-known vapor-to-liquid isotopic equilibrium fractionation factor, α_{K} has still not yet been properly characterized for soil water evaporation. In this study, we investigated the α_{K} daily dynamics during a series of three laboratory experiments differing in soil water availability and aerodynamic conditions. For this, we applied a commonly-used isotopic evaporation model and tested it in two different approaches. First, a two-end member mixing model ("Keeling plot") was fitted to the measured isotopic composition of the laboratory air water vapor to obtain α_{K}. In a second approach, α_{K} was obtained from the slope of the "evaporation line" in a dual isotopic coordinate system. For both methods, the isotopic composition of the soil water was determined non-destructively and online by sampling the soil water vapor with gas-permeable microporous tubing. Results highlighted the limitation of the first approach, as the determination of the isotopic composition of *E* with the Keeling plot was challenging with the laboratory setup. The second approach provided α_{K} values within the range ($\alpha_{\mathrm{K}}^{^{2}\mathrm{H}}$ = 1.0132 ±0.0013; $\alpha_{\mathrm{K}}^{^{18}\mathrm{O}}$ = 1.0149 ±0.0012) reported in the literature and pointed to the prevalence of turbulent water vapor transport under water-saturated soil conditions, but also at soil water content significantly lower than the saturated value. In a third experiment, temporal dynamics of the atmospheric water vapor intrusion in the topmost soil layer could be observed during an isotopic labeling pulse.

1 Introduction

Kinetic isotopic effects during evaporation (*E*) greatly impact the stable isotopic composition (δ) of environmental water pools (e.g., soil, plant, surface waters, groundwater, and atmospheric water vapor) and fluxes (e.g., evaporation and plant transpiration) (Horita et al. 2008, Sprenger et al. 2016, Xiao et al. 2017). A better understanding of the implications of these effects, in addition to the well characterized equilibrium effects (Majoube 1971, Lin and Horita 2016), is required for using the isotopologues $^{1}H^{2}H^{16}O$ and $^{1}H_2{}^{18}O$ as tracers of processes in the water cycle.

The kinetic fractionation factor (α_K) introduced in the Craig and Gordon (1965) model is theoretically defined as the ratio of the transport resistances from the evaporating water surface to the ambient air of $^{1}H^{2}H^{16}O$ or $^{1}H_2{}^{18}O$ to that of the most abundant isotopologue $^{1}H_2{}^{16}O$. The same authors first experimentally determined α_K to be inversely proportional to the ratio of the molecular diffusivities of $^{1}H_2{}^{16}O$ and of either $^{1}H^{2}H^{16}O$ or $^{1}H_2{}^{18}O$. Dongmann et al. (1974) proposed the following expression, assuming that (i) turbulent transport was a non-fractionating process and (ii) molecular diffusion resistances were inversely proportional to the *nth* power of the corresponding diffusivities (*D*):

$$\alpha_K = \left(\frac{D_w}{D_i}\right)^n \qquad (1)$$

where w stands for $^{1}H_2{}^{16}O$ and i for either $^{1}H^{2}H^{16}O$ or $^{1}H_2{}^{18}O$. The dimensionless exponent *n* accounts for the aerodynamic regime above the liquid–vapor interface (i.e., where the relative humidity is 100%). While the diffusivity ratio is considered constant in Eq. (1), *n* ranges from 0.5 (fully turbulent) to 1 (fully diffusive), with a value of 2/3 corresponding to laminar flow conditions (Dongmann et al. 1974). From two independent methods (i.e., evaporation of water under laminar flow conditions and water vapor transport through a diffusion tube), Merlivat (1978) determined the ratio of diffusivities D_w/D_i to be equal to 1.0251 and 1.0285 for $^{1}H^{2}H^{16}O$ and $^{1}H_2{}^{18}O$. These results disagree with those obtained from the kinetic theory of gases (i.e., 1.0168 and 1.0323) and were then explained to be due to different collision diameters of $^{1}H_2{}^{16}O$, $^{1}H^{2}H^{16}O$, and $^{1}H_2{}^{18}O$. It was only much later that Cappa et al. (2003) reconciled these observed differences with the kinetic theory by invoking water surface cooling during evaporation, as measured by Fang and Ward (1999), that plays a crucial role in fractionation of evaporating water. More recently, Luz et al. (2009) conducted evaporation experiments in air, argon, and helium, over 10 to 70 degrees temperature range, and found results similar to those of Merlivat (1978). Their experiments confirmed that these discrepancies could not be due to different collision diameters of the three isotopologues.

Even though the values to be used for D_w/D_i seem to have reached a certain consensus in the isotopic community (currently, the most widely used are those of Merlivat (1978), see review of Horita et al. (2008)), the value for *n* can only be either an educated guess by the user (depending on the aerodynamic conditions prevailing between the evaporation front and the free atmosphere) or deduced quantitatively from atmospheric measurements (e.g., wind velocity) and the application of an evaporation model (e.g., Merlivat and Jouzel 1979).

Rothfuss et al. (2012) suggested that n should vary in time for an evaporating soil even if atmospheric conditions remained the same: the non-saturated air layer developing at the soil surface enhances purely diffusive transport of water vapor and its isotopologues towards the free atmosphere, leading to a progressive increase of n.

Unfortunately, direct laboratory or in situ measurements of kinetic fractionation factors during soil evaporation by applying the Craig and Gordon (1965) model (Braud et al. 2009a, Braud et al. 2009b, Rothfuss et al. 2012, Dubbert et al. 2013), suffer from the following two issues:

(i) The isotopic composition of the net evaporation flux (δ_E, expressed in ‰ on the VSMOW scale, Gonfiantini (1978) has to be disentangled from the isotopic composition of the background atmosphere (δ_a). This is now facilitated by the emergence of laser absorption spectrometry applied to chamber measurements (Dubbert et al. 2013, Dubbert et al. 2014, Dubbert et al. 2017) or the 'Keeling plot' approach (Keeling 1958, Iannone et al. 2010, Good et al. 2014). Under controlled conditions in the laboratory (Braud et al. 2009b, Rothfuss et al. 2010, Rothfuss et al. 2012), δ_E can then directly be measured, while environmental conditions simulated in such climatic chambers may not be encountered in nature;

(ii) The time-consuming and labor-intensive methods frequently used for the determination of soil liquid water isotopic composition $\left(\delta_\mathrm{s}^\mathrm{l}\right)$, i.e., destructive sampling and vacuum distillation or direct equilibration methods (Araguás-Araguás et al. 1995, Garvelmann et al. 2012, Orlowski et al. 2013) do not allow frequent measurements of soil water isotopic composition. However, Rothfuss et al. (2013), Volkmann and Weiler (2014) and Gaj et al. (2016) recently developed non-destructive methods for monitoring $\delta_\mathrm{s}^\mathrm{l}$ online with high precision and accuracy via measurements of the soil water vapor isotopic composition ($\delta_\mathrm{s}^\mathrm{v}$) considering thermodynamic equilibrium at the sampling depth. The method of Rothfuss et al. (2013) was further applied in the laboratory (Gangi et al. 2015, Rothfuss et al. 2015).

Rothfuss et al. (2015) also showed that α_K could be determined using a simplified formula for the slope of the "evaporation line" (i.e., the linear regression of δ^{18}O versus δ^{2}H of the soil liquid water in a dual isotope space) derived from the Craig and Gordon (1965) model and first proposed by Gat (1971). This method (referred to as "G71") has the advantage over the Craig and Gordon (1965) model (referred to as "CG65") that it only relies on measurements of δ_a, $\delta_\mathrm{s}^\mathrm{l}$ and not on measurements of δ_E.

In this study, we determined α_K by applying both CG65 and G71 formulas in an inverse mode during a soil evaporation experiment conducted in the laboratory. The abovementioned limitations of the isotopic methodology were overcome with (i) a Keeling plot technique for the determination of δ_E and (ii) by using the method of Rothfuss et al. (2013) for the non-destructive determination of $\delta_{\mathrm{s}}^{\mathrm{v}}$.

2 Material and Methods

2.1.Soil measurements

The evaporation experiment was carried out using the setup of Gangi et al. (2015) which consists of a 0.127 m^3 PVC tube (0.48 m in diameter, 0.70 m height) sealed at the bottom (Figure 1a) and coated with insulating sheets (Armaflex$^{\mathrm{TM}}$, 0.05 m wall thickness, Armacell International S.A., Luxembourg). Three connecting ports were available at six different depths (i.e., –0.01, –0.03, –0.07, –0.15, –0.30, and –0.57 m): one inlet for the carrier gas, i.e., synthetic dry air (20.5 % O_2 in N_2 with approx. 20–30 ppmv water vapor, Air Liquide, Germany), one sample air outlet, and one duct for a combined soil volumetric water content (θ) and temperature (T_{s}) probe (SMT-100, truebner GmbH, Neustadt, Germany; precision for soil water content and temperature was 3% and 0.2°C, respectively). Each gas inlet and outlet was connected to a 0.3 m long piece of microporous polypropylene tubing (Accurel® PP V8/2HF, Membrana GmbH, Germany). The tubing is water-tight, yet gas-permeable (pore size of 0.2 µm) and allows the sampling of soil water vapor and the measurement of $\delta_{\mathrm{s}}^{\mathrm{l}}$ in a non-destructive manner with high precision and accuracy as detailed in Rothfuss et al. (2013).

The soil column was filled with a silt loam soil (20.1 % sand, 65 % silt, 14.9 % clay) sieved to 2 mm grain size and dried at 110°C for 24 hours. The soil column was saturated with water of known isotopic composition from the bottom through a perforated acrylic glass plate covered with a water-permeable nylon membrane (ecoTech Umwelt-Messsysteme GmbH, Bonn, Germany) by applying slight overpressure from an external tank.

Two soil water isotopic standards were prepared using the same setup as Rothfuss et al. (2013), consisting of a 2.57 l volume airtight acrylic glass cylinder. These two vessels were filled and packed with the same silt loam soil and saturated with one of the two standard waters of isotopic composition $\delta_{\mathrm{st1}}^{\mathrm{l}}$ (δ^2H = –1.5 ‰, δ^{18}O = 7.2 ‰) and $\delta_{\mathrm{st2}}^{\mathrm{l}}$ (δ^2H = –103.2 ‰, δ^{18}O = –21.3 ‰), respectively. The saturated soil water volumetric content (θ_{sat}) value was determined from the ratio of the volume of water needed for saturation and the volume of the soil water isotopic standards and was equal to 0.45 m^3 m^{-3}. The residual water content value was θ_{res} = 0.00 m^3 m^{-3} (Lutz Weihermüller, personal communication)

2.2. Atmospheric measurements

A second PVC tube of the same dimensions and open at both ends was installed gastight on top of the tube with the soil monolith. Atmospheric water vapor could be sampled at six different heights above the soil surface (0.01, 0.03, 0.07, 0.15, 0.30, and 0.57 m) inside the air column. In addition, the surrounding atmospheric water vapor was sampled at 1.00 m above the soil surface, i.e., outside of the column's volume. Air relative humidity (h, %) and temperature (T_a, °C) were monitored at the same height with a RFT-2 sensor (Meter Group, Munich, Germany; precision of relative humidity and temperature measurements was 2 % and 0.1°C, respectively).

2.3. Sampling protocol

$\delta_\mathrm{s}^\mathrm{l}$ was determined from $\delta_\mathrm{s}^\mathrm{v}$ measurements three times a day at each depth of the soil column according to the method developed and described by Rothfuss et al. (2013). 85 ml min^{-1} of dry synthetic air was directed through the permeable tubing for 30 min. The sampled soil water vapor was diluted with dry synthetic air (Figure 1b) in order to (i) reach a water vapor mixing ratio ranging between 10,000 and 15,000 ppmv and (ii) to generate an excess flow upstream of the cavity ring-down laser spectrometer (L2120-*i*, Picarro, Inc., Santa Clara, CA, USA) to avoid any contamination of sample air with ambient air. A 30 min sampling duration was required to reach steady state values for both $\delta^2\mathrm{H}_\mathrm{S}^\mathrm{v}$ and $\delta^{18}\mathrm{O}_\mathrm{S}^\mathrm{v}$ for a period of at least 10 min. These last 10 min (corresponding to approx. 385 observations) were used to compute the $\delta_\mathrm{S}^\mathrm{v}$ mean value. Computed mean values with standard deviations >2 ‰ and >0.5 ‰ for $\delta^2\mathrm{H}_\mathrm{S}^\mathrm{v}$ and $\delta^{18}\mathrm{O}_\mathrm{S}^\mathrm{v}$, respectively, were not taken into account in the analysis as they pointed to, e.g., condensation in the tubing system. Water vapor mixing ratio dependencies of the laser spectrometer isotopic composition readings (Schmidt et al., 2010) were accounted for by computing the theoretical $\delta_\mathrm{S}^\mathrm{v}$ values at 10,000 ppmv. Finally, the corresponding $\delta_\mathrm{s}^\mathrm{l}$ values were calculated at the measured soil temperature (Rothfuss et al. 2013):

$$^{1}\mathrm{H}^{2}\mathrm{H}^{16}\mathrm{O}: \qquad \delta_\mathrm{s}^\mathrm{l} = 104.96 - 1.0342 \cdot T_\mathrm{s} + 1.0724 \cdot \delta_\mathrm{s}^\mathrm{v} \qquad (2a)$$

$$^{1}\mathrm{H}^{1}\mathrm{H}^{18}\mathrm{O}: \qquad \delta_\mathrm{s}^\mathrm{l} = 11.45 - 0.0795 \cdot T_\mathrm{s} + 1.0012 \cdot \delta_\mathrm{s}^\mathrm{v} \qquad (2b)$$

where T_S is the soil temperature in °C.

δ_a was measured three times a day at each available height above the soil surface. Air was sampled at a rate of 200 ml min^{-1} for 15 min. This flow rate was chosen to minimize (i) memory effects due to the volume of the tubing system between air intake and the laser spectrometer and (ii) disturbance inside the air column. The threshold flow rate value below which sampling from one of the three lowest atmospheric layers (i.e., centered at

0.01, 0.03, and 0.07 m above the soil surface) did not impact the other (or the other two) was estimated at 241 ml $\min^{-1}$. This threshold value corresponded to the volume of a cylindrical air layer with 0.02 m height (3619 ml) divided by the sampling duration (15 min). The last three minutes (corresponding to approx. 115 observations) were used to compute the mean value of the isotopic composition of atmospheric water vapor (δ_a) which was, as for $\delta_\mathrm{s}^\mathrm{v}$, corrected for water vapor mixing ratio dependency. δ_a and $\delta_\mathrm{s}^\mathrm{l}$ values were finally corrected for a potential laser analyzer drift using the isotopic compositions $\delta_\mathrm{st1}^\mathrm{l}$ and $\delta_\mathrm{st2}^\mathrm{l}$ of the two water standards as anchor points.

Water vapor of the atmosphere column, of both soil standards, and from the different tubing sections in the soil column were sampled sequentially in the following order: standard1 – standard2 – soil (–0.60 m) – atmosphere (0.01 m) – soil (–0.03 m) – atmosphere (0.30 m) – soil (–0.15 m) – atmosphere (0.60 m) – soil (–0.30 m) – atmosphere (0.03 m) – soil (–0.07 m) – atmosphere (0.15 m) – soil (–0.01 m) – atmosphere (0.07 m) – atmosphere (1.00 m) – standard1 – standard2. This order was chosen to avoid consecutive sampling of neighbor atmospheric heights and soil depths. The 5.75 hour-long sampling sequence was completed by 2.25 hours of sampling the atmosphere at 1.00 m and the whole was repeated three times per day (i.e., to add up to a 24 hour-long daily sampling period).

2.4. Determination of δ_E and δ_EF for the computation of α_K from the Craig and Gordon model

Using the classical approach of Rideal-Langmuir (Sverdrup 1952), Craig and Gordon (1965) modeled the evaporation of $^1H^2H^{16}O$ and $^1H_2{}^{18}O$ from a free surface water body through a series of consecutive layers as the ratio of isotopic composition differences and transport resistances. When we apply this model to soil pore water we derive the following expression for the isotopic kinetic fractionation factor α_K:

$$\alpha_\mathrm{K} = \frac{\frac{(\delta_\mathrm{EF}+1)}{\alpha_\mathrm{eq}} - h'(\delta_\mathrm{a}+1)}{(1-h')(\delta_E+1)} \qquad (3)$$

where δ_EF is the isotopic composition of the soil liquid water at the evaporation front (e.g., the surface under fully saturated conditions) and δ_a is the vapor isotopic composition of the laboratory air measured at 1 m height above the soil column. α_eq is the isotopic equilibrium fractionation factor between soil liquid and vapor at the soil temperature T_S (Majoube 1971) and h' is the relative humidity of the air normalized to the saturated vapor pressure (P_sat [Pa]) (Soderberg et al. 2012) at the temperature of the evaporation front T_EF:

$$h' = h\frac{P_\mathrm{sat}(T_\mathrm{a})}{P_\mathrm{sat}(T_\mathrm{EF})} \qquad (4)$$

where h [%] is the relative humidity in the laboratory.

δ_E was determined with a Keeling plot approach (Keeling 1958) considering the moisture inside the air column (of volumetric concentration C_{col} [kg m^{-3}] and isotopic composition δ_{col}) as a mixture of evaporated soil moisture (of concentration C_E [kg m^{-3}] and isotopic composition δ_{E}) and laboratory air moisture (of concentration C_{a} [kg m^{-3}] and isotopic composition δ_{a}, measured at 1 m height above the soil surface):

$$\delta_{\text{col}} = \frac{1}{C_{\text{col}}}\left[C_{\text{a}}(\delta_{\text{a}} - \delta_E)\right] + \delta_E \tag{5a}$$

The laser spectrometer measures water vapor mixing ratios (MR, -, usually expressed in ppmv) rather than concentrations. Assuming that $C_{\text{a}}/C_{\text{col}} \cong MR_{\text{a}}/MR_{\text{col}}$, where MR_{a} and MR_{col} are the water vapor mixing ratios measured in the ambient laboratory air (a) and in the atmospheric column (col), Eq. (5a) becomes:

$$\delta_{\text{col}} \cong \frac{1}{MR_{\text{col}}}\left[MR_{\text{a}}(\delta_{\text{a}} - \delta_E)\right] + \delta_E \tag{5b}$$

δ_E was determined from the y-intercept of the linear regression between δ_{col} and $1/MR_{\text{col}}$. Only significant linear relationships with a p-value lower than 0.05 were used (an exemplary Keeling plot is shown in Fig. B1 of Appendix B).

Another approach to calculate α_{K} used the slope of the so-called "evaporation line" (S_E) proposed by Gat (1971):

$$S_E = \frac{\left[h\left(\delta_a - \delta^l_{s_{init}}\right) + \varepsilon_{eq} + \Delta\varepsilon\right]_{^2H}}{\left[h\left(\delta_a - \delta^l_{s_{init}}\right) + \varepsilon_{eq} + \Delta\varepsilon\right]_{^{18}O}} \tag{6}$$

where $\delta^{\text{l}}_{\text{s}_{\text{init}}}$ is the initial soil liquid water isotopic composition (e.g., before water vapor is removed from the soil via evaporation). ε_{eq} is the equilibrium enrichment, i.e., the deviation of α_{eq} from unity. $\Delta\varepsilon$ is the kinetic isotopic effect which is associated with the $^1H^2H^{16}O$ and $^1H_2{}^{18}O$ vapor transport. Under the assumptions that (i) the turbulent transport is a non-fractionating process and that (ii) the ratio of the molecular resistance to the total resistance equals one, $\Delta\varepsilon$ is defined as (Gat 1996):

$$\Delta\varepsilon = (1 - h)\left(\frac{D_w}{D_i} - 1\right)n \tag{7}$$

Rearranging Equations (6) and (7) gives the following expression for n:

$$n = \frac{\left[h\left(\delta_a - \delta_{s_{init}}^{l}\right) + \varepsilon_{eq}\right]_{^2H} - S_E\left[h\left(\delta_a - \delta_{s_{init}}^{l}\right) + \varepsilon_{eq}\right]_{^{18}O}}{(1-h)\left(S_E\left(\frac{D_w}{D_{^{18}O}} - 1\right) - \left(\frac{D_w}{D_{^2H}} - 1\right)\right)} \tag{8}$$

Mathieu and Bariac (1996) proposed a formulation incorporating the soil surface water content (θ_{EF}, in $\mathrm{m}^3\ \mathrm{m}^{-3}$) to simulate the evolution of n. The latter is modeled to range from $n_{\mathrm{a}} = 0.5$, i.e., soil is saturated at the evaporation front and evaporation is atmosphere controlled ($\theta_{\mathrm{EF}} = \theta_{\mathrm{sat}} = 0.45\ \mathrm{m}^3\ \mathrm{m}^{-3}$), to $n_{\mathrm{S}} = 1$, i.e., soil water content at the evaporation front reaches the residual value and evaporation is soil-controlled ($\theta_{\mathrm{EF}} = \theta_{\mathrm{res}} = 0.00\ \mathrm{m}^3\ \mathrm{m}^{-3}$):

$$n = \frac{(\theta_{\mathrm{EF}} - \theta_{\mathrm{res}})n_{\mathrm{a}} + (\theta_{\mathrm{sat}} - \theta_{\mathrm{EF}})n_{\mathrm{s}}}{\theta_{\mathrm{sat}} - \theta_{\mathrm{res}}} \tag{9}$$

Due to the fact that the computation of α_{K} with the different methods relies on simultaneous measurements of δ_{EF}, δ_{a}, and δ_E, synchronous values for all three variables were determined from the measured values by linear interpolation for time points 04:00, 12:00, and 20:00 hours each day and used for the calculation of α_{K}. The time gap between the actual measurements and interpolated data ranged between 0.25 and 4 hrs.

In this study, α_{K} was (i) calculated with the Craig and Gordon (1965) model (Equation (3), method "CG65") and (ii) determined from S_{E} values measured at a daily temporal step (Equations (1) and (8), method "G71"). For the latter method values of diffusivity ratios $D_{\mathrm{w}}/D_{\mathrm{i}}$ were taken from Merlivat (1978). The α_{K} estimates derived from CG65 and G71 were compared to those of Mathieu and Bariac (1996) (Eq. 9) by calculating the model-to-data fit (root mean square error – RMSE). The proportion of α_{K} estimates falling into the theoretical range (corresponding to $0.5<n<1$) of Dongmann et al. (1974) was determined by calculating the hit rate (Doswell et al. 1990). Note that α_{K} values outside the theoretical range but for which either α_{K} +1standard error or α_{k} –1 standard error fell into the theoretical range was counted as a hit. The error associated with the calculation of α_{K} was determined by taking into account the effect of all variable and parameter uncertainties, i.e., by propagation of errors, and is detailed in Appendix C.

2.5. Sensitivity of α_{K} to aerodynamic conditions

The sensitivity of α_{K} to (i) the aerodynamic conditions prevailing in the laboratory and to (ii) the development of a dry soil surface layer was investigated during three successive experiments, lasting 40 days each. In a first experiment (E1), the soil column was initially saturated with water ($\theta = 0.45\ \mathrm{m}^3\ \mathrm{m}^{-3}$ across all depths). In a second experiment (E2), water was withdrawn from the bottom after re-saturation of the soil column until water content reached 0.25 m^3 m^{-3} at the soil surface. Subsequently, in a third experiment (E3) water was withdrawn from the bottom after re-saturation until θ = 0.34 m^3 m^3 was reached at the soil surface. Additionally, the relative humidity and isotopic composition of the laboratory air were artificially increased by evaporating 1 L of ^{2}H-enriched water over three days. The isotopic compositions of the ^{2}H-enriched water solution was linearly extrapolated at δ^2H = 4469,370.0 ±611,811.0 ‰ and δ^{18}O = 2,507.9 ±327.0 ‰ from a series of dilution experiments with the standard 1 liquid water (i.e., of isotopic composition $\delta_{\mathrm{st1}}^{\mathrm{l}}$).

3 Results

3.1. Atmosphere column

Figure 2a shows the evolution of the laboratory air temperature and relative humidity during all three experiments. Figure 2a underlines the semi-controlled conditions prevailing during the experiments, i.e., both T_a and h fluctuated on a daily basis in response to outside weather conditions. The mean T_a (resp. h) value during E1, E2, and E3 was 19.6 ±0.9°C (37.9 ±5.3%), 21.8 ±1.3°C (45.4 ±4.6%), and 20.2 ±0.9°C (52.1 ±3.25%), respectively. E1 was started on 22 February 2017 (Day of Experiment, DoE 1) and ran until 2 April 2017 (DoE 40). Here we observed the lowest mean T_a and h values compared to E2 and E3. E2 was conducted in the late spring/early summer (from 3 May 2017 to 11 June 2017) which was characterized by rapidly changing weather conditions (until DoE 92) and by dry and hot conditions (from DoE 92 to 110). Highest values for h were observed during E3, which was carried out from 30 August 2017 to 8 October 2017.

The isotopic composition of the atmospheric water vapor (δ^2H_a and $\delta^{18}O_a$) inside the atmosphere column and at 1 m above the soil surface almost exclusively varied during E1 and E2 due to changing weather conditions outside the laboratory (Fig. 2b and c). In E2 from DoE 86 to DoE 87, strong fluctuations of δ^2H_a and $\delta^{18}O_a$ occurred due to a late spring storm. Following the labeling pulse, δ^2H_a ($\delta^{18}O_a$) increased from –130.0 ±1.3 ‰ (–17.4 ±0.2 ‰) on DoE 211 to –7.2 ±1.4 ‰ on DoE 213 (–16.1 ±0.3 ‰ on DoE 215) at height 0.01 m (E3). Note that water vapor mixing ratio and isotopic compositions data at height 0.01 m in the atmospheric column was not available during E1 due to technical problems.

3.2. δ^{18}O-δ^{2}H relationship for laboratory air water vapor and soil liquid water

Figure 3 displays the isotopic composition results for laboratory air water vapor (blue symbols) and soil liquid water (red symbols) in dual isotopic (δ^{18}O, δ^{2}H) plots. The slope values of the linear regression (LRS) fitted to the atmospheric data were 6.1, 7.0, and 6.2 for E1, E2, and E3 (excluding the data during the ^{2}H labeling period; black dots), respectively, which was significantly lower than the slope of the local meteoric water line (black dashed line; Andreas Lücke, personal communication). This was certainly due to the fact that a significant portion of the laboratory air humidity was provided by the evaporation of soil water (characterized by lower LRS slopes due to kinetic effects). Similar results were observed by Rothfuss et al. (2015).

The slope of the δ^{18}O-δ^{2}H relationship for soil liquid water remained unchanged during E1 and E2 (LRS ≈ 4.4, with $R^2 \approx 1$, p-value = 0.00) and within the expected theoretical range (Sprenger et al. 2016). The labeling of the laboratory air moisture in E3 had a remarkable influence on the water isotopic composition of the upmost soil layer. As a consequence, the LRS slope was significantly higher (7.0, $R^2 = 0.96$, p-value=0.00), which highlighted the influence of the laboratory air water vapor on the isotopic composition of the soil water within the column.

3.3. Soil and atmospheric profiles

Figure 4 shows the vertical profiles of laboratory air mixing ratio (*MR*) (Fig. 4a), soil water content (Fig. 4d) and isotopic compositions (Fig. 4b-c,e-f) measured during E1. Water vapor *MR* was nearly constant across sampling heights above 0.03 m. Water vapor *MR* and isotopic composition profiles shifted during the course of the experiment towards higher values. The hydrogen (oxygen) isotopic composition of the water vapor in the atmosphere column $\delta^{2}H_{col}$ ($\delta^{18}O_{col}$) below 0.03 m was higher (lower) than that of the laboratory air. The direct influence of fractionating evaporation on the water vapor isotopic compositions could be measured near the soil surface only (i.e., at 0.01, 0.03 and 0.07 m heights). The differences between δ_{col} heights at 1 m and 0.01 m were greater at the beginning of the experiment when there was a water film on the soil surface which was evaporating freely.

Figure 4d-f illustrates the soil water content (θ) profiles and the corresponding soil liquid water δ^{2}H and δ^{18}O during E1. The soil surface water content (i.e., measured at –0.1 m, θ_{surf}) was stable throughout E1 and decreased slightly from 0.45 m³ m⁻³ (saturated initial conditions) to 0.42 m³ m⁻³ (DoE 40). During the first 30 days, only the first 0.05 m of soil was impacted by evaporation, i.e., soil water content value decreased from 0.45 (DoE 1) to 0.42 m^3 m^{-3} (DoE 30), while θ remained nearly constant in soil layers below 0.30 m. During the last 10 days of E1, the soil dried faster at 0.30 m depth compared to the other soil layers. The mean evaporation rate computed by mass balance from the temporal changes of the θ profiles over the 40 days of experiment was 0.41 mm d^{-1}. Soil liquid water (Fig. 4e and 4f) became isotopically enriched at the surface relative to the deeper layers, with $\delta^2\mathrm{H}_\mathrm{s}^\mathrm{l}$ ($\delta^{18}\mathrm{O}_\mathrm{s}^\mathrm{l}$) increasing from –47.0 ±1.6 ‰ (–6.2 ±0.2 ‰) to –8.9 ±1.5 ‰ (2.2 ±0.2 ‰) at –0.01 m.

During E2 the water vapor *MR* and isotopic composition (Fig. 5a-c) profiles behaved similarly as during E1. Due to the drier soil (compared to E1) the observed gradient in *MR* between the column atmosphere at 0.01 m and the ambient laboratory air at 1.00 m was significantly smaller. The soil dried almost uniformly (Fig. 5d) across the profile from 0.25 to 0.22 $m^3\ m^{-3}$. The calculated mean evaporation rate (0.59 mm d^{-1}) was significantly higher than during E1 although the soil was much drier (Fig. 2). This can be explained by a greater vapor pressure deficit (due to higher temperature and comparable relative humidity) of the laboratory air and by the existence of capillary rise. Maximum depth gradients of soil liquid water isotopic composition ($\Delta(\delta^2\mathrm{H}_\mathrm{s}^\mathrm{l})/\Delta z$, where z stands for soil depth) were observed in the upmost soil layer (0.01 m), indicating that the evaporation front was located at the soil surface (Rothfuss et al., 2015). At depth 0.01 m, $\delta^2\mathrm{H}_\mathrm{s}^\mathrm{l}$ ($\delta^{18}\mathrm{O}_\mathrm{s}^\mathrm{l}$) ranged between –30.9 ±1.5 ‰ (–2.9 ±0.2 ‰) and –9.6 ±1.6 ‰ (1.4 ±0.2 ‰).

During E3, water vapor *MR* in the laboratory was slightly higher compared to during E1 and E2 (Fig. 6a). The ^{2}H labeling pulse led to an enrichment of the atmosphere column water vapor of –12.9 ‰ (at height 1 m) on DoE 213. Afterwards, the $\delta^2\mathrm{H}_\mathrm{a}$ profiles returned to their normal range (–149.7 ‰ < $\delta^2\mathrm{H}_\mathrm{a}$ < –122.3 ‰ at 1 m height) before labeling. In E3, the soil dried almost uniformly across depths from 0.38 to 0.32 $m^3\ m^{-3}$ (Fig. 6d) with a mean evaporation rate of 1.14 mm d^{-1}. $\delta^2\mathrm{H}_\mathrm{s}^\mathrm{l}$(–0.01 m) varied from –53.4 ±1.5 ‰ (DoE 190) to –18.7 ±1.6 ‰ (DoE 206) (maximum value observed after the ^{2}H labeling pulse) and decreased to –33.1 ±1.7 ‰ (DoE 229). $\delta^{18}\mathrm{O}_\mathrm{s}^\mathrm{l}$ increased from –7.4 ±0.2 ‰ at the beginning of the experiment to –4.1 ±0.2 ‰ at DoE 229.

3.4. Isotopic composition of evaporation and kinetic fractionation factor

As a consequence of the progressive water isotopic enrichment in the upper soil layers (Fig. 7a and b), $\delta^2\mathrm{H}_E$ increased with time from –149.7 ±2.9 ‰ to –82.2 ±8.2 ‰ during the first 40 days of experiment, whereas $\delta^{18}\mathrm{O}_E$ increased from –40.9 ±3.0 ‰ to –26.2 ±2.8 ‰ in the same time. α_K mean values (Table 2) obtained with the CG65 method were 1.0375 ±0.0049 and 1.0238 ±0.0034 for $^1\mathrm{H}^2\mathrm{H}^{16}\mathrm{O}$ and $^1\mathrm{H}_2{}^{18}\mathrm{O}$, respectively. Only 4% of the calculated $\alpha_\mathrm{K}^{2\mathrm{H}}$, but 100% of the $\alpha_\mathrm{K}^{18\mathrm{O}}$ values were within the theoretical range given by Dongmann et al. (1974). By using the G71 method, the mean $\alpha_\mathrm{K}^{2\mathrm{H}}$ value was equal to 1.0132 ±0.0011, while the mean $\alpha_\mathrm{K}^{18\mathrm{O}}$ values was 1.0149 ±0.0012, with a hit rate of 96 % (92 % for $\alpha_\mathrm{K}^{2\mathrm{H}}$). A trend in both data as simulated by the model of Mathieu and Bariac (1996) was not visible. As a measure of model-to-data fit, the root mean square error (RMSE) was estimated at 0.0247 for α_{K}^{2H} and 0.0096 for $\alpha_{\mathrm{K}}^{18O}$ (CG65), and 0.0009 for $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ and to 0.0011 for $\alpha_{\mathrm{K}}^{18\mathrm{O}}$ (G71), respectively.

During E2 (Fig. 8), water in the upper soil layers was initially isotopically enriched compared to that of the deeper soil layers, and the enrichment increased continuously. δ_E showed no significant (upward) trend during the course of experiment and was on average –88.6 ±8.2 ‰ ($\delta^2\mathrm{H}_E$) and –24.2 ±2.2 ‰ ($\delta^{18}\mathrm{O}_E$). The observed decrease of $\delta^2\mathrm{H}_\mathrm{a}$ and $\delta^{18}\mathrm{O}_\mathrm{a}$ between DoE 85 and 87 translated into an increase of the computed values of $\delta^2\mathrm{H}_E$ and $\delta^{18}\mathrm{O}_E$, and ultimately to a decrease of $\alpha_\mathrm{K}{}^2\mathrm{H}$ and $\alpha_\mathrm{K}{}^{18}\mathrm{O}$ estimates. Mean α_K values were 1.0386 ±0.005 and 1.0232 ±0.0052 for $^1\mathrm{H}^2\mathrm{H}^{16}\mathrm{O}$ and $^1\mathrm{H}_2{}^{18}\mathrm{O}$, respectively, when using CG65. The hit rate for $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ ($\alpha_\mathrm{K}{}^{18}\mathrm{O}$) values was 3% (100%) and the RMSEs were 0.0208 (0.0055) for $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ ($\alpha_{\mathrm{K}}^{18\mathrm{O}}$). By using the G71 method, the mean $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ and $\alpha_{\mathrm{K}}^{18\mathrm{O}}$ values were 1.0132 ±0.0015 and 1.0149 ±0.0017, respectively. 84 % and 90 % of the values were within the theoretical range, and the RMSEs were 0.0054 and 0.0061 for $^1\mathrm{H}^2\mathrm{H}^{16}\mathrm{O}$ and $^1\mathrm{H}_2{}^{18}\mathrm{O}$, respectively. During E2, the isotopic kinetic fractionation factor increased with a slope of 0.0001 d^{-1} for both isotopologues using the G71 method, while in the case of using the CG65 no systematic increase was observed.

In E3 (Fig. 9), $\delta^2\mathrm{H}_E$ ($\delta^{18}\mathrm{O}_E$) increased from –155.5 ±7.0 ‰ (–37.2 ±5.0 ‰) on DoE 190 to –47.6 ±3.3 ‰ (–5.7 ±0.6 ‰) on DoE 210. The ^{2}H labeling pulse on DoE 211 caused two depleted values for $\delta^2\mathrm{H}_E$ (i.e., –166.6 ±39.0 ‰ on DoE 212 and –149.1 ±40.9 ‰ on DoE 213). Before and after this peak, the $\delta^2\mathrm{H}_E$ ($\delta^{18}\mathrm{O}_E$) mean value was –60.9 ±7.0 ‰ (–9.1 ±1.1‰). The mean $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ was 0.9887 ±0.0336 and was affected by the rapid change in $\delta^2\mathrm{H}_E$ and $\delta^2\mathrm{H}_\mathrm{a}$ shortly following the labeling pulse (DoE 212) and reached a minimum value of 0.87 ±0.01. $\alpha_{\mathrm{K}}^{18\mathrm{O}}$ was not significantly impacted by the labeling pulse using the CG65 model, yielding a mean value of 1.0011 ±0.0051. The associated hit rate was 15% for $\alpha_\mathrm{K}{}^2\mathrm{H}$ values and 8% for $\alpha_\mathrm{K}{}^{18}\mathrm{O}$ values. When using the G71 method, $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ and $\alpha_{\mathrm{K}}^{18\mathrm{O}}$ values were affected by the labeling pulse. $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ ($\alpha_{\mathrm{K}}^{18\mathrm{O}}$) values increased up to 1.0391 ±0.002 (1.044 ±0.002) on DoE 212 with mean values of 1.0078 ±0.0077 for $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ values and 1.0089 ±0.0086 for $\alpha_{\mathrm{K}}^{18\mathrm{O}}$ values. The hit rate of $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ and $\alpha_{\mathrm{K}}^{18O}$ values decreased to 4%. The RMSE for $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ ($\alpha_{\mathrm{K}}^{18\mathrm{O}}$) values was 0.0434 (0.0187) when considering CG65, whereas the RMSE for $\alpha_{\mathrm{K}}^{2\mathrm{H}}$ ($\alpha_{\mathrm{K}}^{18\mathrm{O}}$) values decreased to 0.0061 (0.0061) when considering G71.

4 Discussion

The coupling between soil gas-permeable tubing and laser-based spectroscopy allowed measuring $\delta_{\mathrm{s}}^{\mathrm{l}}$ profiles in a non-destructive manner during a series of experiments differing in the soil water and atmospheric forcing status. We estimated α_{K} values by using the Craig and Gordon (1965) model in an inverse mode (method CG65). α_{K} values could also be determined from the approximation of the slope of the evaporation line (Gat 1971), also based originally on the Craig and Gordon (1965) model (method G71). The main difference between these two approaches is the requirement or not of δ_E as input variable. δ_{E} was determined via a Keeling plot approach (Keeling 1958) as the y-intercept of the linear regression of δ_{col} versus $1/MR_{\mathrm{col}}$. δ_E is therefore statistically the more accurate (i) the greater the $1/MR_{\mathrm{col}}$ and δ_{col} vertical gradients are, but also (ii) the higher the MR_{col} values are measured directly above the evaporation front (i.e., at 0.01 m height). Mean values of the differences $MR_{\mathrm{col}}(0.01) - MR_{\mathrm{col}}(1.00)$, $\delta^2\mathrm{H}_{\mathrm{col}}(0.01) - \delta^2\mathrm{H}_{\mathrm{col}}(1.00)$, and $\delta^{18}\mathrm{O}_{\mathrm{col}}(0.01) - \delta^{18}\mathrm{O}_{\mathrm{col}}(1.00)$ were equal to 3 045 ppmv, 6.9 ‰, and –1.6 ‰ during experiment E1 and equal to 1 988 ppmv, 3.6 ‰, and –0.5 ‰ during E2. We assumed no occurrence of water vapor condensation in the atmosphere column, which is a prerequisite for using the Keeling plot approach. This was the case under the laboratory conditions, where no measureable temperature gradient existed between the atmosphere column and the free laboratory air. This approach also assumes no change of δ_{a} during the sampling sequence (from 0.01 to 1.00 m). Mean changes of δ_{a} during one sampling sequence were 2.8 ± 2.1 ‰ (3.3 ± 3.2 ‰) for $\delta_{\mathrm{a}}{}^2\mathrm{H}$ ($\delta_{\mathrm{a}}{}^{18}\mathrm{O}$) and 0.4 ± 0.3 ‰ (0.6 ± 0.5 ‰) during E1 and E2. A too strong increase (or decrease) of δ_{a} which resulted in a keeling plot linear regression with a p-value > 0.05 was systematically excluded from the analyses. Finally, the column air should be perfectly mixed at each sampling height in the atmosphere column, i.e., no lateral isotopic gradients should exist. Only then is δ_{col} a representative value of the water vapor in the sampled air layer inside the atmosphere column. This last assumption could unfortunately not be verified during the experiments as it would have required several intake lines at each height.

One limitation of the experimental setup was the sequential sampling of water vapor across heights in the atmosphere column. This reduced the temporal resolution of the δ_{col} profile, with a temporal gap between sampling at 0.01 m (closest to the surface) and at 1.00 m (laboratory "free air") of six hours. As the computation of α_{K} values following the CG65 method theoretically requires the simultaneous determination of the isotopic composition of soil water and of evaporated water vapor, $\delta_{\mathrm{s}}^{\mathrm{l}}$ and δ_{col} measurements across depths and heights were linearly interpolated in time to provide three daily profiles (i.e., at 04:00, 12:00, and 20:00 hours). While it was reasonable to assume that change of $\delta_{\mathrm{s}}^{\mathrm{l}}$ at a given depth was a linear function of time, this might be questionable for changes of δ_{col}, even if the conditions in the atmosphere column remained close to laminar throughout the experiments. Together with the limited temporal resolution, this could have affected the representativeness of δ_E estimates and ultimately those of α_{K} values using the CG65 method.

Oerter et al. (2017) showed that both soil (gravimetric) water content and clay (gravimetric) content should be taken into account for the calculation of $\delta_{\mathrm{s}}^{\mathrm{l}}$ on basis of

δ_s^v. However, in the present study, only a temperature correction was applied. On the one hand, the clay content value was the same across soil layers in the column as well as in the two soil standards. Therefore, the effect of clay particles on the isotopic composition of the equilibrated soil pore water vapor could be neglected. On the other hand E1, E2, and E3 were run under different conditions of soil water availability for evaporation, which would require a soil water content correction. However, we can safely assume that the soil water content effect on the value of δ_s^v was not visible during the series of experiments. The value of δ_s^l measured at 0.60 m depth was constant for all experiments, even though the soil water content was not, i.e., varied between 0.21 and 0.45 m^3 m^{-3}.

A systematic bias was observed between α_K^{2H} and α_K^{18O} estimates during E1 and E2 obtained with the CG65 method. While α_K^{18O} was in general within its theoretical range (1.0141-1.0285, corresponding to 0.5<n<1), α_K^{2H} values were almost always higher than 1.0251 (corresponding to the maximum value n=1, see Table 2). These differences could be explained by potential underestimation/overestimation of δ^2H_E. The precise characterization of the local gradients of δ_{col} (especially close to the soil surface), on which the determination of δ_E depends, was enabled by finding the optimal combination of sampling duration and intake flow rate. On the one hand, greater sampling duration and flow rate values ensure minimizing memory effects from previous sampling. On the other hand, they might lead to overlapped sampling, e.g., sampling of water vapor at 0.01 and 0.03 m simultaneously from the 0.01 m column intake line. Duration and flow rate were set to 15 min and 200 ml min^{-1}, respectively, during all experiments, which corresponded to a sampled air layer of 0.016 m height in the atmosphere column, i.e., lower than 0.02 m, which is the difference between the lowest and second lowest air column sampling height. This means, that there was theoretically no overlapped sampling at 0.01 m, where the vertical resolution was the greatest. Despite these settings, α_K^{2H} results might have been, at least partly, influenced by a stronger memory effect of the δ^2H_{col} measurements of the laser spectrometer than for $\delta^{18}O_{col}$ measurements (Schmidt et al. 2010).

Results of both methods were compared to those of the model of Mathieu and Bariac (1996), which conceptualizes the exponent n simply as the mean between the end-member values n_a (=0.5) and n_s (=1.0), weighted by the absolute deviation of the soil water content measured at the evaporation front (θ_{EF}) from residual and saturated water contents (θ_{res} and θ_{sat}, see Eq. (9)), respectively. This model assumes therefore that only fully turbulent conditions occur when the soil is saturated ($\theta_{EF} = \theta_{sat}$, leading to $n = n_a$), which is not necessarily the case, i.e., laminar flow boundary conditions can exist in such cases. The model of Mathieu and Bariac (1996) also considers that, when the soil is at its driest at the evaporation front ($\theta_{EF}=\theta_{res}$, leading to $n=n_s$), molecular diffusion entirely controls water vapor transport to the atmosphere. This assumption might also not be justified as it does not take into account the thickness of the evaporation front nor the aerodynamic conditions in the free atmosphere above.

Contrary to CG65 and G71, the model of Mathieu and Bariac (1996) predicted for all experiments steady monotonic increases of n (and therefore of α_K values) as a consequence of marginal (E1 and E2) or slow (E3) decreases of θ_{EF} with time. θ_{EF} was measured at high temporal resolution and accuracy. The determination of $\theta_{\text{res}} = 0.00$ m³ m^{-3} and $\theta_{\text{sat}} = 0.45$ m³ m^{-3} was not straightforward and, in the present study, depended on how well the soil was sieved, homogenized, and finally repacked in the column. The overall uncertainty of the calculation of α_{K} values using CG65 obtained from the error propagation calculations was 2.9 ‰ (2.4 ‰), 3.6 ‰ (2.6 ‰) and 4.4 ‰ (1.4 ‰) for $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{2H}}$ ($\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{18O}}$) during E1, E2 and E3. This is approximately two times higher than the estimates of the G71 method (1.1 ‰, 1.4 ‰ and 0.8 ‰ for $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{2H}}$ and 1.3 ‰, 1.5 ‰ and 0.9 ‰ for $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{18O}}$ during E1, E2 and E3, respectively). Figures 7, 8, and 9 illustrate these observations well.

The value of n obtained from G71 was by nature less sensitive to the uncertainties associated with isotopic input variables (i.e., $\delta_{s_{init}}^{l}$ and δ_{a}, ε, and $\Delta\varepsilon$) as it was determined on basis of a ratio of δ^{18}O and δ^{2}H data (Eq. (6), Table 1). Since n evolution was determined in a dual isotopic space it was therefore common for both isotopologues. As a consequence, for example on DoE 213 (experiment E3) the rapid change in $\delta^{2}\text{H}_{E}$ led to sudden variations of $\alpha_{\text{K}}^{\text{2H}}$ as well as of $\alpha_{\text{K}}^{\text{18O}}$. G71 results were, in contrast to CG65 results, always within theoretical ranges. They also matched well the values of the model of Mathieu and Bariac (1996) during E1 (RMSE = 0.0009) and reasonably well during E2 (0.0054<RMSE<0.0061). For the latter experiment, G71 α_{K} estimates ($1.0103 < \alpha_{\text{K}}^{\text{2H}} < 1.0161$ and $1.0117 < \alpha_{\text{K}}^{\text{18O}} < 1.0183$) systematically plotted below those of the Mathieu and Bariac (1996) model ($1.018 < \alpha_{\text{K}}^{\text{2H}} < 1.0189$ and $1.0204 < \alpha_{\text{K}}^{\text{18O}} < 1.0215$), which would still indicate that turbulent transport of water vapor prevailed, even though soil water content was significantly lower. CG65 estimates of $\alpha_{\text{K}}^{\text{18O}}$ were greater than those by the model of Mathieu and Bariac (1996) during E1 and E2, and suggest, again contrary to G71 results, a more predominant role of molecular diffusion in the transport of water vapor.

Although relative humidity in the atmosphere has no impact on the value of α_{K}, it partly controls $\delta_{\text{s}}^{\text{l}}$ via the kinetic isotopic effect term introduced in Eq. (7). The primary objective of experiment E3 was to significantly increase the relative humidity of the laboratory free air to observe its effect on the soil water isotopic enrichment. Even though relative humidity was significantly higher during E3 (52.1 ±3.3%) than during E1 (37.9 ±5.3%) and E2 (45.4 ±4.6%), the impact on both soil hydrogen and oxygen water isotopic surface enrichments was not clear before the intrusion of the enriched atmospheric water vapor occurred. In contrast, the labeling pulse in E3 was shortly (1 day) followed by the intrusion of laboratory air water vapor into the first centimeters of the soil. The maximum $\delta^{2}\text{H}_{\text{s}}$ value was observed on DoE 215, i.e., 3 days after the isotopic composition of the laboratory air reached its maximum value (Fig. 9). This illustrates how conditions in the atmosphere column contrasted with the well-mixed aerodynamic conditions inside the laboratory. The response time of the isotopic composition of soil to the isotopic composition of the atmosphere had clear effects on both methods for determining α_{K} values. CG65 and G71 systematically underestimated MB96 results after the labeling pulse during E3 (to the exception of the DoE 212-213 period for G71). Possible reason for this was the non-attainment of thermodynamic equilibrium conditions in the soil pore space at the evaporation front (EF) upon invasion of the enriched column air water vapor in the upper soil layers. This could have led to errors in the determination of δ_{EF} values, and, ultimately in those of δ_E and α_K.

Only a handful of studies aimed at estimating and/or modeling α_K values during bare soil evaporation. Braud et al. (2009a) could retrieve $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}$ values by using the CG65 method as upper boundary condition for their soil-vegetation-atmosphere model SiSPAT-Isotope during a series of long-term drying experiments in the laboratory. For this, they precisely calibrated the soil water transport module of SiSPAT-Isotope. They simulated a general decreasing trend for $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}$ with highest ($\sim1.020<\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}<\sim1.030$) values at soil water saturation and lowest values – sometimes even lower than 1.000 – ($0.980<\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}<1.020$), when the evaporation front was located the furthest away from the soil surface. This is inconsistent with both the general belief that *n* should increase with increasing thickness of the soil surface dry layer and decreasing soil water content (Barnes and Allison 1983), and the model of Mathieu and Bariac (1996). Rothfuss et al. (2012) determined values for $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}$ under strictly controlled conditions in a climatic chamber, assuming isotopic steady-state evaporation from their soil monolith. They calibrated SiSPAT-Isotope using multiple objective functions and found $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}$ to range between 1.021 and 1.033. Rothfuss et al. (2015) used the G71 method for determination of both $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{18}O}}$ and $\boldsymbol{\alpha}_{\mathbf{K}}^{\mathbf{^{2}H}}$ with help of novel online laser spectroscopy and non-destructive monitoring of $\boldsymbol{\delta}_{\mathbf{s}}^{\mathbf{l}}$. They also found an overall decreasing trend for both kinetic fractionation factors, corresponding to *n* values ranging from 0.95 to 0.6. The authors could partly reconcile their results with theory by considering that relative humidity value at the evaporation front was no longer equal to 100 %. Soderberg et al. (2012) pointed out the need to account in the Craig and Gordon (1965) model for the effect of very low soil water tension (pF>5) on the value of the relative humidity at the evaporation front following the Kelvin equation (Gee et al. 1992). In the present study during E2 where soil was the driest, soil water tension minimum value was calculated with the van Genuchten-mualem model (Mualem 1976, van Genuchten 1980) on basis of the minimum recorded volumetric water content value and the soil retention curve parameters (Lutz Weihermüller, personal communication). It was estimated to range between 2077 and 2611 hPa, which corresponded to a pF value between 3.32 and 3.42 Therefore, soil water tension was not considered to have an impact on the value of α_K computed with the CG65 method via its impact on the isotopic kinetic effect $\Delta\boldsymbol{\varepsilon}$.

When determining δ_E by using the Craig and Gordon (1965) model in a forward mode for, e.g., evapotranspiration (ET) partitioning in the field, G71 should be used together with the model of Mathieu and Bariac (1996) as independent assessment for setting the value of α_K correctly. Sensitivity of the isotopic partitioning of ET to α_K values should be done, if applicable, in light of the potential discrepancies between results of the two methods. For this purpose, $\boldsymbol{\delta}_{\mathbf{s}}^{\mathbf{l}}$ measurements should not be restricted to the upper few centimeters of soil (where evaporation takes place), but rather be conducted throughout the entire soil profile to be able to compute slopes of the evaporation line. Measurements of $\boldsymbol{\delta}_{\mathbf{s}}^{\mathbf{l}}$ should finally be performed at high temporal resolution to evaluate α_K dynamics.

5 Conclusion

In this study, we were able to monitor soil and atmospheric isotopic composition profiles non-destructivly at a high temporal and vertical resolution during a series of bare soil evaporation experiments differing in soil water content and atmospheric forcing. In combination with meteorological measurements and by using a Keeling plot approach, we could determine the isotopic composition of the evaporated water vapor and finally compute the hydrogen and oxygen kinetic fractionation factors from the Craig and Gordon (1965) model with two different inverse modeling approaches on a daily basis.

Our results show that the application of the Keeling plot approach (Keeling 1958) in the laboratory remains highly challenging, with direct consequences for the isotopic composition of evaporated water vapor and its uncertainty using the CG65 approach. This was particularly true for the computation of the hydrogen kinetic fractionation factor, as measurements of δ^2H seemed to suffer from greater analytical memory effects than those of δ^{18}O. The determination of α_K values from the computation of the slope of the so-called "evaporation line" in a dual isotope space (G71) was independent from information on δ_E, and as such provided the best model-to-data fit with the simple two-end member formulation of Mathieu and Bariac (1996) during the first experiment. The discrepancy in results between G71 and the model of Mathieu and Bariac (1996) indicated, e.g., that turbulent transport of water vapor would have still played a preponderant role in the removal of moisture by evaporation during the second experiment, even at a soil water content much below saturation.

Our series of experiments call for further investigation of the temporal dynamics of α_K values with novel non-invasive and/or non-destructive isotopic monitoring tools. They also underline the need for repetitive and thorough determination of soil water isotopic composition profiles in the field for determination of α_K values using both the G71 model and the Mathieu and Bariac (1996) model approaches. This should be useful for providing δ_E estimates in the context of the partitioning of evapotranspiration into soil evaporation and plant transpiration.

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Appendix A. Example of measuring sequence

An example of one measuring sequence (performed on day of experiment – DoE 14) is shown in Fig. A1. The isotopic compositions were measured in the vapor stream collected from soil across depths (–0.57 to –0.01 m), of both standards (“STD1” and “STD2”), and in the atmosphere column across heights (0.01 to 1.00 m). To avoid overlapping sampling inside the atmosphere column measuring time fast set to a maximum of 15 minutes. Figure A1 highlights the steady behavior of soil water vapor measurements and, in contrast, the fluctuations of the atmospheric vapor measurements. .

Appendix B. Example of Keeling plot regression lines on DoE 73

Appendix C: Error calculation on the kinetic fractionation factor α_K

The value for the kinetic fractionation factor α_{K} is given by:

$$\alpha_K = \frac{(\delta_{\mathrm{s}}^{\mathrm{l}}+1)/\alpha_{\mathrm{eq}}^{\mathrm{i}} - h'(\delta_{\mathrm{a}}+1)}{(1-h')\,(\delta_E+1)} \tag{C1}$$

The kinetic fractionation factor α_k depends on errors made in the determination of the following variables: relative air humidity h’ normalized to the saturated vapor pressure (P_{sat} [Pa]) (Soderberg et al. 2012) at the temperature of the evaporation front T_{EF} and temperature T_a, as well as the isotopic compositions of soil evaporation δ_E , atmospheric water vapor δ_{a} and soil water at the evaporation front $\delta_{\mathrm{s}}^{\mathrm{l}}$. The equations for h’ and $\alpha_{\mathrm{eq}}^{\mathrm{i}}$ are given below:

$$h' = h\frac{\exp\left(13.7-\frac{5120}{T_a}\right)}{\exp\left(13.7-\frac{5120}{T_{\mathrm{EF}}}\right)} \qquad \text{and} \tag{C2}$$

$$\alpha_{\mathrm{eq}}^{\mathrm{i}} = \exp\left[-\left(\frac{A}{T_{\mathrm{EF}}^2}+\frac{B}{T_{\mathrm{EF}}}+C\right)\right] \tag{C3}$$

with constants $A = 1137, B = -0.4156\ and\ C = -0.0020667$ for i = ^{18}O and $A = 24844, B = -76.25\ and\ C = 0.05261$ for i = ^{2}H.

We assumed that the errors of all measurements are independent so the standard error $\sigma^2_{\alpha_k}$ can be calculated as:

$$\sigma^2_{\alpha_\mathrm{K}} = \left(\frac{\partial \alpha_\mathrm{K}}{\partial h}\right)^2 \sigma^2_h + \left(\frac{\partial \alpha_\mathrm{K}}{\partial T_\mathrm{a}}\right)^2 \sigma^2_{T_a} + \left(\frac{\partial \alpha_\mathrm{K}}{\partial T_\mathrm{EF}}\right)^2 \sigma^2_{T_\mathrm{EF}} + \left(\frac{\partial \alpha_K}{\partial\, \delta_\mathrm{E}}\right)^2 \sigma^2_{\delta_\mathrm{E}} + \left(\frac{\partial \alpha_\mathrm{K}}{\partial\, \delta_\mathrm{a}}\right)^2 \sigma^2_{\delta_a} + \left(\frac{\partial \alpha_\mathrm{K}}{\partial\, \delta^\mathrm{l}_\mathrm{s}}\right)^2 \sigma^2_{\delta^\mathrm{l}_\mathrm{s}} \qquad \text{(C4)}$$

The first three partial derivate terms can be obtained using the chain rules:

$$\frac{\partial \alpha_\mathrm{K}}{\partial h} = \frac{\partial \alpha_\mathrm{K}}{\partial h'}\frac{\partial h'}{\partial h} \qquad \text{(C5)}$$

$$\frac{\partial \alpha_\mathrm{K}}{\partial T_\mathrm{a}} = \frac{\partial \alpha_\mathrm{K}}{\partial h'}\frac{\partial h'}{\partial T_\mathrm{a}} \qquad \text{(C6)}$$

$$\frac{\partial \alpha_\mathrm{K}}{\partial T_\mathrm{EF}} = \frac{\partial \alpha_\mathrm{K}}{\partial \alpha_\mathrm{eq}}\frac{\partial \alpha_\mathrm{eq}}{\partial T_\mathrm{EF}} + \frac{\partial \alpha_\mathrm{K}}{\partial h'}\frac{\partial h'}{\partial T_\mathrm{EF}} \qquad \text{(C7)}$$

with:

$$\frac{\partial \alpha_\mathrm{K}}{\partial h'} = \frac{(-\delta_\mathrm{a}-1)}{(1-h')(\delta_E+1)} + \frac{\frac{\delta^\mathrm{l}_\mathrm{s}+1}{\alpha_\mathrm{eq}} - h'(\delta_\mathrm{a}+1)}{(1-h')^2(\delta_E+1)} \qquad \text{(C5-1)}$$

$$\frac{\partial h'}{\partial h} = \frac{\exp\left(13.7-\frac{5120}{T_\mathrm{a}}\right)}{\exp\left(13.7-\frac{5120}{T_\mathrm{EF}}\right)} \qquad \text{(C5-2)}$$

$$\frac{\partial h'}{\partial T_\mathrm{a}} = h\ \frac{5120}{(T_\mathrm{a})^2}\frac{\exp\left(13.7-\frac{5120}{T_\mathrm{a}}\right)}{\exp\left(13.7-\frac{5120}{T_\mathrm{EF}}\right)} \qquad \text{(C6-1)}$$

$$\frac{\partial \alpha_\mathrm{K}}{\partial \alpha_\mathrm{eq}} = \frac{\delta^\mathrm{l}_\mathrm{s}+1}{(h'-1)\,(\delta_E+1)\,{\alpha^\mathrm{i}_\mathrm{eq}}^2} \qquad \text{(C7-1)}$$

$$\frac{\partial \alpha_{eq}}{\partial T_{\mathrm{EF}}} = \alpha_{eq} \left(\frac{2A}{T_{\mathrm{EF}}^{3}} + \frac{B}{T_{\mathrm{EF}}^{2}} \right) \tag{C7-2}$$

$$\frac{\partial h'}{\partial T_{\mathrm{EF}}} = -h \, \frac{5120}{(T_{\mathrm{EF}})^{2}} \frac{\exp\left(13.7 - \frac{5120}{T_{\mathrm{a}}}\right)}{\exp\left(13.7 - \frac{5120}{T_{\mathrm{EF}}}\right)} \tag{C7-3}$$

Combining equation C4-1 to C6-3 leads to

$$\frac{\partial \alpha_{\mathrm{K}}}{\partial h'} = \frac{\exp\left(13.7 - \frac{5120}{T_{a}}\right)}{\exp\left(13.7 - \frac{5120}{T_{\mathrm{EF}}}\right)} \left(\frac{(-\delta_{a}^{v} - 1)}{(1-h')(\delta_{E}^{v}+1)} + \frac{\frac{\delta_{s}^{l}+1}{\alpha_{eq}} - h'(\delta_{a}^{v}+1)}{(1-h')^{2}(\delta_{E}^{v}+1)} \right) \tag{C8}$$

$$\frac{\partial \alpha_{\mathrm{K}}}{\partial T_{a}} = h \, \frac{5120}{(T_{a})^{2}} \frac{\exp\left(13.7 - \frac{5120}{T_{a}}\right)}{\exp\left(13.7 - \frac{5120}{T_{\mathrm{EF}}}\right)} \left(\frac{(-\delta_{a}^{v} - 1)}{(1-h')(\delta_{E}^{v}+1)} + \frac{\frac{\delta_{s}^{l}+1}{\alpha_{eq}} - h'(\delta_{a}^{v}+1)}{(1-h')^{2}(\delta_{E}^{v}+1)} \right) \tag{C9}$$

$$\frac{\partial \alpha_{\mathrm{K}}}{\partial T_{\mathrm{EF}}} = \frac{\delta_{\mathrm{s}}^{\mathrm{l}}+1}{(h'-1)\,(\delta_{E}+1)\,{\alpha_{\mathrm{eq}}^{\mathrm{i}}}^{2}} \, \alpha_{eq} \left(\frac{2A}{T_{\mathrm{EF}}^{3}} + \frac{B}{T_{\mathrm{EF}}^{2}} \right) -$$

$$\frac{\exp\left(13.7 - \frac{5120}{T_{\mathrm{a}}}\right)}{\exp\left(13.7 - \frac{5120}{T_{\mathrm{EF}}}\right)} \left(\frac{(-\delta_{\mathrm{a}} - 1)}{(1-h')(\delta_{E}+1)} + \frac{\frac{\delta_{\mathrm{s}}^{\mathrm{l}}+1}{\alpha_{\mathrm{eq}}^{\mathrm{i}}} - h'(\delta_{\mathrm{a}}+1)}{(1-h')^{2}(\delta_{E}+1)} \right) h \, \frac{5120}{(T_{\mathrm{EF}})^{2}} \frac{\exp\left(13.7 - \frac{5120}{T_{\mathrm{a}}}\right)}{\exp\left(13.7 - \frac{5120}{T_{\mathrm{EF}}}\right)} \tag{C10}$$

The last first three partial derivate terms are given below:

$$\frac{\partial \alpha_{\mathrm{K}}}{\partial \, \delta_{E}} = \frac{(\delta_{\mathrm{s}}^{\mathrm{l}}+1)/\alpha_{\mathrm{eq}}^{\mathrm{i}} - h'(\delta_{\mathrm{a}}+1)}{(1-h')\,(\delta_{E}+1)^{2}} \tag{C11}$$

$$\frac{\partial \alpha_{\mathrm{K}}}{\partial \, \delta_{\mathrm{a}}} = \frac{-h'}{(1-h')\,(\delta_{E}+1)} \tag{C12}$$

$$\frac{\partial \alpha_{\mathrm{K}}}{\partial \, \delta_{\mathrm{s}}^{\mathrm{l}}} = \frac{1/\alpha_{\mathrm{eq}}^{\mathrm{i}}}{(1-h')\,(\delta_{E}+1)} \tag{C13}$$

Table 1

Overview on equations used in this study to calculate the kinetic fractionation factor with their corresponding references.

Reference	α_K	*n*
Dongmann et al. (1974)	$\alpha_{\mathrm{K}} = \left(\frac{D_{\mathrm{w}}}{D_{\mathrm{i}}}\right)^n$	$n = 0.5$ (fully turbulent) $n = 2/3$ (laminar) $n = 1$ (fully diffusive)
Mathieu and Bariac (1996)	$\alpha_{\mathrm{K}} = \left(\frac{D_{\mathrm{w}}}{D_{\mathrm{i}}}\right)^n$	$n = \frac{(\theta_{\mathrm{EF}} - \theta_{\mathrm{res}})n_{\mathrm{a}} + (\theta_{\mathrm{sat}} - \theta_{\mathrm{EF}})n_{\mathrm{s}}}{\theta_{\mathrm{sat}} - \theta_{\mathrm{res}}}$
Gat (1971) (G71)	$\alpha_{\mathrm{K}} = \left(\frac{D_{\mathrm{w}}}{D_{\mathrm{i}}}\right)^n$	$n = \frac{\left[h\left(\delta_a - \delta^l_{s_{init}}\right) + \varepsilon_{eq}\right]_{^2H} - S_E\left[h\left(\delta_a - \delta^l_{s_{init}}\right) + \varepsilon_{eq}\right]_{^{18}O}}{(1-h)\left(S_E\left(\frac{D_w}{D_{^{18}O}} - 1\right) - \left(\frac{D_w}{D_{^2H}} - 1\right)\right)}$
Craig and Gordon (1965) (CG65)	$\alpha_{\mathrm{K}} = \frac{\frac{(\delta_{\mathrm{EF}} + 1)}{\alpha_{\mathrm{eq}}} - h'(\delta_{\mathrm{a}} + 1)}{(1-h')(\delta_E + 1)}$	-

Table 2

Mean kinetic fractionation factor (α_K) values, hit rate (%), i.e., the proportion of α_K estimate lying within the theoretical range (1.0125<α_K^{2H}<1.0251 and 1.0141<α_K^{18O}<1.0285) and goodness of fit (RMSE) between α_K estimates and simulated values using the model of Mathieu and Bariac (1996). "CG65" and "G71" refer to the two different methods of calculation of α_K values.

	E1		**E2**		**E3**	
	α_K^{2H}	α_K^{18O}	α_K^{2H}	α_K^{18O}	α_K^{2H}	α_K^{18O}
CG65						
mean value (±1sd) [-]	1.0375 ±0.0049	1.0238 ±0.0034	1.0386 ±0.005	1.0232 ±0.0052	0.9887 ±0.0336	1.0011 ±0.0051
hit rate [%]	4	100	3	100	15	8
RMSE [-]	0.0247	0.0096	0.0208	0.0055	0.0434	0.0187
G71						
mean value (±1sd) [-]	1.0132 ±0.0011	1.0149 ±0.0012	1.0132 ±0.0015	1.0149 ±0.0012	1.0078 ±0.0077	1.0089 ±0.0086
hit rate [%]	96	92	84	90	4	4
RMSE [-]	0.0009	0.0011	0.0054	0.0061	0.0061	0.0061
Mathieu and Bariac (1996)						
mean value (±1sd) [-]	1.0129 ± 0.0003	1.0146 ± 0.0003	1.0185 ±0.0003	1.0209 ±0.0003	1.0152 ± 0.0005	1.0173 ± 0.0006

Figure 1.

Experimental setup: (a) PVC soil monolith with system for applying water suction at the bottom, atmosphere column, and available measurements; (b) experimental setup for sampling water vapor at the different soil depths, from the two soil water standards, and from the atmosphere.

Figure 2

(a): Time series of temperature (T_a, °C) and relative humidity (h, %) of the ambient air in the laboratory (sampled one meter above the soil surface, i.e., outside the atmosphere column); (b): time series of the hydrogen (δ^2H_a, ‰) and (c) oxygen ($\delta^{18}O_a$, ‰) stable isotopic compositions of the water vapor across heights within the atmosphere column for experiments E1 to E3. Grey shaded stripes indicate missing data due to encountered technical problems.

Figure 3

Measurements of the laboratory air water vapor isotopic composition (blue symbols) 1 m above the soil surface and soil liquid water isotopic composition (red: –0.01 m; dark orange: –0.03 m; orange: –0.07 m; light orange: –0.15 m; dark yellow: –0.30 m; yellow: –0.60 m) from all depths along with their respective linear regression lines (atmosphere: blue solid line; soil: red solid line) in dual isotopic plots for experiment (a) E1, (b) E2, and (c) E3. Data collected in the period following the ^2H labeling pulse (black symbols) were excluded from the regression for E3 (c). Linear regression slopes (LRS) and coefficients of determination (R^2) as well as the equation for the local meteoric water line (LMWL) are reported (black dotted line).

Figure 4

Experiment 1 (day of experiment – DoE 1 to 40): profiles of (a) water vapor mixing ratio (MR) and (b) hydrogen and (c) oxygen isotopic compositions (δ^2H_a and $\delta^{18}O_a$) in the atmosphere column across heights. Profiles of (d) soil water volumetric content (θ, $m^3\ m^{-3}$) and (e) hydrogen and (f) oxygen isotopic compositions (δ^2H_s and $\delta^{18}O_s$) across depths.

Figure 5

Experiment 2 (day of experiment – DoE 71 to 110): profiles of (a) water vapor mixing ratio (MR) and (b) hydrogen and (c) oxygen isotopic compositions (δ^2H_a and $\delta^{18}O_a$) in the atmosphere column across heights. Profiles of (d) soil water volumetric content (θ, $m^3\ m^{-3}$) and (e) hydrogen and (f) oxygen isotopic compositions (δ^2H_s and $\delta^{18}O_s$) across depths.

Figure 6

Experiment 3 (day of experiment – DoE 190 to 229): profiles of (a) water vapor mixing ratio (MR) and (b) hydrogen and (c) oxygen isotopic compositions (δ^2H_a and $\delta^{18}O_a$) in the atmosphere column across heights. Profiles of (d) soil water volumetric content (θ, $m^3\ m^{-3}$) and (e) hydrogen and (f) oxygen isotopic compositions (δ^2H_s and $\delta^{18}O_s$) across depths.

Figure 7

Experiment 1: Isotopic composition of the soil liquid water ($\delta^2H_S^l$ and $\delta^{18}O_S^l$, in ‰) at depth 0.01 m (a-b), of the laboratory air water vapor (δ^2H_a and $\delta^{18}O_a$ in ‰) at 1 m above the soil surface (c-d), of the evaporated water vapor (δ^2H_E and $\delta^{18}O_E$ in ‰, e-f) calculated with the Keeling plot method (only results with a p-value lower than 0.05 are shown); α_K results by using the inverse Craig and Gordon (1965) model (method "CG65", g-h); α_K results obtained from the value of the slope of the "evaporation line" given by Gat (1971) (method "G71", i-j). Theoretical ranges of α_K values are represented by the grey shaded horizontal stripes, and results of the model of Mathieu and Bariac (1996) are displayed for comparison (black stars).

Figure 8

Experiment 2: Isotopic compositions of the soil liquid water ($\delta^2\mathrm{H}_\mathrm{S}^\mathrm{l}$ and $\delta^{18}\mathrm{O}_\mathrm{S}^\mathrm{l}$, in ‰) at depth 0.01 m (a-b), of the laboratory air water vapor ($\delta^2\mathrm{H}_\mathrm{a}$ and $\delta^{18}\mathrm{O}_\mathrm{a}$ in ‰) at 1 m above the soil surface (c-d), of the evaporated water vapor ($\delta^2\mathrm{H}_E$ and $\delta^{18}\mathrm{O}_E$ in ‰, e-f) calculated with the Keeling plot method (only results with a p-value lower than 0.05 are shown); α_K results by using the inverse Craig and Gordon (1965) model (method "CG65", g-h); α_K results obtained from the value of the slope of the "evaporation line" given by Gat (1971) (method "G71", i-j). Theoretical ranges of α_K values are represented by the grey shaded horizontal stripes and results of the model of Mathieu and Bariac (1996) are displayed for comparison (black stars).

Figure 9

Experiment 3: Isotopic compositions of the soil liquid water ($\delta^2\mathrm{H}_\mathrm{S}^\mathrm{l}$ and $\delta^{18}\mathrm{O}_\mathrm{S}^\mathrm{l}$, in ‰) at depth 0.01 m (a-b), of the laboratory air water vapor ($\delta^2\mathrm{H}_\mathrm{a}$ and $\delta^{18}\mathrm{O}_\mathrm{a}$ in ‰) at 1 m above the soil surface (c-d), of the evaporated water vapor ($\delta^2\mathrm{H}_E$ and $\delta^{18}\mathrm{O}_E$ in ‰, e-f) calculated with the Keeling plot method (only results with a p-value lower than 0.05 are shown); α_K results by using the inverse Craig and Gordon (1965) model (method "CG65", g-h); α_K results obtained from the value of the slope of the "evaporation line" given by Gat (1971) (method "G71", i-j). Theoretical ranges of α_K values are represented by the grey shaded horizontal stripes and results of the model of Mathieu and Bariac (1996) are displayed for comparison (black stars). Note for 9c-j: y-axes scales differ from Figs 7 and 8.

Figure A1

Linear Regression line (Keeling plot) of δ^2H (left) and δ^{18}O (right) against the inverse MR on Day of Experiment 73, values for the y-Intercept (I), the coefficient of determination (R²) and the p-value are reported.

Figure B1

Water vapor mixing ratio (in ppmV) and isotopic composition (δ^2H and δ^{18}O in ‰) of the water vapor sampled on Day of Experiment 14 from the ambient air "atm", both standards ("STD1" and "STD2") and soil depths ("soil"), the numbers representing the depth/high regarded to the soil surface