Using storage selection functions to assess mixing patterns and water ages of soil water, evaporation and transpiration

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Using StorAge Selection functions to assess mixing patterns and water ages of soil water, evaporation and transpiration

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Abstract. Understanding internal flow mechanisms within the critical zone relies heavily on characterising the interactions between evaporation and vegetation uptake of soil water; however, the magnitude, sources, and ages of these water fluxes are rarely well-constrained. We adapted the StorAge Selection (SAS) function framework to estimate the water residence time of storage, and transit times of eco-hydrologic fluxes, at multiple soil depths in typical soil-vegetation units in a humid, energy-limited environment in the Scottish Highlands. Modelling water and stable isotope fluxes within the soil-vegetation units indicated that rapid movement of young water through the soils occurred at both sites creating relatively stable water residence times in the soils with depth and time. Estimation of the evaporation profile had limited temporal variability with a high preference for near-surface water (0 – 5 cm soil depth, long-term mean age: 50 – 65 days) due to relatively frequent precipitation. Root uptake profile revealed higher temporal variability, favouring deeper water (5 – 15 cm) during drier periods and near-surface (0 – 5 cm) during wet periods (long-term mean age: 6 – 15 days older than evaporation). The model structure provides a tool to help constrain water storage–flux–age interactions in the upper part of the critical zone and understand how soil–vegetation systems regulate groundwater recharge and catchment-scale hydrology.

1 Introduction

Recent studies in soil-vegetation interactions have suggested that soil water contributing to recharge and streamflow, and soil waters available for vegetation root uptake, may be effectively de-coupled systems, giving rise to the “two-water worlds hypothesis” (McDonnell, 2014; Evaristo et al., 2015; Berry et al., 2017). Water stored in the soil profile is continuously changing and is subject to multiple fluxes (e.g. evaporation, root uptake, and recharge). Each flux has a distinct characteristic age distribution which affects the age of water remaining in storage. Whilst isotopic data in some regions has inferred a clear separation of plant water from soil water, this is not apparent in all cases (Ellsworth and Williams, 2007; Vargas et al., 2017). Consequently, identifying the source of water for vegetation uptake and evaporation needs both further theoretical and methodological developments which can be empirically tested (Rothfuss and Javaux, 2017).

Exploring ecohydrologic separation in contrasting soil-vegetation units is essential for understanding the influence of evaporation, vegetation uptake, and mixing processes in the critical zone on catchment scale-water fluxes. Within the critical zone, soil water movement is complex due to heterogeneous soil properties resulting in highly preferential flow and depth-dependent soil sources of evaporation and transpiration (e.g. Sprenger et al., 2018a). In large catchment scale modelling approaches, the heterogeneities of vegetation and soil water influencing bulk evapotranspiration (ET) are generally simplified to a net flux mainly driven by atmospheric demand (Zhao et al., 2013). Due to the complexity of water mixing in soils, the partitioning of evaporation and root uptake into discrete profiles in soils and potentially contrasting ages has been subject to limited investigation. Such separation is difficult due to the often unknown root densities and soil moisture distributions that
influence the spatial location of root uptake volumes (Brantley et al., 2017). Isotopes have been shown to be a useful tool to help identify such root uptake profiles through mixing estimations of soil and xylem isotopes (Ogle et al., 2014; Geris et al., 2017; Sprenger et al., 2017b). Similarly, evaporation fluxes and ages from depth are difficult to quantify due to the limited availability of measured energy fluxes (i.e. in situ soil latent and sensible heat fluxes, Xiao et al., 2011, 2012). Studies have previously inferred the age of evaporative water using simple flux tracking and assuming complete mixing, with model results suggesting removal of significantly younger water via evaporation relative to stream water at the catchment outlet (e.g. Soulsby et al., 2016).

Storage Selection (SAS) functions provide a simple method for identifying the likely sources and ages of water, based on a probabilistic analysis of how each source of different composition and age might have mixed (Botter et al., 2011). The framework for using SAS functions as time-variant tools to temporally account for water flux and storage age is defined by the “master equation” (Botter et al., 2011), and can identify how water preferentially moves through storage. Although the majority of time-variant approaches for assessing water age have focused on the catchment scale, some reductionist empirical studies have inferred changes in the transit and residence times of soil water using controlled lysimeter measurements with tracer injections and estimated breakthrough curves in outflows (Rinaldo et al., 2011; Harman and Kim, 2014; Benettin et al., 2015; Queloz et al., 2015; Kim et al., 2016). These have helped identify time-variant changes in transit times due to different soil properties and moisture conditions (Ali et al., 2014; Tezlaflf et al., 2014; Sprenger et al., 2016; Pangle et al., 2017). With these recent breakthroughs in soil water transit times, a modification of the SAS function framework has the potential for assessing the time-variant age and soil water mixing at discrete depths of specific soil properties and fluxes.

Here, the SAS framework was used, in conjunction with a year’s climatic, hydrometric and isotopic data for two typical soil-vegetation units in the Scottish Highlands (heather shrubs overlying podzolic soils) to explore the interactions between the ages of stored soil water and fluxes in evaporation, root water uptake, and recharge. The SAS approach was modified to include multiple linked storages and account for internal (between storage) water age exchanges. The study had three objectives. First, to use the modified SAS approach to assess the mixing of water ages within the soil profile. Second, to characterise the relationship between the age of water at different soil depths against all soil water to differentiate the water age distribution for fluxes from soils in larger-scale approaches. Third, to identify the seasonal changes in the profile and age of evaporation and root-water uptake water as well as recharge ages. This approach uses calibrated soil water isotope simulations with isotopic xylem water to identify the time variance of root uptake and evaporation water from different soil depths.

2 Theory and Methodology

Within this theory section, there are two key aspects, 1) the profile of evaporation and root uptake from the soil, and 2) the SAS functions (terms listed in Appendix A). The profile is defined as the fraction of evaporation or root uptake from a spatial location in the soil (e.g. 20% of evaporation from 5 cm), whereas the SAS function describes the age of water from a location within the soil (e.g. age of 10 days from 5 cm). In the following sections, soil layers are defined as equidistant soil depths with thickness Δz, to describe the volume of water in multiple soil storages to the maximum simulated soil depth of Z.

2.1 Evaporation and root uptake profiles

Tracer-aided studies have shown that the profiles of both evaporation (E) and root uptake (R) likely change in time over the course of the year, principally due to changes in water availability to sustain atmospheric water demands (Ogle et al., 2014; Volkmann et al., 2016; Barbeta and Peñuelas, 2017). Soil water models which include E and R typically estimate the flux profile with respect to depth using a simple time-invariant relationship (e.g. linear or exponential distributions; e.g. Sprenger et al. 2018b, Fig. 1a). For E, a change of the profile from dominant surface evaporation is derived from the diffusion capacity
evaporated vapour through the soil (Xiao et al., 2011). The use of a time-variant function relationship of $E$ and $R$ facilitates the assessment of biological (e.g. root densities) and physical restrictions (e.g. vapour diffusion through soil and suction potential) on water available by the atmosphere and by plants. A probability distribution (e.g. Gamma, beta, exponential) can estimate the fraction of $E$ and $R$ from each soil layer:

$$f_{E \text{ or } R}(t, i) = \int_{\Delta z \cdot i}^{\Delta z \cdot (i-1)} p(t, z, i) \cdot dz$$

(1)

where $f_{E \text{ or } R}(t, i)$ is the fraction of $E$ or $R$ from soil layer $i$, $\Delta z$ is the depth of the soil layer $i$, $z$ is the depth below the soil surface, and $p$ is a probability distribution. The summation of $f(t, i)$ for all soil layers is equal to 1. Here we use the beta distribution as the probability distribution ($p(t, z)$) due to its definition over a defined interval from 0 to 1 (i.e. equal to the range of the normalized volume of a soil layer) and the parameterization which can replicate the shape of other distributions. The beta distribution is defined by normalizing the average depth of the soil layer ($z(i)$) by the maximum soil depth ($Z$):

$$p(t, z, i) = \left(\frac{z(i)}{Z}\right)^{k-1} \left(1 - \frac{z(i)}{Z}\right)^{u(t)-1}$$

$$B(k, u(t))$$

(2)

where $B$ is the complete beta function, $k$ and $u(t)$ are beta distribution shape parameters controlling the shape of the distribution. It is important to note that Eqs. (1) and (2) are not SAS functions, but functions describing the profile of $E$ and $R$ from within the soil profile. The parameter $k$ was held constant in time to maintain shape consistency for the profile of $E$ and $R$ with depth (i.e. forced higher proportion of $E$ from near-surface soils). Permitting temporal variability of $k$ results in lower constraints for the combination of $k$ and $u(t)$ to represent the physical processes of $E$ and $R$ profiles from depth. The parameters $k$ and $u(t)$ are assumed to be independent for the different fluxes $E$ and $R$. Since the profiles of $E$ and $R$ have been observed to change due to soil moisture conditions (e.g. Ogle et al., 2014), parameterisation of $u(t)$ in Eq. (2) was enabled as a function of soil moisture (e.g. Harman, 2015):

$$u(t) = \lambda \cdot N(\theta_m(t)) + \tau$$

(3)

where $\lambda$ is a linear slope parameter, $\tau$ is an intercept parameter, and $N(\theta_m(t))$ is the normalized soil moisture using the mean ($\mu_\theta$) and standard deviation ($\sigma_\theta$) of the measured soil moisture $\theta_m$ ($N(\theta_m(t)) = (\theta_m(t) - \mu_\theta)/\sigma_\theta$). Deviation of $\lambda$ from zero results in temporal variability of the $E$ and $R$ profiles (Fig. 1b), while as $\lambda$ approaches zero, the maximum and minimum values of $\lambda \cdot N(\theta(t))$ similarly approach zero, and $u(t)$ approaches $\tau$ (time-invariance). Using soil moisture to control the temporal variance results in deeper $E$ and $R$ profiles during drier conditions (e.g. April – October, Fig. 1b). The parameterisation of $\lambda$, $\tau$, and $k$ should be carefully chosen to ensure that $E$ and $R$ profiles are physically representative (e.g. highest $E$ near the surface and $R$ similar to the root depth profile).
2.2 Estimation of water and mass balance

At scales smaller than catchments, the quantification of internal fluxes is more significant for tracer-based estimates of transit times. The fluxes at small scales are dominated by downwards vertical flows ($Q$) regulated by the soil structure and may contain mixing exchange ($J$) between water in faster and slower flowing domains (Gerke and van Genuchten, 1993; Sprenger et al., 2018b), evaporation ($E$), and root uptake ($R$). Each of these fluxes ($Q$, $E$, $R$, and $J$) likely change with depth and time due to soil properties and moisture conditions. Discretization of the soil water column into discrete soil layers of volume, $V(t,i)$, and soil thickness $\Delta z$, provides a series of water and mass balance estimations progressing downwards from the surface.

2.2.1 Assessment of fast and slow domain storage

The estimation of soil layer mass-balance using larger and smaller soil pore volumes and exchange between them may have a significant effect on the simulation of conservative tracers (Gerke and van Genuchten, 1993; Sprenger et al., 2018b). The definition of fast and slow flow domain in this theory differs slightly from previous studies (e.g. Sprenger et al., 2018b), here, the fast flow domain is defined as the volume of water in the soil layer which contributes to downward vertical fluxes, while the slow flow domain yields no vertical fluxes but sustains storage in the layer (Fig. 2). The separation of the fast and slow domain storages is obtained using the fluxes into and out of each soil layer:

$$\frac{\Delta V(t,i)}{\Delta t} = Q(t,i-1) - E(t) \cdot f_E(t,i) - R(t) \cdot f_R(t,i) - Q(t,i)$$

Figure 1: Evaporation (or root uptake) profiles from 1cm soil layers with a) an example time-invariant function (triangular distribution) and c) an example time-variant beta distribution (Eqs. 1 – 3) over the same period ($\alpha = 0.6$ and $\beta = 2$ and 7 for the green and blue curve respectively). The colour bars indicate a high (black) and low (white) contribution of soil depths to the total $E$ and $R$ fluxes. Discrete low moisture conditions (green) and high moisture conditions (blue) are shown as a profile with depth for b) the time-invariant function and d) time-variant beta distribution.
where $Q(t, i-1)$ is the flux coming into soil layer $i$ (from either precipitation or the soil layer above), and $Q(t, i)$ is the downward flux out of the soil layer. For the soil layer at the surface (i.e. $i=0$), $Q(t, i-1)$ is equal to the precipitation of the day. For each soil layer, the change in volume, $\Delta V(t, i)/\Delta t$, can be estimated as the change in measured soil moisture ($\Delta V(t, i)/\Delta t = \Delta \theta(t, i)/\Delta t$ per unit surface area). To simplify the water balance for each soil layer, the matric pressure is assumed to be sufficiently high to yield for free drainage to the next layer regardless of the saturation state (Nimmo, 2005). Using a combination of closing the water balance and predictor-corrector methods the fluxes for each soil layer and time-step are solved. With measured soil moisture ($\Delta V(t, i)/\Delta t$, $E$ and $R$ (and estimated $f_E$ and $f_R$), the water balance can be closed (i.e. solve for $Q(t, i)$) if the loss due to $E$ and $R$ in the layer is less than the net volume change to the layer (i.e. $E(t) \cdot f_E(t, i) + R(t) \cdot f_R(t, i) \leq Q(t, i-1) - \Delta V(t, i)/\Delta t$) (see Appendix B for more details). In all other cases, the predictor-corrector method is used by estimating $Q(t, i)$ using a power function fit to soil moisture and outflow relationship for each soil layer:

$$Q(t, i) = \sqrt{2 - b(i)} \cdot a(i) \cdot \left[\frac{V(t, i)}{\Delta t} - E(t) \cdot f_E(t, i) - R(t) \cdot f_R(t, i) + Q(t, i-1)\right]$$

Where $V_d(i)$, $a(i)$ and $b(i)$ are fitting parameters, which is similar to the change in hydraulic conductivity with soil moisture in unsaturated soils (Mualem, 1976). By the definition, the value of $b(z)$ must be less than 2 for a slow domain volume to exist.

Thereby, the maximum slow flow domain volume ($V_s(t, i)$) should be equal to $V_o(i)$ (with $\theta_o$ denoting the soil moisture of $V_o$).

The estimated $Q(t, i)$ is used to correct $E$ and $R$ for each soil layer to close the water balance relative to the measured soil moisture (see Appendix B for more details).

### 2.2.2 Estimation of the fast and slow domain water balance

The water balance of each layer (Eq. 4) may be used to estimate the fast and slow flow domains by parameterising the $E$ and $R$ profiles (Eq. 3), estimating the slow flow domain volume ($V_o$, Eq. 5), and determining the domain source (fast or slow flow domain) for $E$ and $R$ (Fig. 2). By the definition of slow flow domain here, there is no vertical flux ($Q(t, i)$) out of the slow flow domain and thereby no vertical flux into the slow flow domain (Fig. 2). The vertical fluxes ($Q(t, i)$) can be estimated with the water balance of each layer (Eq. 4), measured soil moisture ($\theta(t, i)$), and estimated $E$ and $R$ from the layer (Eqs. 1 – 3). Since incoming flow/precipitation replenishes only the fast flow domain, the slow flow domain is replenished from a lateral exchange ($L(t, i))$ with the fast domain. The water balance for the fast flow domain is:

$$\frac{V_f(t+1, i)}{\Delta t} = Q(t, i-1) - \frac{V_f(t, i)}{V(t, i)} \cdot \left[ E(t) \cdot f_E(t, i) + R(t) \cdot f_R(t, i) \right] - L(t, i) - Q(t, i) + \frac{V_f(t, i)}{\Delta t}$$

where $Q(t, i-1)$ and $Q(t, i)$ are estimated from Eq. (4), $f_E(t, i)$ and $f_R(t, i)$ are estimated from Eq. (1), and $V_f(t, i)$ is estimated as $V_f(t, i) = \max(\{V(t, i) - V_o\}, 0)$. The water balance for the slow flow domain is:

$$\frac{V_s(t+1, i)}{\Delta t} = L(t, i) - \left[ 1 - \frac{V_f(t, i)}{V(t, i)} \right] \cdot \left[ E(t) \cdot f_E(t, i) + R(t) \cdot f_R(t, i) \right] + \frac{V_s(t, i)}{\Delta t}$$

where $f_E(t, i)$ and $f_R(t, i)$ are estimated from Eq. (1) (same values as in Eq. 6), and $V_s(t, i) = \min(V(t, i), V_o)$. The lateral flux effectively replenishes the slow flow domain for losses from $E$ and $R$. In wet climates, $V(t, i)$ is likely always greater than $V_o$, therefore $\Delta V_s(t, i)/\Delta t = 0$ and there is no change in the slow flow domain volume. If $V_s(t, i) < V_o$, $V_s(t, i)$ cannot be greater than 0 and $L(t, i)$ is increased to remove excess $V_s(t, i)$ (i.e. $L(t, i) + V_s(t, i)$). An example of the water balance estimation for various soil conditions is shown in Appendix B.
2.2.3 Water age estimation with StorAge Selection functions

In typical StorAge Selection (SAS) function applications (i.e. at the lysimeter, hillslope or catchment scale), the water age is defined relative to the time precipitation input enters storage (initial age of zero days). The precipitation input is designated as a pulse function. The age of water leaving storage is defined by the elapsed time \( T \) water has spent in the model domain (Botter et al., 2011; van der Velde et al., 2012; Harman, 2015). For simplification, in the following equation, the age-ranked storage \( S_{T}(T,t,i) \) is shown as \( S_{T} \). With multiple soil layers, a similar approach is applied where \( S_{T} \) represents the storage of a single soil layer, ranked by the time it has spent in the layer (not ranked by \( T \), see Appendix C). For the fast flow domain, the age-ranked storage is distinguished as \( S_{f}(T,t,i) \) (shown herein as \( S_{f} \)) and slow flow domain age-ranked storage as \( S_{s}(T,t,i) \) (shown herein as \( S_{s} \)); therefore, \( S_{f} = S_{f} + S_{s} \). Herein, equations that are shown that apply to either the fast or slow flow domain are denoted with subscript d. Values of \( S_{T} \) (or \( S_{f} \) or \( S_{s} \)) represent the youngest cumulative sum of water in storage (e.g. \( S_{T}(T,t,i) = 100 \) mm, which indicates the youngest 100 mm of water in storage layer \( i \)). Incoming water is assigned as a pulse of water age 0 (new water to the soil layer) and ranked by the elapsed time it has spent in the layer. For soil layers not sharing a boundary with the surface, the downward flux has a total age evaluated as the sum of the elapsed times in the layers. Each inflow is additionally labelled with the mean age of the downward water from the layer above. For example, on \( t = 100 \) days there is a downward flux of water leaving the first soil layer with a mean age of 50 days. At \( t = 150 \) days the parcel of water in the second soil layer has an elapsed time in the second layer of 50 days, and a total age of 100 days \( (T) \) (an additional example is provided in Appendix C). Using this concept, the age-ranked storage of the model domain (soil depth \( 0 – Z \)) is the sum of \( S_{T} \) of each soil layer \( (S_{TZ}(T,t) = \sum_{i=1}^{n} S_{T}(T,t,i)) \). The relationship between the normalized fast and slow domain water age in

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**Figure 2:** Water balance approach used in this study, with downward flux in the fast flow domain and evapotranspiration in the fast and slow domain.
each layer \((N_f = S_f/V_f \text{ and } N_s = S_s/V_s, \text{ respectively})\) and the normalized water age of the soil profile \((N_{TZ} = \sum_{i=1}^{n} V(i))\)

provide an indication of water age storage under varying wetness conditions. The \(S_f\) from each flow domain and soil layer may also be used to aggregate the water of age \(T\) from all layers and domains to approximate the distribution of water ages of \(E\) and \(R\) from the model domain (soil depth \(0 - Z\)) (shown for \(E\) below):

\[
P_E(T, t) = \left( \sum_{i=1}^{N} \left( \frac{\Omega_E(S_F, t) \cdot V_F(t, i) + \Omega_E(S_S, t) \cdot \left(1 - \frac{V_f(t, i)}{V(t, i)}\right)}{V(t, i)} \right) \right) \cdot \frac{E(t) \cdot f_E(t, i)}{E(t)}
\]

where \(P_E\) (or \(P_R\)) is the distribution of water ages \((T)\) of \(E\) estimated at the surface from all of the soil domain and \(\Omega\) \((\Omega_E(S_F, t)\) or \(\Omega_E(S_S, t)\)) are the cumulative uniform SAS functions of \(E\) (or \(R\)).

In addition to the one-directional flux exchange between the fast and slow flow domain \((L(t,i))\), there may be some vapour exchange which is not measured with \(\theta_m\) (e.g. Criss 1999; Sprenger et al., 2018b). The vapour exchange results in an equalization of isotope mass in the fast and slow domain over long periods. The potential exchange between the fast and slow domain is introduced using a one-parameter linear diffusion flux term \((J(t,i))\), estimated with an exchange parameter, \(\xi\), and \(V_j(t,i) = \xi \cdot V_d(t,i))\). To ensure that there is no net volume change in either flow domain due to the diffusive flux, the volume of diffusive flux \((J(t,i))\) is equal and opposite between the domains, with the only difference occurring in the water age. The diffusive flux is introduced to equilibrate the mass of isotopes in the fast and slow flow domains rather than for volumetric balance. The exchange between the fast and slow flow domains with a linear diffusion term produces non-linear curves towards mass equalization similar to those produced with other physically based equations as described in Criss (1999) (e.g. linear diffusion in closed systems, Chapra, 1998). The governing equations of mass-balance using the cumulative SAS function \((\Omega(S_f,t))\) for the fast domain and \(\Omega(S_s,t)\) for the slow domain) are defined for the fast and slow flow domains, respectively:

\[
\frac{\partial S_f}{\partial t} = Q(t, i - 1) + J(t, i) \cdot \Omega_f(S_s, t) - J(t, i) \cdot \Omega_f(S_f, t) - L(t, i) \cdot \Omega_L(S_f, t) - Q(t, i) \cdot \Omega_Q(S_f, t)
\]

\[
\frac{\partial S_s}{\partial t} = L(t, i) \cdot \Omega_L(S_f, t) + J(t, i) \cdot \Omega_f(S_f, t) - J(t, i) \cdot \Omega_f(S_s, t)
\]

where the water age of each domain (fast and slow) is dependent on each other via the linear diffusion term \((J_f \text{ and } J_s)\) and subscripts \(f\) and \(s\) indicate exchange from the fast to slow flow domain, and slow to fast flow domain respectively. The definition of the form of the SAS function \((\Omega)\) used for each flux may substantially change the estimated water age and mass-balance of fluxes. For example, in comparison to a uniformly mixed flux, a young water dominated flux has a higher proportion of younger water movement and a lower proportion of older water movement.

### 2.2.4 Conservation of Mass

Similar to the governing mass-balance equations for water age (Eqs. 9 & 10), the mass of tracers can be estimated using SAS functions and by tracking and age-ranking the tracer mass of each input, as done with the age-ranked storage. When using the stable isotopes of water, the mass refers to the mass of a rare isotope (e.g. \(^2\)H or \(^18\)O). The rare isotopes are given as a ratio of the common isotope (e.g. \(^2\)H/\(^1\)H or \(^18\)O/\(^16\)O) and normalized against a standard (Vienna Standard Mean Ocean Water standard). The normalized ratios and are expressed in delta per mil (δ, %o) and termed isotopic compositions. Fractionation of stable isotopes during root uptake is generally assumed to be negligible (Ehleringer and Dawson, 1992) and soil isotopic compositions in each soil layer are unaffected by the root uptake flux. The influence of soil evaporation on isotopic
compositions is more complex because evaporation results in kinetic fractionation, thereby affecting the conservation of mass. To simplify the conservation of mass estimation, the conservation of mass was evaluated for the volume of each water age, \( T \), estimated by Eqns (9) and (10), where the volume of each age \( T \) is \( V_d(T,t,i) = S_d(T,t,i) - S_d(T-(T-\Delta t),t,i) \), in mm as with \( S_d \). The isotopic fractionation due to evaporation is estimated using the Craig-Gordon (1965) model for the volume of water in of each water age, \( T \), modified from Gibson (2002), evaluated in the soil layers affected by upward vapour loss (evaporative flux, Eqs. 1-3, Fig. 2):

\[
\delta_d(T, t + \Delta t, i) = \delta^* - (\delta^* - \delta_d(T, t, i)) \cdot \frac{m \cdot e_d(T,t,i)}{e_d(T,t,i) + e_d(T,t,\Delta t,i)}
\]

(11)

where \( \delta_d(T+t+\Delta t,i) \) is the isotopic composition of water age \( T \) at \( t+\Delta t \) in layer \( i \) and domain \( d \) (fast or slow), \( \delta^* \) is the limiting isotopic composition \( (\delta^* = (h \cdot \delta_A + e)/(h \cdot e/1000), \text{Gibson 2002}) \), \( \delta(T,t,i) \) is the isotopic composition at \( t \) in layer \( i \) and domain \( d \), \( m = (h - e/1000)/(1 - h - e/1000) \), \( h \) is the relative humidity, \( e_d(T,t,i) \), is the upward diffusive vapour loss of water age \( T \) at time \( t \) from layer \( i \) and domain \( d \) (from Eqs. 9 and 10), \( O_d \) is the remaining outflow of water age \( T \) at time \( t \) from layer \( i \) and domain \( d \) (eg. downward flow, root uptake, and lateral exchange, from Eqs. 9 and 10), and \( \epsilon^* \) and \( \epsilon_5 \) are equilibrium and kinetic fractionation, respectively (modified from Mathieu and Bariac, 1996 and Good et al., 2014 using \( \epsilon^* \) rather than \( \epsilon^* \) by the approximate relationship of \( \epsilon^* \approx \epsilon^* \), IAEA, 2013). The full derivation along with the atmospheric aerodynamic diffusion and soil relative humidity of the Craig-Gordon model modified for evaporation in soils is shown in Appendix D. In soils without direct evaporation, a simplified form of Eq. (11) can be used since fractionation does not occur:

\[
\delta_d(T, t + \Delta t, i) = \frac{\delta_d(T,t,i) \cdot \frac{\omega_d(T,t,i) \cdot V_d(T,t,i)}{\omega_d(T,t,i) \cdot V_d(T,t,i) + Q_{od}(T,t,i)}}{Q_{od}(T,t,i)}
\]

(12)

where \( Q_{od}(T,t,i) \) is the total inflow to layer \( i \) and domain \( d \) with water age of \( T \), and \( \delta_d(t) \) is the flux-weighted inflow of \( Q \) (derivation and example calculations shown in Appendix D). As the forms of Eqs. (11) and (12) only estimate the change in the isotopic composition of each water age (evaluated for each \( T \)) by the fluxes, the mean isotopic compositions of the fluxes and storages must also be estimated:

\[
\delta_{dQ}(t, i) = \int_0^{V_d} \omega_Q(S_d,t) \cdot \delta_d(S_d, t, i) \cdot dS_d
\]

(13)

for the downward flux, where \( \delta_{dQ} \) is the mean isotopic composition of the flux in domain \( d \) (fast or slow) at time \( t \) and layer \( i \), and \( \omega_Q \) is the SAS function used in Eqs (9) and (10), and for the mean isotopic composition of a soil layer (\( \delta(t,i) \)):

\[
\delta(t, i) = \frac{V_f(t,i)}{V(t,i)} \cdot \left( \int_0^{S_f} \frac{1}{S_f} \cdot \delta_f(S_f, t, i) \cdot dS_f \right) + \frac{V_s(t,i)}{V(t,i)} \cdot \left( \int_0^{S_s} \frac{1}{S_s} \cdot \delta_s(S_s, t, i) \cdot dS_s \right)
\]

(14)

where the integrals yield the weighted isotopic composition within the flow domain (fast or slow), and the isotopic composition of the soil layer is the weighted sum of the fast and slow domain isotopic compositions. The isotopic composition of \( R \) integrates the fluxes from the fast and slow domain as well as multiple soil layers. Modifying the equation used for estimating stream isotopes (as shown in Benettin et al., 2017), the estimation of the isotopic composition of \( R \) is:

\[
\delta_R(t) = \sum_{i=1}^{N} f_R(i,t) \cdot \left[ \frac{V_f(t,i)}{V(t,i)} \left( \int_0^{S_f} \omega_R(S_f, t) \cdot \delta_f(S_f, t, i) \cdot dS_f \right) + \frac{V_s(t,i)}{V(t,i)} \left( \int_0^{S_s} \omega_R(S_s, t) \cdot \delta_s(S_s, t, i) \cdot dS_s \right) \right]
\]

(15)

where \( \omega_R \) is the probability SAS function of \( R \) and the integration of \( \omega_R \cdot \delta \) is the isotopic composition of \( R \) from layer \( i \) (for each flow domain, fast and slow), and \( f_R(i,t) \) is the profile of \( R \) (Eq 1). The isotopic composition of \( R \) is weighted by the quantity of flux from the fast and slow domains and the volume of each age-ranked water age.
3 Model Application

3.1 Study Site

The depth-dependent SAS approach was applied to data collected from two sites representative of the dominant soil-vegetation (podzol-heather) units in the Bruntland Burn experimental catchment (3.2 km²) in the Scottish Highlands (Fig. 3). Continuous precipitation and hydroclimatic data for estimation of potential evapotranspiration were available, along with daily precipitation isotope samples, from October 2015-September 2016 to drive the model. The Bruntland Burn is energy limited, given the latitude (57° 8' N, 3° 20' E), with high annual relative humidity (> 80 %), resulting in low annual potential evapotranspiration ($ET$, ~ 400 mm yr⁻¹) (Tetzlaff et al., 2014). Annual precipitation is ~ 1000 mm yr⁻¹ with < 5 % snowfall. Previous hydrometeorological studies have partitioned $ET$ at these podzol-heather units into 56 % transpiration (root-water uptake) and 44 % total evaporation (interception and soil evaporation) (Wang et al., 2017). The dominant soils in the catchment are free-draining podzols, with rankers on the upper hillslopes and peat in the valley bottom (Fig. 3). Soil water isotope sampling and moisture measurements were conducted in two podzol profiles; one overlying sandy-silt drift (Site A), the other over coarse scree deposits (Site B). The soil profile has a high organic content, with a minero-genic component increasing below 10 cm. At each location, heather (Calluna sp. and Erica sp.) shrubs are the dominant vegetation with extensive shallow root systems and fine roots typically do not exceed 20 cm soil depth (Sprenger et al., 2017b). Soil moisture was continuously measured at 10, 20, and 40 cm depths, while bulk water samples were collected once per month within each plot at 2.5, 7.5, 12.5, and 17.5 cm depths, composite of 2.5 cm above and below each sample depth, providing a unique dataset covering markedly contrasting wetness conditions. Soil samples (~ 100 g) were taken to the laboratory and water vapour was sampled for isotope analysis by the direct equilibration method (see full details in Sprenger et al., 2017a). Heather xylems samples were collected as cut twigs from the vegetation bimonthly during the growing season, and water was cryogenically extracted (Gerais et al., 2017). Replicate soil water and xylem samples (ns = 5) were taken for each depth and plant material. These, along with the daily rainfall samples, were analysed for $\delta^2$H and $\delta^{18}$O values using an off-axis Integrated Cavity Output Spectroscopy (OA-ICOS) (Triple Water-Vapor Isotope Analyzer TWIA-45-EP, Model#: 912-0032-0000 Los Gatos Research, Inc., USA) running in liquid mode with a precision of ± 0.4 ‰ for $\delta^2$H and ± 0.1 ‰ for $\delta^{18}$O as given by the manufacturer. In addition to $\delta^2$H and $\delta^{18}$O, line-conditioned excess (lc-excess) was used to interpret the isotopic compositions in each soil layer. Lc-excess (lc-excess = $\delta^2$H – SL*$\delta^{18}$O - INT) is a measure of the Euclidean distance of a single isotopic sample (of coordinates $\delta^2$H and $\delta^{18}$O) from the regression of the local meteoric water line (LMWL, linear regression of precipitation $\delta^2$H and $\delta^{18}$O, SL = slope, and INT = intercept; Landwehr and Coplen, 2006). Negative lc-excess values indicate kinetic fractionation effects (i.e evaporation) whereas lc-excess > 0 indicates differing sources of precipitation. Since lc-excess is derived from precipitation isotopic compositions, the seasonal variability of precipitation compositions is not explicitly observed in soil water lc-excess values. Lc-excess is very sensitive to changes in $\delta^2$H and $\delta^{18}$O, and a slight bias of $\delta^2$H and $\delta^{18}$O (e.g. over-estimation of $\delta^2$H and underestimation of $\delta^{18}$O) can result in large changes in lc-excess.

3.2 Model set-up and calibration

3.2.1 Soil profile water balance, structure, and input data

All simulations of soil water balance, water age, and isotopic composition were run on a daily time-step using precipitation, temperature, relative humidity, and potential evapotranspiration (PET) collected at a weather station located between the two sites (weather station location on Fig. 3). The initial water age of the soil water storage was set to the same age for all soil layers. To ensure that water older than the simulation did not influence the results, a year-long spin-up period was used prior to the start of the simulation. The potential evapotranspiration and the partitioning into $E$ and $R$ were estimated using the Penman-Monteith and the maximum entropy production methods, respectively (values used from Wang et al., 2017).
rooting depth of 20 cm for both sites and the limit of soil water isotope sampling (20 cm) were used to prescribe the bottom boundary of the modelled soil profile. Since the soil water samples were comprised of aggregated depths (i.e. soil at 5 cm includes soil sampled between 0 – 5 cm), the modelled soil profile was discretized into 5 cm depths for the modelled soil layers (Δz = 5 cm). From the surface, the layers are herein referred to by the mean soil depth of each layer, 2.5 cm (0 – 5 cm), 7.5 cm (5 – 10 cm), 12.5 cm (10 – 15 cm), and 17.5 cm (15 – 20 cm). To conduct the water balance at 2.5 and 12.5 cm, the measured soil moisture at 10, 20, and 40 was used to construct a spline extrapolation and interpolation, respectively. The water balance in the fast and slow flow domain was solved for each layer by defining evaporation to occur only from the fast flow domain. For wet soils, similar to those observed throughout the year in Scottish catchments, evaporation predominantly occurs in soil pores with lower resistances (Yan et al., 2012), consistent with the definition of the fast flow domain here. Temporal variability of evaporation to soil moisture was considered due to the observed soil water fractionation at soil depths below the upper 5 cm, potentially indicating fractionation below the upper soil layer (Figs. 3c and d). For the root-water uptake, the use of a multi-source mixing model for estimating the root-water uptake sources (Appendix E; Eq. E.1; Fig. E.1; Rothfuss and Javaux et al., 2017) indicated that the bulk water isotope of soils were able to reasonably reproduce the xylem water while closely following the root-distribution. The replication of bulk water isotopes to produce the measured xylem water indicates that root uptake water sources involve both the fast and slow flow domain. In each layer, $R_f(t, i)$ was equally proportioned by the ratio of water in the fast and slow flow domains (Eqs (6) and (7)). The estimation of the water balance (including Q, E, and R fluxes) was conducted using the method in Appendix B. The multi-source mixing model additionally revealed temporal variability of the root uptake profile from the soils, confirming the use of temporally variable parameterization of the $R$ profile (Appendix E, Eq. E.1, Fig. E.1). Parameterization of $E$ and $R$ profiles (Eqs. 1-3, $k_E$, $\lambda_E$, $\tau_E$, $k_R$, $\lambda_R$, and $\tau_R$) were restricted to imitate the shape of the rooting density profile through all soil moisture conditions (> 50% of $R$ in the upper 10 cm), and similarly highest $E$ (>50%) occurring in the upper 10 cm for all soil moisture conditions. Values of $\lambda$ are positive for all simulations to best emulate evaporation and root uptake conditions. For example, under wet conditions evaporation likely originates from the surface while during dry condition evaporation may originate below the surface (e.g. 5 cm). Parameters influencing the water balance are shown in Table 1.

<table>
<thead>
<tr>
<th>Flux</th>
<th>Calibrated parameters</th>
<th>Parameter function</th>
<th>Parameter Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation</td>
<td>$k_E$ [-]</td>
<td>Beta shape parameter: changes the profile of evaporation from the soil depth as a function of soil moisture</td>
<td>[0.1, 2]</td>
</tr>
<tr>
<td></td>
<td>$\lambda_E$ [-]</td>
<td>Slope of linear function using soil moisture</td>
<td>[0, 5]</td>
</tr>
<tr>
<td></td>
<td>$\tau_E$ [-]</td>
<td>Intercept of the linear function using soil moisture</td>
<td>[1, 6]</td>
</tr>
<tr>
<td>Root uptake</td>
<td>$k_R$ [-]</td>
<td>Beta shape parameter: changes the profile of root uptake from the soil depth as a function of soil moisture</td>
<td>[0.1, 2]</td>
</tr>
<tr>
<td></td>
<td>$\lambda_R$ [-]</td>
<td>Slope of linear function using soil moisture</td>
<td>[0, 5]</td>
</tr>
<tr>
<td></td>
<td>$\tau_R$ [-]</td>
<td>Intercept of the linear function using soil moisture</td>
<td>[0, 1.8]</td>
</tr>
<tr>
<td>Diffusion</td>
<td>$\xi$ [-]</td>
<td>Linear diffusion rate of exchange between the fast and slow flow domains</td>
<td>[0.001, 0.1]</td>
</tr>
</tbody>
</table>

### 3.2.2 Functional forms and parameterisation of SAS functions

The simulation of water age (Eqs. 9, 10) and isotopic composition (Eqs. 13, 14) is accomplished by updating the age-ranked storage and isotopic composition in the fast and slow domains at each time-step using inflow and outflow. Water ages and isotopic composition are solved for each soil layer proceeding downward. The functional form of the cumulative SAS functions ($\Omega$) in Eq. (9) and Eq. (10) is fundamental to the estimation of water age. The SAS function may vary from young water- to old water-dominated. In relation to a uniform distribution (dominance of water age equal to water volume, $S_T/V$),
young water-dominated has a higher proportion of younger water and a lower proportion of older water. The beta distribution is one of the most versatile distributions since it may imitate the shapes of other distributions, and was therefore used to identify young- and old-water dominated flow paths. As the beta distribution is defined on the interval [0, 1] and fluxes are evaluated with age-ranked storages (Eqs. 9 and 10), the age-ranked storages of \( S_f \) and \( S_s \) should be normalized by \( V_f \) and \( V_s \), respectively, (e.g. \( S_f(T, t, i)/V_f(t, i) \) and \( S_s(T, t, i)/V_s(t, i) \)) to yield volume ratios for each water age, \( T \), between zero and one. Other SAS function studies have shown the significance of incorporating a non-uniform distribution for water fluxes of vertical soil water movement (Kim et al., 2016). A similar approach was therefore applied in which a parameterized form of the beta distribution was used for downward flow (\( Q(t, i) \)). The beta distribution for downward flow (\( Q(t, i) \)) has two shape parameters (\( \alpha \) and \( \beta \)). Similar to the approach taken with other studies (e.g. Harman, 2015), \( \beta \) was allowed to vary linearly with respect to soil moisture (i.e. storage) while \( \alpha \) was held temporally constant. The linear variability was incorporated with two parameters, \( \lambda \) and \( \tau \) (\( \beta = \lambda \cdot N(\theta_m(t)) + \tau \)), where \( \lambda \) is a slope parameter and \( \tau \) is an intercept parameter. The calibration parameter ranges are shown in Table 2 (\( \lambda \) parameter range is inclusive of 0). An additional, separate calibration was conducted by restricting the SAS function to time-invariance by \( \beta = \tau \). At each site, the similarities of the soil matrix characteristics with depth suggested that the downward flux SAS function parameters (i.e. \( \alpha, \lambda, \) and \( \tau \)) may be similar for each depth but different between Site A and Site B. Therefore the values of \( \alpha, \lambda, \) and \( \tau \) were kept constant between each soil layer. For all simulations, the value of \( \alpha \) was limited to a minimum value of 0.5 due to errors in numerical convergence when \( \alpha \) was less than 0.5. The use of non-uniform mixing for vertical flow builds off of the uniform mixing assumption previously used in the catchment (Sprenger et al., 2018b). Similar to other two-pore domain studies (e.g. Sprenger et al., 2018b), the assumed mixing between the fast and slow flow domain (\( J \) or \( L \)) was uniform (uniform SAS function) (e.g. \( \omega = S_f/V_f \) for the fast flow domain). The uniform mixing SAS function yields no additional parameterization (Table 2). Additionally, consistent with other studies, \( E \) and \( R \) water age mixing is conducted with a uniform mixing approach (uniform SAS function). Besides the consistency with other studies, there is insufficient information to parameterize both the \( E \) and \( R \) profile with a SAS function, and estimations of the \( R \) profile with uniform mixing (Appendix E) provide a reasonable approximation of the water source.

### Table 2: SAS function parameters and calibration parameter range for all fluxes in Figure 2.

<table>
<thead>
<tr>
<th>Flux</th>
<th>SAS function (variant/invariant)</th>
<th>Parameters</th>
<th>Parameter Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge</td>
<td>Time-variant beta distribution</td>
<td>( \alpha )</td>
<td>[0.5, 5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \lambda )</td>
<td>[-5, 5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \tau )</td>
<td>[0.1, 4]</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Time-invariant uniform distribution</td>
<td>[*]</td>
<td>[*]</td>
</tr>
<tr>
<td>Root Uptake</td>
<td>Time-invariant uniform distribution</td>
<td>[*]</td>
<td>[*]</td>
</tr>
<tr>
<td>Lateral flux</td>
<td>Time-invariant uniform distribution</td>
<td>[*]</td>
<td>[*]</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Time-invariant uniform distribution</td>
<td>[*]</td>
<td>[*]</td>
</tr>
</tbody>
</table>

### 3.2.3 Model calibration and evaluation

Simulations of \( \delta^2 \)H, \( \delta^{18} \)O, and line-conditioned excess (lc-excess) were conducted by varying the downward flow SAS function parameters (\( \alpha, \lambda, \tau \), \( E \) and \( R \) profile parameters (\( k_E, \lambda_E, t_E, k_R, \lambda_R, t_R \); Eqs. 1-3), and the diffusion parameter (\( \xi \)). The diffusion and SAS function parameters were assumed to be the same for each soil layer. The simulations of \( \delta^2 \)H, \( \delta^{18} \)O, and lc-excess were calibrated at each depth (2.5, 7.5, 12.5, and 17.5 cm) and for root uptake water against the bulk soil water samples and xylem water samples on each sample day. To test the sensitivity of the model parameters, Morris sensitivity analysis was
conducted for the parameters ($\alpha$, $\lambda$, $\tau$, $k_E$, $\lambda_E$, $\tau_E$, $k_R$, $\lambda_R$, $\tau_R$, and $\xi$) using root mean square error with 10 radial point trajectories (Appendix F, Soheir et al., 2014).

The Nash-Sutcliffe criteria (NSE, Nash and Sutcliffe, 1972) was used to best address the isotopic variability in the near-surface soil waters. The replicate samples (ns = 5) resulted in differing ranges of isotopic composition for a given sampling day, fluctuating from 4.5‰ in drier conditions to 44.5‰ in wet conditions for $\delta^2$H. Due to the high temporal variation of replicate sample ranges, using the mean value for calibration may not best represent the measured soil isotopic compositions. Studies have utilized temporally varying uncertainty in modelling results by directly incorporating the measurement uncertainty via a correlation matrix (e.g. Kupfel et al., 2013). A similar approach was applied by modifying the NSE to incorporate the uncertainty and variability of the replicate samples of soil and xylem samples into the evaluation metric:

$$\text{NSE}_{\text{adj}}(i) = 1 - \frac{\sum_{t=1}^{e} \left(1 - \frac{p(\delta(t,i)|\mu_m(t,i),\sigma_m(t,i))}{p(\mu_m(t,i)|\mu_m(t,i),\sigma_m(t,i))} \cdot (\delta(t,i) - \mu_m(t,i))\right)^2}{\sum_{t=1}^{e} (\mu_m(t,i) - \bar{\mu}(t,i))^2}$$

(16)

where $\mu_m(t,i)$ is the mean measured isotopic composition at time $t$ and soil layer with depth $i$, $\bar{\mu}(t,i)$ is the mean of $\mu_m(t,i)$ through all time-steps, $\sigma_m(t,i)$ is the standard deviation of isotopic compositions at time $t$ and soil layer depth $i$, $\delta(t,i)$ is the simulated isotopic composition at time $t$ and soil layer depth $i$, $p$ is a Gaussian probability distribution with a mean of $\mu_m(t,i)$ and standard deviation $\sigma_m(t,i)$, and $\epsilon$ is the length of the simulation. The simulated composition, $\delta(t,i)$, is evaluated within the Gaussian distribution with respect to the $\mu_m(t,i)$ and $\sigma_m(t,i)$ and normalized between zero and one using the probability of the distribution evaluated at $\mu_m(t,i)$. On days with high measurement uncertainty (e.g. range of $\delta^2$H = 44.5‰), $\sigma_m(t,i)$ is large and the deviation of $\delta(t,i)$ from $\mu_m(t,i)$ on the efficiency criteria has less weight. Calibration consisted of 50,000 Monte Carlo simulations, and NSE$_{\text{adj}}$ was evaluated for simulated for $\delta^2$H, $\delta^{18}$O, and le-excess values in each soil layer and in xylem water. The Monte Carlo simulations were ranked using the NSE$_{\text{adj}}$ for all measurements ($\delta^2$H, $\delta^{18}$O, and le-excess for 2.5, 7.5, 12.5, and 17.5 cm soil water, and xylem) and normalized scores (from Ala-Aho et al., 2017a). The normalized scores ($y$) were developed for each efficiency criterion with the largest NSE$_{\text{adj}}$ resulting in a value of one ($y = \text{NSE}_{\text{adj}}/\text{max(NSE}_{\text{adj}})$). The parameter sets were ranked by iteratively solving the union of events:

$$\text{Nu}(Y) = \left(\prod_{i=1}^{5} \prod_{j=1}^{3} y_{ij} (Y \leq y)\right) / 100$$

(17)

where Nu(Y) is the fraction of samples with normalized scores greater than $Y$, $i$ is the layer and xylem simulations (e.g. layer: 1, 2, 3…xylem), and $j$ is the simulation output (i.e. $\delta^2$H, $\delta^{18}$O, or le-excess). The value of $Y$ is sequentially increased by increments of 0.01 (dNu(Y)/dY = 0.01). Under these conditions, the largest value of $Y$ (Eq. 17) will yield Nu(Y) = 1 and the smallest value of $Y$ will yield Nu(Y) = 0.01. The 100 best simulations using Eq. (16) were retained while ensuring a minimum efficiency criteria threshold ($\text{NSE}_{\text{adj}} \geq 0.4$) for $\delta^2$H, $\delta^{18}$O, and le-excess simulations for all layers (2.5, 7.5, 12.5, and 17.5 cm) and root uptake.

The uncertainty of model simulations of water ages and isotopic compositions was assessed for each soil layer and for root uptake and evaporation using a variation on the GLUE methodology. At each time-step, a weighted kernel density function (Guillamon et al., 1998) was developed using the 100 “best” calibration parameter sets for median water age and isotopic composition. With a smaller sample size (100 simulations), the weighted kernel density estimation provides an approximation closer to the actual probability density than the weighted eCDF shown in the GLUE method (Beven and Binley, 1992). Similar to the GLUE method, the probability function was weighted by a likelihood function (N(X)), which provides greater weight to the highest-ranked simulations. The uncertainty bounds were determined using the 95% bounds of the estimated...
kernel density function for each day. For water age, the shape of the kernel density function (probability density form) evaluated on each day, is shown to visually depict the occurrences of simulated water age. The kernel density approach helps to visually identify daily changes in the shape of the uncertainty distribution (comparison of tails and maximum probability).

4 Results

4.1 Temporal dynamics of soil water isotopes

For each site, the partitioning of the fast and slow flow domains using the storage-discharge equation (Eq. 5) indicated a higher proportion of water stored in the fast flow domain in the upper 10 cm, and a higher proportion of water stored in the slow flow domain at greater depths (Fig. 3a and b). Comparisons of the downward fluxes from the fast domain in each layer to simulations conducted with HYDRUS 1-D (Sprenger et al., 2018b) show similar net exchange throughout the simulation period (Fig. B.1). Generally, the greatest uncertainty of this partitioning occurs within the upper 5 cm of the soil, which is dominated by organic matter in the O horizon. Soil water isotope samples generally plot along the LMWL throughout the year (Fig. 3c and d). However, water in the upper 10 cm significantly (p <0.05) deviates below the LMWL (e.g. negative lc-excess) during the spring and summer periods indicating evaporative enrichment (Fig. 3e). Soil waters below 10 cm did not generally deviate from the LMWL (p> 0.05). The deviation of δ²H and δ¹⁸O from the LMWL and the degree of variability of was also observed to change with depth, where near-surface soils had the highest variability (box plots, Fig. 3c and d). Soil water isotopic compositions at both sites were lower during large winter precipitation events in December 2015 and January 2016, though soil isotopic compositions remained above the LMWL (positive lc-excess) as did the precipitation isotopic compositions (Fig. 5a). Xylem samples generally plotted significantly below the LMWL (95% confidence), similar to the upper 10 cm soil samples (Fig. 3e). This is consistent with the higher rooting densities of heather within the upper 10 cm relative to the top 20 cm soil profile, suggesting the upper 10 cm soil water is the main source of plant water (Fig. 3a and b).
Figure 3: The location of the two sites and weather station in the Bruntland Burn. Plots (a) and (b) show the estimated proportions of fast (green) and slow (grey) flow domain water for each depth (shaded areas), the measured fine root densities of heather (red line, Sprenger et al., 2017b), and soil moisture below the heather (blue line) for Site A and Site B, respectively. The black dashed lines on (a) and (b) show the uncertainty on the estimation of $\theta_o$, smoothed between the mid-layer estimations (2.5, 7.5, 12.5, and 17.5 cm). Subplots (a) and (b) also show the average soil moisture with depth at Site A and B. Plots (c) and (d) show the dual-isotope space for each location for 2.5 cm (●), 7.5 cm (■), 12.5 cm (▲), 17.5 cm (♦), and xylem (★) waters colour coded in time (blue show the earliest samples and red show the oldest) or site A and B, respectively, and (e) shows the mean sign of the lc-excess (− or +), with * indicating a significant deviation from the LMWL.
4.2 Model parameter evaluation

The distributions of calibrated parameters were generally consistent between the two sites (Fig. 4); although some deviation between sites was apparent with the downward flow SAS function parameters ($\alpha$, $\lambda$, and $\tau$) and root uptake with depth parameter ($k_R$). Sensitivity analysis revealed that these parameters were also the most sensitive calibration parameters (Fig. F.1). The mean of the distribution of $\alpha$ at Site B was on average slightly higher than 1 (approaching Gaussian distribution shape of the beta distribution) and Site A was on average slightly lower than 1 (more representative of exponential distribution shape). The sites differed with the calibration of $\lambda$ (amount of temporal variability of the SAS function) with Site A showing more temporal variability (larger $\lambda$). With a smaller value of $\tau$ and larger $\lambda$ at Site A (Eq. 3), the temporal variability of the SAS function is much larger than at variant parameter for the downward flow SAS function ($\lambda$) did not approach zero at either site, which indicates preference of the calibration to utilize the time-variance of soil storage to describe the changes in isotopic composition. While there is a mild bimodal distribution tendency of $\lambda$ at both sites (Fig 4), there were very few simulations with $\lambda$ less than zero and the simulations showed less temporal variability in simulated soil isotopic compositions (not shown). Comparison of time-variant calibration to time-invariant calibration showed noticeable differences in model performance (shown with Akaike Information Criteria) particularly with the under-estimation of $\delta^{2}H$ at Site B (NSE$_{adj} \geq 0.1$, Appendix G, Fig. G.1).

![Estimated posterior probability distributions of the model parameters](image)

Figure 4: Estimated posterior probability distributions of the model parameters for the 100 best time-variant simulations at Site A and B (red and blue lines, respectively) for the soil SAS shape parameter ($\alpha$), soil SAS temporal variability parameter ($\lambda$), soil SAS constant ($\tau$), $E$ and $R$ profile parameters ($k_E$, $\lambda_E$, $\tau_E$, $k_R$, $\lambda_R$, $\tau_R$), and diffusive flux parameter ($\xi$).

While some temporal variability was estimated for both evaporation and root uptake profiles ($\lambda_E$ and $\lambda_R$, Fig. 4), the low values of $k_E$ (both Sites) and $k_R$ (Site B only), restrict the amount of variability with depth. The greatest difference in the parameter calibration of the two sites was for the $k_R$ and $\tau$ parameters. Site B showed very high sensitivity to values of $k_R < 0.5$,
representing a high preference of root uptake water near the surface (beta distribution scale parameter). Conversely, Site A showed low sensitivity to $k_R$, with a higher distribution of parameters near three.

4.3 Simulated isotopes in soil and xylem water

Stable water isotopes in precipitation at the sites were highly variable during the study year, ranging from -170 to 0 ‰ for $\delta^{2}H$ and from -15 to 15 ‰ for lc-excess (Fig. 5a). Much of the variability occurred during large precipitation events between December 2015 and January 2016. Simulations of $\delta^{2}H$ and lc-excess generally captured the measured dynamics for each variable within each of the soil layers of the two profiles and replicated the greatly damped isotopic variability relative to the precipitation (Fig. 5b - i). The mean NSE$_{adj}$ of $\delta^{2}H$ (lc-excess) in soils (2.5, 7.5, 12.5, and 17.5 cm) was 0.75 (0.51) and 0.53 (0.34) for Site A and B, respectively. The most notable deviation of the simulation from measured composition was the 2015/2016 event for the upper 5 cm soil layer, where the simulations were more enriched than the measured isotopic composition. The simulated lc-excess followed the general trend of the measured signal, with higher lc-excess during the winter and lower lc-excess during the summer. However, the simulated lc-excess had much narrower uncertainty bounds relative to the range of the lc-excess derived from measured daily replicate samples (Figs. 5b - d, 5f - h). There were some deviations of the simulations from the measured lc-excess which occurred primarily during the winter months. Similar to $\delta^{2}H$, the simulated lc-excess during the 2015/2016 event at Site A was over-estimated. However, the simulated lc-excess moved in the direction of the precipitation lc-excess of the large event (above zero). Lastly, both sites show some under-estimation of the lc-excess in deeper soil layers (17.5 cm, Fig. 5d and h) during the winter months. The high measured lc-excess during these months was not observed in any of the soil layers above (2.5-12.5 cm) throughout the study period.
Simulated xylem water originating from the upper 20 cm was able to capture the majority of measured xylem δ²H and lc-excess as a function of soil moisture conditions (Fig. 5e and i). Xylem water compositions not captured by the simulation were similarly not explained using the soil measurements (Appendix E, Fig E.1). Measured and simulated xylem waters (δ²H) were both less variable than the near-surface waters (5 cm) despite the high percentage of fine root densities in the upper 5 cm (Fig. 3a and b). The simulations of xylem lc-excess were able to capture the bounds of the measured lc-excess; however, the daily mean measured lc-excess was much more variable than the simulation (either for xylem or soil waters). Some deviation of the simulations from the measurements occurred in mid-June 2016 (δ²H), where measurements revealed much more depleted water in the bulk soil water of any of the soil layers. As such, the simulations of root uptake water δ²H, which are dependent on the soil water δ²H, were unable to capture the measured depletion of δ²H. Similarly, some of the lc-excess measurements of root uptake water were more negative than the measured soil water lc-excess.

Figure 5: (a) Rainfall amount and isotopic composition for the study period. (b) 95% confidence bounds for simulated δ²H and lc-excess at 2.5, 7.5, 17.5 cm and xylem waters with time-variant SAS function calibrations.
4.4 Temporal variability of soil water and percolation water ages

The variability of soil moisture storage was site-dependent, reflecting the different subsurface drainage properties and the resulting soil moisture profile at each site (Fig. 6a). These differences in drainage properties and soil moisture distributions were reflected in the simulated median water ages for the soil layers at each site (Fig. 6b and d). At both sites, median water ages in storage were on average < 200 days for all depths in both the fast and slow flow domain, with restricted periods (notably in the drier spring of 2016) where median water ages in some depths were greater than 200 days. For both sites, median water ages in the slow domain were, on average, greater than those in the fast domain, and showed less temporal variability. Median water ages in each soil layer generally increased with depth at Site A, which was most apparent in the slow domain (Fig. 6b). The median soil water ages at the more freely draining Site B were generally younger than those at their equivalent depths at Site A (Fig. 6d). For Site A at 2.5, 7.5 and 17.5 cm, the fast domain was significantly younger than the slow domain through 58, 51, and 89% of the simulation period, respectively (Appendix H, Fig. H.1). Conversely, the fast and slow domain at 2.5, 7.5, and 17.5 cm for Site B were significantly different through 91, 68, and 79% of the simulation period, respectively. The younger soil water ages at Site B were also characterised by much larger variability. For both sites, the mean age of water retained in the top 20 cm was markedly older than the ages of fluxes leaving as percolation from the soil profile (bottom of Fig. 6b and d). The outflow of the soil profile was different for each site, where Site B had, on average, younger water than Site A moving towards groundwater recharge. The water ages of outflow were also more variable at Site A than Site B, with multiple days of median outflow age > 25 days.

Figure 6: (a) Measured soil moisture at 10 and 20cm for Site A and Site B. (b) Median water ages in the fast and slow domain for Site A at 2.5, 7.5, and 17.5 cm and outflow from 17.5 cm, shown with daily kernel density functions (red is high probability, blue is low probability). (c) The estimated relationship between layer residence age and the soil profile residence ages for each flow domain and depth at Site A, averaged for the 5 highest (HM) and 5 lowest (LM) moisture conditions. (d) Median water ages in the fast and slow domain for Site B at 2.5, 7.5, and 17.5 cm and outflow from 17.5 cm. (e) The estimated relationship between layer residence age and the soil profile residence age for each flow domain and depth at Site B, averaged for the 5 highest (HM) and 5 lowest (LM) moisture conditions.
To best highlight the relationship between fast (or slow) domain residence age \( (N_d(t,i) = S_d/V_d) \) and the soil profile residence age \( (N_{TZ} = S_{TZ}/V_{TOT}) \), the ratio of \( N_d(t,i) \) to \( N_{TZ} \) is used to infer the proportion of water age \( T \) from the soil profile present in each soil depth (Fig. 6c and e). \( N_d(t,i)/N_{TZ} > 1 \) indicates a higher proportion of water age \( T \) in the flow domain storage relative to the soil profile water age, while \( N_d(t,i)/N_{TZ} < 1 \) indicates a lower proportion of water age \( T \) in the flow domain storage relative to the soil profile water age. The ratio \( (N_d(t,i)/N_{TZ}) \) showed a dominance of the youngest water in the modelling domain (0 – 20 cm) in the upper soil layer fast flow domain storage (Fig. 6c and e), although a greater dominance of young water in the upper soil layer relative occurred at Site A (Fig. 6c). Deeper soil water storages (at 17.5 cm) exhibited different ratios at Site A and B (Fig. 6c and e). The deepest soil layer at both sites showed younger water in the fast domain relative to the slow domain. The slow domain of 17.5 cm at Site A showed the highest occurrence of the oldest water (\( N_d \) ratios at Site A and B (Fig. 6c and e). The deepest soil layer at both sites showed younger water in the fast domain relative to the soil profile water age. The ratio \( (N_d(t,i)/N_{TZ}) \) showed a dominance of the youngest water in the modelling domain (0 – 20 cm) in the upper soil layer fast flow domain storage (Fig. 6c and e), although a greater dominance of young water in the upper soil layer relative occurred at Site A (Fig. 6c). Deeper soil water storages (at 17.5 cm) exhibited different ratios at Site A and B (Fig. 6c and e). The deepest soil layer at both sites showed younger water in the fast domain relative to the slow domain.

4.5 Evaporation and root uptake water profile and ages

The \( E \) and \( R \) fluxes were quite similar between sites, with slightly higher \( E \) at Site A relative to Site B (Fig. 7a and b). Calibration of flux profiles (\( k_E, \lambda_E, \) and \( \tau_E \), Eqs. 1 – 3) resulted in high estimates of near-surface \( E \) flux at both sites (Fig. 7c and d). While \( \lambda_E \) was relatively insensitive and had values much greater than 0 (indicating time-variance of the evaporation profile), simulations for both sites indicated that the \( E \) profile was relatively stable and occurred only in the upper 5 cm of the soil. The temporal insensitivity of the \( E \) profile occurred despite high values of \( \lambda_E \) due to the high influence of \( k_E \) which kept the highest probability of \( E \) profile in the upper 5cm through changing conditions over the year. The high proclivity of near-surface water for the \( E \) profile, as well as the random selection from water in the fast domain, resulted in similar median \( E \) ages to the median water ages of the fast domain in the upper 5 cm soil layer (Fig. 6b and d). During periods of reduced rainfall (spring 2016), the median age of \( E \) water increased for both sites (Fig. 7e and f). On average, the median \( E \) age was between 50 and 65 days.

The estimated profile of the \( R \) (parameters, \( k_R, \lambda_R, \) and \( \tau_R \)) showed temporal variability; during wet periods there was a higher selection of \( R \) near the surface soil whereas during drier periods the selection of \( R \) varied from a wider range of soil depths (Fig. 7g and h). In general, the profile of \( R \) at each site was relatively similar to the fine root densities measured (Fig. 3a and b). Slight deviations between Site A and Site B were noticeable throughout the year. At Site B, the \( R \) profile was greater in the upper 5 cm throughout the year and showed less temporal variability than Site A. A similar result for root uptake was obtained when using the measured isotopic compositions of soil water to estimate the measured xylem water (Fig. E.1). Similar to the effect of \( k_E \) for evaporation, the low estimated values of \( k_R \) for Site B limited the change in water profile over time. The profile of deeper soil water at Site A relative to Site B, and the older water at Site A, resulted in slightly greater estimates of median \( R \) age (79.9 ± 13.8 and 56.4 ± 8.9 days for Site A and B, respectively) relative to median \( E \) age. The differences between the median \( R \) age of the two sites were also statistically significant (95% confidence, 2-sided Student’s t-test, Fig. H.1). Similar to median \( E \) water ages, the median \( R \) water age was generally the oldest in the spring of 2016 (Fig. 7i and j), which coincided with the period of the least precipitation input (Fig. 5a). At Site A, the water ages of \( E \) and \( R \) were not significantly different during the winter months which resulted in a smaller proportion of the simulation period where the median \( E \) and \( R \) age were estimated profile of the soil, as well as the random selection from water in the fast domain, resulted in similar median \( E \) ages to the median water ages of the fast domain in the upper 5 cm soil layer (Fig. 6b and d). During periods of reduced rainfall (spring 2016), the median age of \( E \) water increased for both sites (Fig. 7e and f). On average, the median \( E \) age was between 50 and 65 days.

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significantly different (41%, Fig. H.1). Conversely, the water ages of $E$ and $R$ at Site B were significantly different through more than 90% of the simulation period.

Figure 7: Simulations and measurements of evaporation and root uptake at Sites A and B. (a and f) total soil evaporation and transpiration, (b and g) median simulated evaporation water age, (c and h) average probability of evaporation profile from depth, (d and i) median simulated root uptake water age, (e and j) average probability of root uptake profile from depth.

Assessing the depth-dependent $E$ and $R$ profiles with soil storage (Eq. 1) provided a novel opportunity to examine the water ages of $E$ and $R$ as a function of the water age in storage. While the SAS functions of $E$ and $R$ were assumed to be derived from uniform (random) sampling in each soil layer, the combination of temporal variability of the $E$ and $R$ profiles with the non-uniform recharge SAS function (Fig. 6c and e), provides potential for examining the temporal changes of water ages of $E$ and $R$ relative to the soil water ages. The upper and lower bounds were an accumulation of the $E$ and $R$ water age relationship with the soil water storage at both sites for all accepted parameter sets (Section 3.2.3). The relationships are shown as an average of the five highest soil moisture condition (red bounds), and five lowest soil moisture conditions (blue bounds) in the simulation (Fig. 8). Regardless of soil saturation, $E$ contained the youngest water in the soil modelling domain (0 – 20 cm) (Fig. 8a). This is consistent with the scarcity of temporal variability in the $E$ profile with the high proclivity of younger soil water in the near-surface soils (Fig 6). The relationship of $E$ water age to soil profile residence ages in the wettest conditions (red bounds, Fig. 8a) had relatively narrow upper and lower bounds relative to the lower soil moisture conditions (blue
The lower soil moisture conditions showed wide variability, from a very high preference for young water to a uniform sampling of water in storage (Fig 8a). The relationship of \( R \) water ages to the soil profile residence ages was slightly more variable with soil saturation, and showed a higher affinity for the median residence age of the soil profile (at \( N_{TZ} = 0.5 \)) under low soil moisture conditions (blue bounds, Fig. 8b), while there was a greater inclination for young water under higher soil moisture conditions (red bounds, Fig. 8b). Unlike the upper and lower bounds of the \( E \) water age-soil residence age relationship, the upper and lower bounds of the \( R \) water age-soil residence age relationship was relatively similar for both the wet and dry periods.

**Figure 8:** The relationship between (a) evaporation and (b) root uptake water ages to the soil profile residence age under the 5 highest soil moisture (red) and 5 lowest soil moisture (blue) conditions

**5 Discussion**

**5.1 Ecohydrologic controls on root uptake and evaporation from soils**

This study used a novel adaptation of StorAge Selection functions linked with stable water isotope data to help identify the profiles and ages of \( E \) and \( R \) from contrasting locations. This is an innovation which may: (a) help interpret physical mechanisms of root uptake and evaporation, (b) inform on the age preferences of fluxes at larger scales and (c) test hypotheses regarding the potential for ecohydrologic separation of “energetically available” water for uptake (McDonnell, 2014; Good et al., 2015; Brantley et al., 2017).

We observed only limited temporal differences between the evaporation profile from the two sites, while root uptake profiles had clear differences, corresponding to differences in the rooting profile and soil moisture at each site. The soils were relatively wet in the organic-rich near-surface horizons throughout the simulation period, which directly correlates to the highly dominant near-surface \( E \) (0 - 5 cm soils), consistent with other studies showing that measured soil \( E \) is limited to the near-surface under wet conditions (Sakai et al., 2011; Xiao et al., 2011). While it was assumed that deeper soil layers experienced limited evaporation, negative lc-excess was evident in both simulations and measurements, indicating a significant influence of the percolation of fractionated near-surface water to depth.

The root uptake profile was more temporally variable than evaporation; however, one site (Site A) showed noticeably more temporal variability to the root uptake profile, with a slightly more temporally consistent root uptake profile at the other site (Site B). The differences between the estimated root uptake profiles are likely the result of contrasting wetness conditions both temporally and with depth (Ogle et al., 2014; Volkmann et al., 2016; Barbeta and Peñuelas, 2017). Site B was characterised by much higher root uptake near the surface and was relatively constant throughout the year, which corresponds well to the more consistently wet near-surface soil layer, and more limited water availability at depth. Conversely, the time-variability of the
root uptake profile at Site A is likely the result of more significant soil surface drying relative to Site B, and the relatively high soil moisture availability with depth.

While the simulations reasonably capture the dynamics of the sampled xylem compositions, some limitations of the approach and model structure become apparent. This is reflected in the over-estimation of $\delta^2$H of xylem samples in June 2016. The limitations of the relationship between root uptake profile and soil moisture were met during this period since measured xylem composition was more depleted than the measured soil water isotopic composition. This divergence of soil water and xylem compositions (Fig. 5e and i; Fig D.1) may be due to a number of different conditions in the soils that were simplified in the estimated water balance. Some of these differences include (not limited to) the redistribution of soil water due to root water potential (Domec et al., 2010; Volpe et al., 2013) (e.g. upward flux of water from deeper soils) and upward soil water movement due to matrix potential and suction forces. Additional differences may be caused by methodological or biological differences, including the potential differences in the equilibrium and cryogenic extraction methods (for soil and xylem, respectively), or isotopic fractionation in the vegetation, similar to evaporation. There is growing evidence that xylem water may be subject to fractionation due to a wide range of biophysical processes that may obscure direct connections with soil water sources (Berry et al., 2017). Some of these biophysical processes may include: effects of evaporative fractionation on xylem isotopic compositions during summer months (Simonin et al., 2014), the potentially longer residence and transit times of water within the xylem (Brandes et al., 2007), or possible fractionation/discrimination of $^{18}$O and $^2$H during root-water uptake (Ellsworth and Williams, 2007; Vargas et al., 2017). While not a large concern in most shrubs, long residence times in larger vegetation (potentially over 20% of the year, Meinzer et al., 2006) may result in a mixed isotopic composition of root uptake integrated over numerous days.

The relationship of $R$ water ages to the soil residence age indicating young water during high soil moisture conditions and median soil residence age water during lower soil moisture conditions is a divergence from young water only SAS functions previously used for $ET$ (e.g. Harman, 2015). However, the young water age of $E$ relationship to the soil residence age has previously been observed in lysimeter studies (e.g. Queloz et al., 2015). The variability of $E$ water age was similar to that derived by other recent catchment-scale studies at the site (Soulsby et al., 2016; Kuppel et al., 2018) and recent physically-based modelling (Sprenger et al., 2018a). These approaches have all adopted similar model structures with uniform mixing of fluxes, only changed in this study with a non-uniform mixing (SAS function) for downward fluxes and show the youngest $E$ water ages during periods of high soil moisture. The modification of non-uniform mixing here resulted in a higher preference for younger water percolating, and a slightly older soil water age than complete mixing approaches and thereby slightly older water age of $E$ and $R$ than previous study estimations. The broad similarities of the variability of $E$ and soil water ages estimated with the SAS approach in this study, and the physically-based 1-D model approaches in the Bruntland Burn catchment (e.g. Sprenger et al., 2018a) provides some additional “soft” validation of the SAS function approach to estimating soil water and flux ages.

While the shape of the relationship of $E$ or $R$ water age to the soil profile residence age is dependent on the defined model domain, the $E$ and $R$ water ages on larger scales (e.g. catchment scales) can be inferred from the trends of the soil water ages and $E$ and $R$ profiles from depth. Catchment-scale approaches do not define a set soil depth, and the water age within the catchment can reach several years to explain base flow composition (average of ~3 years in the Bruntland Burn; Benettin et al., 2017). When considering the deeper soils in the $E$ or $R$ to soil residence age relationship at the catchment-scale, older groundwater will lengthen the “tail” of the distribution (Fig. 8). During high moisture conditions, the shape of the SAS function for $E$ and $R$ will likely shift towards an exponential shape used in previous studies (e.g. Harman, 2015; Queloz et al.,
The method has potential applicability to testing multiple hypotheses of ecohydrological separation and water mixing, including different degrees of partial mixing. Using matric potential (e.g., Sprenger et al., 2018b) may possibly further constrain simulations of the isotopic composition of the fast domain, with the aided calibration tool of suction lysimeter samples. However, the soil type may influence the lysimetric (fast flow) isotopic compositions (Vargas et al., 2017) and measurement methods need careful consideration. Additionally, hypotheses on different profiles of evaporation and root uptake (e.g., fast domain only, slow domain only, proportional mixing of the fast and slow domain, etc.) can be tested to help explain differences in xylem water while also assessing how each hypothesis would affect the isotopic composition of residual soil water. The relatively high sensitivity of soil water isotopes to root uptake profile parameters suggests that there may be a significant influence on the mixing of soil water from different degrees of ecohydrological separation.

While the mixing approaches that are applied in this study (i.e., uniform SAS functions for $E$, $R$, $L$, and $J$) are consistent with other non-SAS based soil study approaches, further testing of different SAS functions would be potentially useful. Calibration using different SAS functions would likely result in differing water ages to those shown in this study. For example, if a predominantly young-water SAS function (exponential distribution) is applied for the other fluxes (in addition to $Q$) the water ages of storage as well as the downward flow would likely increase. Conversely, the age of the other fluxes would decrease relative to the uniform SAS function age estimation. However, a significant amount of soil data (fast and slow domain isotopic samples and percolation isotopic samples), coupled with an assumption of time-invariant $E$ and $R$ profiles, would be necessary to fully test different SAS functions for each flux. An additional consideration of a different parameterization of the SAS functions for each soil layer may be necessary for soils greatly affected by large temporal changes in soil flow conditions (e.g., cracking in drying soils or rapid growth/decay in rooting densities). Lastly, the water balance approach used within this study (E from fast flow domain, and R from both fast and slow flow domain) may have some influence on the estimated water ages within the soils. The use of the whole soil domain for the root uptake here was derived from the multi-source mixing model; however, if root uptake was estimated only from the fast domain, the slow domain storage age could be greater than estimated. The increase in age in the slow domain would likely be a result of no lateral inflow ($L$, Fig. 2) and therefore exchange would be driven only by diffusion ($J$).

### 5.2 Implications of soil water mixing patterns using SAS functions

Modelling using SAS functions showed potential for a coherent, integrated assessment of soil water mixing using stable isotopes. The temporally varying beta distribution used in this study was a more dynamic approach to soil water mixing estimates than repeated testing of mixing assumptions at different depths (e.g., Lindström and Rodhe, 1992). The modelling revealed temporal differences in the age of water fluxes, with generally high tendencies for young water to move rapidly through the soil profile. These results were similar to lysimeter and hillslope studies, which also showed a higher preference for young water movement through soils (Kim et al., 2016; Pangle et al., 2017). The increased preference for young water may be the result of factors such as the limited additional storage in soils while wet and the freely draining nature of the soil structure (Geris et al., 2015; Sprenger et al., 2017b), or rapid lateral transport due to rising water tables (Kim et al., 2016; Pangle et al., 2017). The amplified inclination for young water fluxes during wet periods simulated here has previously been observed in the streamflow within the catchment (Soulsby et al., 2015). While there were noticeable differences between the time-variant and time-invariant downward flow SAS functions (Fig. G.1), the width of the uncertainty bounds of the SAS function combined with the number of temporally different calibration points suggests further testing of the significance of the
temporal variability with the method proposed would be beneficial. Due to the greater movement of young water through the soil, the overall median age of the soil water was greater than expected for shallow soils (upper 5 cm); however, the median water age through all soil depths was broadly consistent to previous estimates of the podzols beneath heather elsewhere in the catchment (< 6 months, Tetzlaff et al., 2014). Despite the similar podzolic profiles at the two sites, the soil water movement was somewhat different. The freely-draining deeper soil conditions at Site B was likely the cause of the smaller slow flow domain relative to Site A (Fig. 3a, 3c), lower soil moisture in deeper layers (Fig. 6a), and younger soil water ages (Fig. 6b and c). The higher proportion of water in the slow flow domain further from the surface at Site A is consistent with high water content in the organic surface horizons and a less freely-draining sub-soil than Site B. The differences were more noticeable with the estimated water ages, which were significant between fast and slow domains, as well as between sites, throughout most of the simulation period. While Site B is more freely draining (younger outflow ages), the water ages in the upper 2.5 cm are on occasion greater than Site A. This may be due to the smaller proportion of fast domain in the upper 2.5 cm of Site B relative to Site A (Fig. 3a, 3c).

However, some complexities remain with the use of SAS functions within soil columns. For simplification, the slow flow domain modelled here only exchanged in the vapour phase with the fast flow domain and did not contribute to vertical fluxes. During some of the wettest periods in the simulations, the ability of the model to reproduce the isotopic compositions of near-surface water (upper 5 cm) was limited. The depleted isotopic composition of soil water measured following the large event was not similar to an isotopic composition implied by vertical infiltration of the precipitation of the large event. It seems plausible that this may be due to lateral flow in the upper soil, which occurs only during rare fully-saturated conditions and may bring in more depleted isotopes from upslope areas (Scheliga et al., 2018). It is notable that rainfall totals at this time had estimated return periods > 200 years (Soulsby et al., 2017). Experimental evidence from hillslope studies has shown a potential influence of lateral mixing from upslope soils and changes in infiltration during precipitation events with observed greater influence in the near-surface waters (Essig et al., 2009; Morbidelli et al., 2015). Furthermore, a general reduction in the uncertainty of the SAS function was observed for both the age estimation (Fig. 6) and $\delta^{2}H$ (Fig. 5) during wet conditions, while during dry conditions the uncertainty is higher. Higher uncertainty during dry conditions is not an anomaly with SAS functions (e.g. Benettin et al., 2017), but exemplifies a general concern for both wet and dry periods regarding the number of data points required to best characterise the SAS function under extreme conditions. Whilst the data set used here is of unusual detail and longevity, the temporal resolution is temporally coarse relative to the dynamics of such changes. Further testing of the model at controlled sites where higher resolution data is available would be useful (e.g. lysimeter studies).

6 Conclusion

The method reported here provides an adaptation of StorAge Selection functions for assessing soil water mixing and providing an approximation of depth-related evaporation and root uptake water profiles. Beta distributions identified dominant flow paths of younger water through all seasonal variations in soil moisture conditions. The estimated profile of soil evaporation fluxes showed mostly near-surface water (0 – 5cm) throughout the year, consistent with the isotopic fractionation of near-surface soil waters. The median evaporation water age was very similar to the median water age of near-surface soil water (63 and 65 days, respectively). Root uptake profiles were variable in time, dependent on the soil moisture, and were derived from the near-surface (0 – 5 cm) soils under wet conditions, but were derived from deeper soils (5 – 10 cm) as conditions dried. The wider distribution of the root uptake water resulted in older transpired water relative to soil evaporation (50 relative to 56 and 65 relative to 79 days for evaporation and root uptake at Site A and Site B, respectively). Median percolation water ages were very young (8 to 11 days). The median age of soil waters is much younger than those estimated in stream waters due to longer transit times in larger groundwater stores (e.g. Ala-aho et al., 2017b); however, the water ages converge under wet, highly
connective catchment conditions. Wider application of the SAS function presented here may provide a framework to test different mixing assumptions and hypotheses regarding ecohydrological separation where parameterizations can be used to explain subtle differences in the mechanisms controlling evaporation, root uptake water, and drainage patterns of soils.

Acknowledgements

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References


## Appendix A: Table of parameters

### Table A.1: Glossary table for water balance, soil terms, StorAge Selection, isotopic fractionation, evaporation and root uptake, and model parameters.

<table>
<thead>
<tr>
<th>Water Balance Terms</th>
<th>Symbol</th>
<th>Description</th>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>ET</td>
<td>Evapotranspiration flux [Length'/Time]</td>
<td>Q</td>
<td>Downward flux [Length'/Time]</td>
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<tr>
<td>E</td>
<td>Evaporation [Length'/Time]</td>
<td>R</td>
<td>Root uptake [Length'/Time]</td>
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<td>D</td>
<td>Diffusive exchange between fast and slow flow domains [Length'/Time]</td>
<td>V_f(t,i)</td>
<td>Total water volume of the fast flow domain of soil layer i at time t [Length^3]</td>
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<td>L</td>
<td>Lateral liquid exchange from the fast to slow flow domain [Length'/Time]</td>
<td>V_d(t,i)</td>
<td>Total water volume of the slow flow domain of soil layer i at time t [Length^3]</td>
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<td>V(t,i)</td>
<td>Volume of water in soil layer i at time t [Length^3]</td>
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<table>
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<tr>
<td>Z</td>
<td>Bottom depth of the soil modelling domain [Length]</td>
<td>θ_m(i,j)</td>
<td>Measured soil moisture in soil layer i [-]</td>
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<td>Δz</td>
<td>Soil thickness of each soil layer [Length]</td>
<td>θ_o(i)</td>
<td>Soil moisture threshold for fast vs. slow flow domain in soil layer i [-]</td>
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<td>z(i)</td>
<td>Mean depth (from soil surface) of soil layer i [Length]</td>
<td>V_d(i)</td>
<td>Volumetric threshold for fast vs. slow flow domain in soil layer i [-]</td>
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<td>a(i)</td>
<td>Fitting parameter in soil layer i</td>
<td>b(i)</td>
<td>Fitting parameter in soil layer i</td>
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<td>i</td>
<td>Soil layer descriptor</td>
<td>Δt</td>
<td>Time-step [Time]</td>
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<tr>
<td>SAS</td>
<td>StorAge Selection</td>
<td>T</td>
<td>Age of water [Time]</td>
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<td>S_f(T,t,i)</td>
<td>Age-ranked storage for soil layer i [Length]</td>
<td>t</td>
<td>Time</td>
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<td>S_D(T,t,i)</td>
<td>Age-ranked storage for the fast flow domain in soil layer i [Length]</td>
<td>Ω(S_f(T,t,i),T)</td>
<td>SAS cumulative density function [-]</td>
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<td>S_S(T,t,i)</td>
<td>Age-ranked storage for the slow flow domain in soil layer i [Length]</td>
<td>φ_o(S_S(T,t,i),T)</td>
<td>SAS probability density function [1/Length]</td>
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<td>V(T,t,i)</td>
<td>Discrete volume of water in storage layer i with age T [Length]</td>
<td>N_f(t or s)</td>
<td>Normalized water ages of the fast or slow flow domain (N = S(T,t,i)/V)</td>
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<td>P_f</td>
<td>Distribution of water ages T of evaporation flux at time t, cumulative from all soil layers</td>
<td>P_R</td>
<td>Distribution of water ages T of root uptake flux at time t, cumulative from all soil layers</td>
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<th>Symbol</th>
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<td>δ_r</td>
<td>Isotopic composition of the fast domain [%]</td>
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</tr>
<tr>
<td>δ_s</td>
<td>Isotopic composition of the slow domain [%]</td>
<td>δ_R</td>
<td>Isotopic composition of root uptake [%]</td>
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<tr>
<td>INT</td>
<td>Intercept of the local meteoric water line [%]</td>
<td>SL</td>
<td>Slope of the local meteoric water line [-]</td>
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<th>Symbol</th>
<th>Description</th>
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</thead>
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<tr>
<td>f(t,i)</td>
<td>Distribution of either evaporation or root uptake from depth</td>
<td>N(0_m(t))</td>
<td>Normalized soil moisture over the time-series</td>
<td></td>
</tr>
<tr>
<td>p(t,z,i)</td>
<td>Probability distribution function describing evaporation or root uptake profile from depth [1/Length]</td>
<td>μ_o</td>
<td>Mean soil moisture of the time-series [-]</td>
<td></td>
</tr>
<tr>
<td>B(k,u(t))</td>
<td>Complete beta function</td>
<td>σ_o</td>
<td>Standard deviation of soil moisture of the time-series [-]</td>
<td></td>
</tr>
<tr>
<td>u(t)</td>
<td>Time-variable beta scale parameter</td>
<td></td>
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<th>Symbol</th>
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<tbody>
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<td>k_e</td>
<td>Parameters for evaporation selection from depth</td>
<td>k_r</td>
<td>Parameters for root uptake selection from depth</td>
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<tr>
<td>λ_e</td>
<td>Parameters for evaporation selection from depth</td>
<td>λ_r</td>
<td>Parameters for root uptake selection from depth</td>
<td></td>
</tr>
<tr>
<td>σ_e</td>
<td>Parameter for evaporation selection from depth</td>
<td>σ_r</td>
<td>Parameter for root uptake selection from depth</td>
<td></td>
</tr>
</tbody>
</table>
Appendix B: Example estimation of water balance in each layer

The estimation of the water balance starts with using Eq. (5) to estimate the fitting parameters \( V_o(i) \) for each soil layer \( (i) \).

For ease of interpretation, the units of volume and fluxes will herein be shown in units of Length or Length/Time (for fluxes) which are with respect to a unit area (resulting in Length\(^3\) and Length\(^3\)/Time). The following provides examples of 2 conditions, the first where the soils remain wet for the whole study period \( (V > V_o \) through all time), and for a drier soil \( (V < V_o \) in some periods). The following examples are shown for the flow conditions shown in Fig 2 with synthetic data.

**Wet Conditions**

For example, a soil with three soil layers has soil water storage ranging from 10 – 17 mm of storage (per unit area) through the simulation period in all three layers. The values of \( V_o(i) \) were estimated as 5, 6, and 5.5 mm for layers 1 – 3, respectively. The volume of fast flow domain in each layer is estimated using measured soil water as:

\[
V_f(i, t) = V_m(i, t) - V_o(i)
\]

Where \( V_m(i, t) \) is the measured soil water volume (\( \theta_m(i, t) \cdot \Delta z \cdot A \)), \( A \) is unit area. Therefore the maximum fast flow domain storages are 12, 11, and 11.5 mm for layers 1 – 3, respectively, with a minimum fast flow domain storage of 5, 4, and 4.5 mm for layers 1 – 3, respectively. Similarly for the slow flow domain:

\[
V_s(i, t) = V_o(i)
\]

which does not temporally change as \( V_f \) does not decrease to 0 in any of the soil layers. On day \( t=30 \), \( V(30,1) \) is 12 mm \((V_f(30,1) = 7 \text{ mm}) \) and there is 5 mm of rain, it is assumed that all of the precipitation infiltrates during the day (regardless of precipitation amount or wetness). \( V(31,1) \) is 13 mm \((V_f(t+1,1) = 8 \text{ mm}) \), indicating that storage only increases by 1 mm and 4 mm leaves layer 1 via either \( E, R \), or \( Q \). The parameterisation of Eq 3 results in the fraction of \( E \) in layer 1 \((f_E(30,1), \text{ Eq 1}) \) equal to 0.95 and fraction of \( R \) in layer 1 \((f_R(30,1), \text{ Eq 1}) \) equal to 0.6. Potential evaporation during the day is 0.4 mm and potential root uptake is 0.6 mm, therefore potential evaporation in layer 1 is 0.38 mm \((0.95 \times 0.4 \text{ mm}) \) and potential root uptake in layer 1 is 0.36 mm \((0.6 \times 0.6 \text{ mm}) \). The cumulative \( E \) and \( R \) in layer 1 is 0.74 mm, which is less than the total outflow of the layer \((4 \text{ mm}) \), therefore \( E \) and \( R \) fluxes are not limited. The flux of \( Q \) is therefore 3.26 mm \((4 \text{ mm} - 0.74 \text{ mm}) \) to close the water balance. The \( E \) and \( R \) from the fast flow domain are 0.22 mm \((7 \text{ mm}/12 \text{ mm} * 0.38 \text{ mm}) \) and 0.21 mm \((7 \text{ mm}/12 \text{ mm} * 0.36 \text{ mm}) \), respectively. In the slow flow domain, \( E \) and \( R \) are 0.16 mm \((5 \text{ mm}/12 \text{ mm} * 0.38 \text{ mm}) \) and 0.15 mm \((5 \text{ mm}/12 \text{ mm} * 0.36 \text{ mm}) \), respectively. Since the lateral flow acts to replenish the slow flow domain, \( L \) is 0.31 mm, equal to the cumulative \( E \) and \( R \) from the slow flow domain \((0.16 \text{ mm} + 0.15 \text{ mm}) \). The following equations show the variable balance \((B.3)\) and value balance \((B.4)\) in the fast flow domain:
\[ V_f(31,1) = V_f(30,1) + P - L - E - R - Q \]
\[ 13 = 12 + 5 - 0.31 - 0.22 - 0.21 - 3.26 \]

And the variable balance (B.5) and value balance (B.6) for the slow flow domain:
\[ V_s(31,1) = V_s(30,1) + L - E - R \]
\[ 5 = 5 + 0.31 - 0.16 - 0.15 \]

Additionally, on day \( t = 67 \), \( V(67,1) \) is 11.2 mm (\( V_f(67,1) = 6.2 \) mm) and \( V(68,1) \) is 10.9 mm (\( V_f(67,1) = 5.9 \) mm), indicating a loss of 0.3 mm via either \( E \), \( R \), or \( Q \). The parameterisation of Eq 3 results in the fraction of \( E \) in layer 1 (\( f_E(67,1), \text{Eq 1} \)) is estimated as 0.92 and fraction of \( R \) in layer 1 (\( f_R(67,1), \text{Eq 1} \)) is estimated at 0.45. Potential evaporation during the day is 0.7 mm and potential root uptake is 1.1 mm, therefore potential evaporation in layer 1 is 0.64 mm (0.92 * 0.7 mm) and potential root uptake in layer 1 is 0.50 mm (0.45 * 1.1 mm). The cumulative \( E \) and \( R \) in layer 1 (1.14 mm) is greater than the total outflow of the layer (0.3 mm), therefore \( E \) and \( R \) are less than the estimates. Since \( E \) and \( R \) fluxes are lower than estimates, the downward flow cannot be estimated as the difference of the soil moisture and \( E \) and \( R \).

Downwards flow is estimated using the regression of the soil water as a first approximation (Eq 5, \( a=0.2, b=1.5 \)), which gives 0.25 mm (\( 0.25 = \frac{2}{1.5} \cdot 0.2 \cdot [(11.2 - 0.64 - 0.5 + 0) - 5] \)). The total loss (\( E, R \) and \( Q \)) is equally split by total weight of fluxes (total potential outflow is 1.39 = 0.64+0.5+0.25), then the fraction of loss that is \( E \) is 0.46 (0.46 = 0.64 / 1.39), the fraction of loss that is \( R \) is 0.36 (0.36 = 0.5 / 1.39) and the fraction of loss that is \( Q \) is 0.18 (0.18 = 0.25 / 1.39). Therefore, with the total loss of 0.3 mm by the soil moisture measurements, total loss of \( E \) from the layer is 0.14 mm (0.14 = 0.3*0.46), total loss of \( R \) is 0.11 mm (0.11 = 0.3*0.36), and total downward flow is 0.05 mm (0.05 = 0.3*0.18). Using the same means as above to separate \( E \) and \( R \) into fast and slow flow fluxes, the \( E \) from the fast flow domain is 0.09 mm (0.09 = 0.14 mm* 6.2mm/10.2mm) and 0.05 mm in the slow flow domain (0.05 = 0.14 mm* 5mm/10.2mm), and for \( R \) in the fast flow domain 0.07 mm (0.07 = 0.11 mm* 6.2mm/10.2mm) and 0.04 mm (0.04 = 0.14 mm* 5mm/10.2mm) in the slow flow domain. Therefore, the lateral transfer from the fast to slow flow domain is 0.09 mm (0.09 mm = 0.05 mm + 0.04 mm). The following equations shows the variable balance (B.7) and value balance (B.8) in the fast flow domain:
\[ V_f(68,1) = V_f(67,1) + P - L - E - R - Q \]
\[ 10.9 = 11.2 + 0 - 0.09 - 0.09 - 0.07 - 0.05 \]

And the variable balance (B.9) and value balance (B.10) for the slow flow domain:
\[ V_s(68,1) = V_s(67,1) + L - E - R \]
\[ 5 = 5 + 0.09 - 0.05 - 0.04 \]

\textit{Dry Conditions}
The flow conditions can similarly be estimated under dry conditions where there is no water in the fast flow domain. The following example uses the same $E$ and $R$ from the Wet Conditions example, with changed soil water volumes. It is important to note that while the synthetic potential $E$ and $R$ are the same as the conditions in the previous section, these estimates would (in reality) be estimated from a decreased soil moisture. The soil has three layers with storage ranging from 3 – 9 mm (per unit area) through the simulation period in all three layers. The values of $V_o(i)$ are the same as in the previous section (5, 6, and 5.5 mm for layers 1 – 3, respectively). The volume of fast flow domain is estimated slightly differently than above:

$$V_f(i, t) = \max(V_m(i, t) - V_o(i), 0)$$ \hspace{1cm} B.11

where a condition is set that if $V_m$ is less than $V_o(i)$ the volume in the fast domain is 0 mm. The maximum fast domain storage is therefore 4, 3, and 3.5 mm for layers 1 – 3, respectively, and a minimum of 0 mm of all. For the slow flow domain:

$$V_s(i, t) = \min(V_o(i), V_m(i, t))$$ \hspace{1cm} B.12

which only changes $V_s$ on days where the soil moisture is less than $V_o(i)$. On day $t=30$, $V(30,1)$ is 3.5 mm ($V_f(30,1) = 0$ mm, $V_s(30,1) = 3.5$ mm) and there is 5 mm of rain, it is assumed that all of the precipitation infiltrates during the day (regardless of precipitation amount or wetness). $V(31,1)$ is 4.5 mm ($V_f(t+1,1) = 0$ mm, $V_s(t+1,1) = 0$ mm), indicating that storage only increases by 1 mm and 4 mm leaves layer 1 via either $E$, $R$, or $Q$. The parameterisation of Eq 3 results in the fraction of $E$ in layer 1 ($f_E(30,1)$, Eq 1) is estimated as 0.95 and fraction of $R$ in layer 1 ($f_R(30,1)$, Eq 1) is estimated at 0.6.

Potential evaporation during the day is 0.4 mm and potential root uptake is 0.6 mm, therefore potential evaporation in layer 1 is 0.38 mm (0.95 * 0.4 mm) and potential root uptake in layer 1 is 0.36 mm (0.6 * 0.6 mm). The cumulative $E$ and $R$ in layer 1 (0.74 mm) is less than the total outflow (4 mm), therefore, the potential $E$ and $R$ are not limited. The flux of $Q$ is therefore 3.26 mm (4 mm – 0.74 mm), which could indicate preferential flow. The $E$ and $R$ from the fast flow domain are both 0 mm (no water in the fast flow domain). The $E$ and $R$ in the slow domain are therefore 0.38 mm and 0.36 mm, respectively, with a lateral flow of 1.74 mm (0.38 mm + 0.36 mm + 1 mm increase in slow flow domain storage). The following equations show the variable balance (B.13) and value balance (B.14) in the fast flow domain:

$$V_f(31,1) = V_f(30,1) + P - L - E - R - Q$$ \hspace{1cm} B.13

$$0 = 0 + 5 - 1.74 - 0 - 0 - 3.26$$ \hspace{1cm} B.14

And the variable balance (B.5) and value balance (B.6) for the slow flow domain:

$$V_s(31,1) = V_s(30,1) + L - E - R$$ \hspace{1cm} B.15

$$4.5 = 3.5 + 1.74 - 0.38 - 0.36$$ \hspace{1cm} B.16

Similarly, on day $t=67$, $V(67,1)$ is 4.2 mm ($V_f(67,1) = 0$ mm, $V_s(67,1) = 4.2$ mm) and $V(68,1)$ is 3.9 mm ($V_f(67,1) = 0$ mm, $V_s(67,1) = 3.9$ mm), indicating a loss of 0.3 mm via either $E$ or $R$. The parameterisation of Eq (3) results in the
fraction of $E$ in layer 1 ($f_E(67,1)$, Eq 1) is estimated as 0.92 and fraction of $R$ in layer 1 ($f_R(67,1)$, Eq 1) is estimated at 0.45. Potential evaporation during the day is 0.7 mm and potential root uptake is 1.1 mm, therefore potential evaporation in layer 1 is 0.64 mm (0.92 * 0.7 mm) and potential root uptake in layer 1 is 0.50 mm (0.45 * 1.1 mm). The cumulative $E$ and $R$ in layer 1 (1.14 mm) is greater than the total layer outflow (0.3 mm), therefore $E$ and $R$ are less than estimated. Since there is no water in the fast flow domain and no incoming flow, there can be no downward flow ($Q(i,67) = 0$ mm). The total loss ($E$ and $R$) is equally split by total weight of fluxes (total potential outflow is 1.14 = 0.64+0.5), then the fraction of loss that is $E$ is 0.56 (0.46 = 0.64 / 1.14), and the fraction of loss that is $R$ is 0.44 (0.36 = 0.5 / 1.14). Therefore, with the total loss of 0.3 mm by the soil moisture measurements, the total loss of $E$ from the layer is 0.17 mm (0.17 = 0.3*0.56), and the total loss of $R$ is 0.13 mm (0.13 = 0.3*0.44). Since there is no water in the fast domain, all $E$ and $R$ originates from the slow domain, so $E$ and $R$ from the slow flow domain are 0.17 mm and 0.13 mm, respectively. As there is no water in the fast domain to replenish the slow flow domain, lateral transfer ($L$) is 0 mm. The following equations show the variable balance (B.17) and value balance (B.18) in the fast flow domain:

$$V_f(68,1) = V_f(67,1) + P - L - E - R - Q \quad \text{B.17}$$

$$0 = 0 + 0 - 0 - 0 - 0 \quad \text{B.18}$$

And the variable balance (B.19) and value balance (B.20) for the slow flow domain:

$$V_s(68,1) = V_s(67,1) + L - E - R \quad \text{B.19}$$

$$3.9 = 4.2 + 0 - 0.17 - 0.13 \quad \text{B.20}$$

Within the model application at the Bruntland Burn, the dry conditions were not met through any time-step as there was always some vertical flow and soil volumes greater than the fast-slow domain thresholds. The parameters $a$, $b$, and $V_0$ were estimated in this study by using the measured hourly change in storage ($V_m(t,i) - V_m(t+\Delta t,i) = Q(t,i)$) and the average soil storage ($((V_m(t,z) + V_m(t+\Delta t,z))/2$) during periods with no $E$, $R$, or $P$ during storage regression periods (Table B.1). The periods of negligible potential $E$ and $R$ were used from a previous study at the site (Wang et al., 2018). The average hourly measured storage was ranked (highest to lowest), and the average storage and change in storage were grouped into equal bin sizes prior to regression. The bin size was determined by the minimum number of hourly data points where the standard deviation of a bin was less than half of its mean. The linear regression on a log-log plot were used to determine the downward flux parameters $a$ and $b$ ($S = \text{slope} = b$ and $L = \text{intercept} = \exp(a)$). The estimated vertical fluxes using the above method were compared to HYDRUS-1D simulations for direct assessment of the approach. There was good agreement between the method used here and the simulation from HYDRUS-1D (Fig B.1). The method applied here assumes that all soil flow is downward. This resulted in some deviations between the simple storage-discharge relationship and the HYDRUS-1D model during low flow conditions and during the peak event in January 2016.
Figure B.1: Comparison of HYDRUS-1D simulations to the soil moisture regression method at 5, 10, 15, and 20 cm depths at Site A. with the corresponding daily precipitation amounts. Evaluation at Site B is similar.

Table B.1: Fitted parameters a, b, and Vo for Site A and Site B for each soil depth

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth (cm)</th>
<th>a</th>
<th>b</th>
<th>b Standard Deviation</th>
<th>b Standard Deviation</th>
<th>Vo</th>
<th>Vo Standard Deviation</th>
</tr>
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<tbody>
<tr>
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<td>0.25</td>
<td>0.03</td>
<td>1.84</td>
<td>0.01</td>
<td>5.00</td>
<td>0.00</td>
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<td></td>
<td>7.5</td>
<td>0.09</td>
<td>0.01</td>
<td>1.72</td>
<td>0.02</td>
<td>5.06</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>0.03</td>
<td>0.00</td>
<td>1.40</td>
<td>0.02</td>
<td>11.43</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>0.01</td>
<td>0.00</td>
<td>1.16</td>
<td>0.02</td>
<td>11.48</td>
<td>0.11</td>
</tr>
<tr>
<td>Site B</td>
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<td>2.03E-03</td>
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<td>0.91</td>
<td>0.06</td>
<td>9.44</td>
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</tr>
<tr>
<td></td>
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<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>5.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>0.05</td>
<td>0.01</td>
<td>1.59</td>
<td>0.04</td>
<td>5.00</td>
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<td>0.08</td>
<td>0.03</td>
<td>1.47</td>
<td>0.10</td>
<td>5.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Appendix C: Example age ranking in each soil layer

In general, catchment age-ranked water in storage is defined by the time that water has resided in storage, in particular, since the time of precipitation. The same definition is applied to each of the storages in this study. At the soil surface (i = 1), the time that water has spent in the soil layer is equal to the time since precipitation. As a synthetic example, Table C.1 shows incoming precipitation, layer 1 storage, and layer 1 outflow for a 30 day (outflow from layer 1 or 2 is \( Q = 0.2 \times Storage^{1.1} \)).
If a temporally constant beta SAS function ($\alpha = 0.7$ and $\beta = 2$) is used for water translating to layer $i+1$ (layer 2), then there is a penchant for more the recent water entering the soil layer to leave the layer fastest. The water is ranked by the time it entered the soil layer, and the time-series of the cumulative water of each age is normalized by the total water storage to produce values between 0 and 1. These fractions are used in the beta distribution ($\alpha = 0.7$ and $\beta = 2$) to estimate the corresponding fraction of water of each age leaving storage. The values of each water entry age in storage and in outflow are shown in Table C.2. and Table C.3. respectively.
As an example calculation we will use the entry time of 10 days (precipitation amount = 0.05 mm). There is a total storage of 0.94 mm, comprised of newly entered precipitation (0.05 mm) and older water (0.04, 0.13, 0.29, 0.2, 0.2 and 0.03 mm from the 1, 2, 4, 6, 8, and 9 days preceding precipitation events, Table C.2.). The cumulative sum of water in storage by the time it entered is then [0.05, 0.09, 0.22, 0.5, 0.71, 0.91, 0.94], and normalized to [0.05, 0.09, 0.23, 0.54, 0.75, 0.97, 1].

For the most recent input (0.05 mm), the beta distribution (Beta(0.05,0.7,2) = 0.21) shows that the input accounts for more than 20% of the output while accounting for only 5% of the storage volume. With output flux of 0.19 mm/day on in the time-step (entry time t = 10 days), the flux uses 0.21 * 0.19 = 0.04 mm of the youngest water (Table C.3.).
Table C.3.: Outflow values from layer 1 for the 30 day example input. Time since entry is specific to the final time-step (30 days).

The mean age (days) relative to the model domain (Table C.3) are the ages ($T$) of water leaving layer 1 at each time-step. These water ages enter layer 2 and are added to the elapsed time water stays in layer 2. For example, on time-step 1 (entry time = 1), water leaving layer 1 has an age ($T$) equal to 0 days (leaves the same day), therefore $T$ in layer 2 is also 0 days.

By the end of 30 days, this parcel has an age of $T = 29$ days (Table C.4.). Note that the diagonal identity of Table C.4. is the same as the mean age from Table C.3. As an additional example, on entry time 10 days, output from layer 1 has an age ($T$) of 2.7 days. This value is equivalent to the diagonal value in Table C.4., and by the end of 30 days results in an age of 22.7 days (2.7 initial age + 20 days in layer 2).
### Table C.4.: Water ages of storage values in layer 2 for the 30 day example input.

<table>
<thead>
<tr>
<th>Entry Time</th>
<th>Time Since Entry</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<tr>
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<td>1</td>
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<tr>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

Storage and flux SAS functions estimations (Table C.5. and Table C.6.) are conducted in a similar means to layer 1

(-ranked by the time water entered the layer). Water age \((T)\) (in and out of) layer 2 is estimated using Table C.4. (water age shown on Table C.6.) with a comparison to the water ages relative to the time that water resided in layer 2. On all time-steps, water age \((T)\) leaving layer 2 is older than or equal to layer 1. Water ages are only equal to the layer above if the outflow from the layer is dominated by the youngest water.

### Table C.5.: Storage values in layer 2 for the 30 day example input. Time since entry is specific to the final time-step (30 days).

<table>
<thead>
<tr>
<th>Time Since Entry</th>
<th>Entry Time</th>
<th>Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00579424</td>
<td>9.06348</td>
</tr>
<tr>
<td>1</td>
<td>0.03187911</td>
<td>9.5876</td>
</tr>
<tr>
<td>2</td>
<td>0.06292375</td>
<td>9.112</td>
</tr>
<tr>
<td>3</td>
<td>0.09377620</td>
<td>8.6376</td>
</tr>
<tr>
<td>4</td>
<td>0.12452075</td>
<td>8.162</td>
</tr>
<tr>
<td>5</td>
<td>0.15526530</td>
<td>7.687</td>
</tr>
<tr>
<td>6</td>
<td>0.18591985</td>
<td>7.212</td>
</tr>
<tr>
<td>7</td>
<td>0.21657440</td>
<td>6.737</td>
</tr>
<tr>
<td>8</td>
<td>0.24722895</td>
<td>6.262</td>
</tr>
<tr>
<td>9</td>
<td>0.27788350</td>
<td>5.787</td>
</tr>
<tr>
<td>10</td>
<td>0.30853805</td>
<td>5.312</td>
</tr>
<tr>
<td>11</td>
<td>0.33919260</td>
<td>4.837</td>
</tr>
<tr>
<td>12</td>
<td>0.36984715</td>
<td>4.362</td>
</tr>
<tr>
<td>13</td>
<td>0.39050170</td>
<td>3.887</td>
</tr>
<tr>
<td>14</td>
<td>0.42115625</td>
<td>3.412</td>
</tr>
<tr>
<td>15</td>
<td>0.45181080</td>
<td>2.937</td>
</tr>
<tr>
<td>16</td>
<td>0.48246535</td>
<td>2.462</td>
</tr>
<tr>
<td>17</td>
<td>0.51312000</td>
<td>1.987</td>
</tr>
<tr>
<td>18</td>
<td>0.54377465</td>
<td>1.512</td>
</tr>
<tr>
<td>19</td>
<td>0.57442930</td>
<td>1.037</td>
</tr>
<tr>
<td>20</td>
<td>0.60508395</td>
<td>0.562</td>
</tr>
<tr>
<td>21</td>
<td>0.63573860</td>
<td>0.087</td>
</tr>
<tr>
<td>22</td>
<td>0.66639325</td>
<td>0.007</td>
</tr>
<tr>
<td>23</td>
<td>0.69704790</td>
<td>0.007</td>
</tr>
<tr>
<td>24</td>
<td>0.72770255</td>
<td>0.007</td>
</tr>
<tr>
<td>25</td>
<td>0.75835720</td>
<td>0.007</td>
</tr>
<tr>
<td>26</td>
<td>0.78901185</td>
<td>0.007</td>
</tr>
<tr>
<td>27</td>
<td>0.81966650</td>
<td>0.007</td>
</tr>
<tr>
<td>28</td>
<td>0.85032115</td>
<td>0.007</td>
</tr>
<tr>
<td>29</td>
<td>0.88097580</td>
<td>0.007</td>
</tr>
<tr>
<td>30</td>
<td>0.91163045</td>
<td>0.007</td>
</tr>
</tbody>
</table>
Table C.6.: Outflow values from layer 2 for the 30 day example input. Time since entry is specific to the final time-step (30 days).

Appendix D: Estimation of isotopic fractionation

The Craig-Gordon model (CG, Craig and Gordon, 1965) is the most commonly applied model for the estimation of evaporation vapour flux, $\delta_e$. The CG model incorporates aerodynamic resistances from the surface to the atmosphere with the phase-change fractionation from liquid to vapour ($\alpha_c$), and the equilibrium and kinetic fractionation ($\epsilon^e$ and $\epsilon_K$, respectively). The liquid-vapour fractionation and equilibrium fractionation are a function of air temperature ($T_a$): for deuterium ($\delta^2H$),

$$\alpha^e(t) = \exp(1158.8((T_a(t))^3/10^{12}) - 1620.1((T_a(t))^2/10^8) + 794.84((T_a(t))/10^6) - 0.16104 + 2.9992(10^6/(T_a(t))^3))$$

and for oxygen-18 ($\delta^{18}O$),

$$\alpha^e(t) = \exp(-0.007685 + 6.7123(1/(T_a(t))) - 1.6664(10^2/(T_a(t))^2) + 0.35041(10^6/(T_a(t))^3))$$

$\epsilon^e(t) = n(t, i) \cdot C_K \cdot (1 - h_A(t))$;
\[ \delta_e(T, t, i) = \frac{1}{(h_z(t) - h_A(t) + \varepsilon)} \cdot \left( \delta_p(T, t, i) - h_A(t) \cdot \delta_A(t) - \varepsilon \right) \]

where \( \delta_e \) is evaluated for each water \( T \) for the fast flow domains, \( h_z \) is the relative humidity in the soil layer, \( \delta_A \) is the atmospheric isotopic composition \( \delta_A = (\delta_P - \varepsilon)/\alpha \) which is a function of the precipitation isotopic composition \( \delta_P \), and is evaluated at each time-step \( t \) and for each water age \( T \). On days without precipitation, the \( \delta_P \) is estimated from the linear interpolation of the previous and next precipitation isotopic compositions. Recent work on soil water evaporative fractionation has modified the CG model (Eq. D.3) to include the effects of soil moisture conditions on the relative humidity and aerodynamic diffusion coefficient \( n \):

\[ n(t, i) = 1 - \frac{1}{2} \cdot \left( \frac{\theta_m(t, i) - \theta_o(i)}{\theta_{sat}(i) - \theta_o(i)} \right) \]

where \( \theta_o(z) \) is the separation of the fast and slow flow domains (from \( V_o \) in Eq. 5), \( \theta_m(t, i) \) is the measured soil moisture in the layer at time \( t \), and \( \theta_{sat}(i) \) is saturated soil moisture of the layer (Mathieu and Bariac, 1996; Good et al., 2014). In many regions, \( h_z \) may be a significant factor by reducing the diffusive flux from the soil to the atmosphere. However, in wet soils such as those evaluated in this study, \( h_z \) is at or near 1, and the Eq. (D.3) is simplified using \( h_z = 1 \).

To estimate the isotopic compositions with the consideration of evaporation and other outgoing/incoming fluxes, the isotopes are first estimated for each water age \( T \) in each flow domain (fast or slow) with Eqs. (D.3 & D.4) and the mass-balance (Eqs 9 & 10). Since the solution is conducted for each individual water age, the fluxes are not distributions of water ages, rather a single value of a single water age. Similar to Gibson (2002), the mass balance can be described with the water balance (Eq 6 & 7, shown here for Eq 6) as:

\[ V_f \frac{d\delta_f}{dt} + \delta_f \frac{dV_f}{dt} = \delta_{in} \cdot Q(t, i - 1) - \frac{V_f(t, i)}{V(t, i)} \cdot (E(t) \cdot f_E(t, i) \cdot \delta_E + R(t) \cdot f_R(t, i) \cdot \delta_R) - (L(t, i) + Q(t, i)) \cdot \delta_f + D(t, i) \cdot \delta_s - D(t, i) \cdot \delta_f \]

where \( V_f \) is the total volume of the fast flow domain of layer \( i \), \( \delta_f \) is the isotopic composition of layer \( i \), \( \delta_{in} \) is the incoming isotopic composition from the layer above, \( \delta_E \) is the isotopic composition of evaporation, and \( \delta_s \) is the isotopic composition incoming from the slow flow domain. Equation D.5 is solved independently for each water age, \( T \), therefore each flux (e.g. \( Q(t, i-1) \) in Eq. (D.5)) represents only a fraction of the total flux. For example, consider a distribution of water ages for outflow ranging from \( T \) of 1 day to 150 days, where the fraction of outflow is greatest with younger water (smaller \( T \)). At time \( t \), the total outflow is 5mm \( (Q(t, i) = 5mm) \), with 0.3 mm of water of age \( T = 25 \) days (\( q = 0.3 = Q \cdot \omega(Q(S_{25}(t, i), t), t) \)). A similar approach can be made for the other fluxes (e.g. \( e = \cdot \omega(E(S_{25}(t, i), t), r = \cdot \omega(R(S_{25}(t, i), t), etc). Equation D.5. can be re-written for the solution of each age \( T \) (shown for the fast flow domain):

\[ V \frac{d(\delta(T, t, i))}{dt} + \delta_f(T, t, i) \frac{dV}{dt} = d_xf \cdot \delta_s - q \cdot \delta_f - l \cdot \delta_f - d_xf \cdot \delta_f - r_f \cdot \delta_f - e \cdot \delta_e(T, t, i) \]

where \( q \) is the downward flux of water age \( T \) at time \( t \) in layer \( i \) (e.g. \( q = Q \cdot \omega(S(t, i), t)) \), \( l \) is the later flux to the slow domain of water age \( T \) at time \( t \) in layer \( i \), \( d_xf \) is the diffusive flux to the slow domain of water age \( T \) at time \( t \) in layer \( i \), \( d_xf \)
is the diffusive flux from the slow domain to the fast domain of water age $T$ at time $t$ in layer $i$, $r_i$ is the root uptake flux of water age $T$ at time $t$ in layer $i$, and $e$ is the evaporation of water age $T$ at time $t$ in layer $i$. Eq. D.6 is then solved for $\delta_i$ for each flow domain to yield Eq. 11 which using the method of substitution shown in Gibson (2002).

**Appendix E: Evaporation and root uptake profile estimation using the stable isotopes of water**

For each measurement period with soil water isotopes at multiple depths and xylem water isotopes, the root uptake source may be approximated by solving for the proportion of root-water uptake from each soil water depth. The proportions are resolved by meeting the criterion that a mixture of bulk soil water reproduces the measured xylem water samples (Eq E.1, modified from Rothfuss and Javaux, 2017).

$$
\delta_R = P_1 \cdot \delta_{z1} + P_2 \cdot \delta_{z2} + P_3 \cdot \delta_{z3} + \cdots + P_n \cdot \delta_{zn}
$$

E.1

Where $P$ is the proportion of root uptake water from soil depth $n$ ($1 = \sum_{i=1}^{n} P_n$), $\delta_m$ is the isotopic composition of bulk soil water at depth $z$, and $\delta_R$ is the estimated xylem water. The proportions of root uptake at each depth are identified as the solutions with the minimal difference to the measured xylem isotopic compositions ($\delta_x$). The estimations of the root uptake profile for each measurement period of the study are shown on Fig E.1. It is important to note that this estimation method used the bulk soil water (combined and amount-weighted fast and slow domain water) with no preference of water age (i.e. uniform mixing of available water).

![Figure E.1: Root uptake proportion with depth at Site A and Site B for each of the 5 xylem measurement periods with the maximum allowable error (Er).](image)

The limited constraints on the proportions ($\sum P_n = 1$), result in some uncertainty of the root uptake profile for most measurement periods (Site A measurement periods 2-4, and Site B measurement periods 2, 3 and 5). The other measurement periods (Site A measurement periods 1 and 5, and Site B measurement periods 1 and 4) were constrained by the shape of the rooting density since the solution of $\delta_n$ did not converge to $\delta_x$ (error > $1 \times 10^{-4}$). It is notable that measurements 2 and 3 have the highest soil moisture and 1 and 5 have the lowest soil moisture at both sites. Similarly, at
both sites, the proportion of root uptake from near-surface water is estimated to increase with soil moisture (exception of
measurement period 1 at Site B).

The application of a linear function to describe changes in root uptake with soil moisture conditions (Eqs. 1-3) results in
larger $u(x,t,z)$ with higher soil moisture and increases the probability of water sourced from near the surface (as $z$
approaches zero). Conversely, while low soil moisture conditions decrease the probability of water sourced from near the
surface. For example in a 20 cm deep modelling domain ($Z = 20$), if $k_x = 2$ under high soil moisture conditions (using a
value of $u(x,t,z) = 10$), 80% of the vapour flux occurs the top 5 cm ($f_1(5-0,t)$) while < 1% occurs between 10 and 15 cm
($f_1(15-10,t)$). Conversely, under low soil moisture conditions (using a value of $u(x,t,z) = 2$), only 15% of the vapour occurs
from the top 5 cm while 35% occurs between 10 - 15 cm.

**Appendix F: Model parameter sensitivity**

The sensitivity of the water age of the fast domain water, the mean deuterium isotopic composition (integration of fast and
slow domain), and mean lc-excess (integration of fast and slow domain) of each layer to changes in model parameters
were assessed using a modification of the Morris Sensitivity analysis (Soheir et al., 2014). To assess the sensitivity, 10
model trajectories were developed, corresponding to each ‘x’ on Fig. (F.1). Each trajectory contained 13 model
simulations, one baseline simulation, and 12 simulations which changed each parameter value sequentially and
independently between simulations. For example, the second simulation only changed the parameter value of $\lambda$ from the
baseline simulation, while the third simulation only changed the parameter value of $\alpha$ from the baseline simulation. The
parameter values of the baseline simulation were determined using Latin Hypercube Sampling and were unique for each
trajectory. For each trajectory, the simulations of water age, deuterium, and lc-excess were compared to the baseline
simulation using root mean square error and bias (ratio of mean values), which determine the elementary effect of
changing the parameter. The parameters were ranked (left to right) by the average elementary effect of all trajectories.
Figure F.1: Morris sensitivity analysis for (a) water age in the fast domain, (b) mean deuterium, and (c) mean lc-excess in different soil layers (5, 10, and 20 cm). Sensitivity was assessed using root mean square error (left column) and bias (right column).

On average, the parameters for the SAS functions ($\lambda$, $\alpha$, and $\tau$) were the most sensitive parameters with respect to water age, $\delta^2H$, and lc-excess. While the parameter sensitivity for isotopic compositions decreased with depth, water age estimation in the fast flow domain had higher sensitivity in deeper soil layers (Fig. F.1). The isotopic compositions of soil water near the surface and at the greatest soil depth (15 - 20 cm) were both sensitive to the root uptake profile parameters ($\lambda_R$, $k_R$, and $\tau_R$, Eq. 1-3), although the sensitivity in the deepest soil layer was much lower than near the surface.

Evaporation profile parameters were not as sensitive as the root uptake profile parameters. On average, the water age and isotopic simulations were not sensitive to changes in the parameters for evaporation profile ($k_E$, $\lambda_E$, and $\tau_E$), potentially due to the small prescribed ranges. Similarly, the water age and isotopic simulations were not sensitive to the diffusion parameter ($\xi$) due to the relatively small parameter range limiting the exchange between the fast and slow domain. Lastly, changes in the molecular diffusion coefficient ($C_K = O^{18}/O^{16}$ or $C_K = H^2/H^1$) resulted in little sensitivity to the water age or deuterium simulations and were held constant for calibration with values described by Merlivat (1978). However, the
lc-excess simulations were very sensitive to changes in the deuterium molecular diffusion coefficient. The sensitivity is predominantly due to a simulation bias (vertical shift in the simulation) without noticeable changes in the dynamics of the lc-excess (either daily or seasonally).

Appendix G: Comparison of time-variant and time-invariant SAS functions

To evaluate the necessity of time-variance of the SAS functions, Monte Carlo simulations were conducted assuming no time-variance and directly compared to the time-variant simulations. The NSE$_{adj}$ were on average 0.1 lower for the time-invariant simulations relative to the time-variant simulations, consistent with the difference in time-variant and time-invariant comparisons at the catchment scale (eg. Harman, 2015). The inclusion of time-variance ($\lambda$) was a significant inclusion to the model for the near surface soils, as represented with the Akaike Information Criteria (AIC) for each soil layer (Table G.1.). The AIC values were estimated for $\delta^2$H, $\delta^{18}$O, and lc-excess using a kernel density function so that no function of the distribution of errors was assumed. AIC values show the importance of time-variance in the shallow soils (upper 10 cm), with only the shallowest soil (2.5 cm) in Site B not showing a tendency for time-variance (AIC is greater for the variant simulations than the invariant simulations at 2.5 cm). With a lower $\lambda$ value (Figure 4) at Site B, there was already a decreased tendency for time-variance at Site B than Site A.

Table G.1.: Values of the Akaike Information Criteria (AIC) for Site A and Site B in each soil layer. Lower values of AIC indicate higher performance of the model.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Site A</th>
<th>Site B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Invariant</td>
<td>Variant</td>
</tr>
<tr>
<td>2.5 cm</td>
<td>6586.12</td>
<td>6164.62</td>
</tr>
<tr>
<td>7.5 cm</td>
<td>6108.80</td>
<td>5987.35</td>
</tr>
<tr>
<td>12.5 cm</td>
<td>5810.10</td>
<td>5722.80</td>
</tr>
<tr>
<td>17.5 cm</td>
<td>5750.25</td>
<td>5965.53</td>
</tr>
</tbody>
</table>

In general, the time-invariant simulations performed reasonably under moderate conditions with little change in storage; however, during very wet conditions and drier conditions, the divergence of time-variant and time-invariant simulations was more pronounced. The performance of time-invariant conditions was dependent on the site. Site A showed smaller differences between the time-invariant and time-variant in deeper soil layers, while Site B had much larger differences between the time-invariant and time-variant conditions at deeper layers. The difference in lc-excess was smaller between time-invariant and time-variant conditions since the evaporation source was estimated similarly between time-invariant and time-variant simulation and the SAS function of evaporation (uniform distribution) was not assumed to be time-variant during either simulation. While not shown, simulations of $\delta^{18}$O were similar to $\delta^2$H.
Figure G.1: Comparison of time-invariant and time-variant calibrations of the downward flow SAS function. Black lines are the mean $\delta^{2}H$ or lc-excess simulation for the time-variant solution, and blue lines are the mean $\delta^{2}H$ or lc-excess simulations for the time-invariant solution. Red square shows the isotopic range of measurements and green stars show the mean of the isotopic measurements (lc-excess only).

Appendix H: Isotopic and water age statistical comparison

Statistical differences of isotopic compositions (measured and simulation) and water ages of each soil layer at the two sites were evaluated on each day time-step using a two-sided Student’s t-test and the 100 best simulations for the time-variant parameterisations. The confidence bounds of the t-tests were set at 95%. To test the differences within the soils, Site A and Site B water ages were evaluated for the fast and slow domains, and the evaporation and root uptake water ages. The null hypothesis for each analysis was equal isotopic mean values for Site A and Site B with unknown variance. Fig (H.1) shows the periods of significant difference (coloured regions) against periods of no significant differences (white regions). The statistical differences between the measured isotopic compositions for Site A and Site B are shown with black “x” while insignificant differences between the measured isotopic compositions between the sites are shown with red “x”. Generally, isotopic compositions between the two sites were significantly different for both measured and simulated values. The greatest similarities are observed between the slow flow domain water ages in Site A and Site B in the shallowest soil layer (5 cm), which is most noticeable during the wet conditions in the winter. Additionally, the evaporation and root uptake water ages in Site A are not significantly different for a large portion of the simulation,
encompassing the wettest conditions during the winter where both fluxes show a selection from the shallowest soil layer (5 cm).

Figure H.1: Colour map showing periods of significant differences between two time-series. Coloured regions indicate significant differences between time-series and white regions indicate no significant differences between the time-series.