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Catchment transit time variability with different SAS function parameterizations for the unsaturated zone and groundwater

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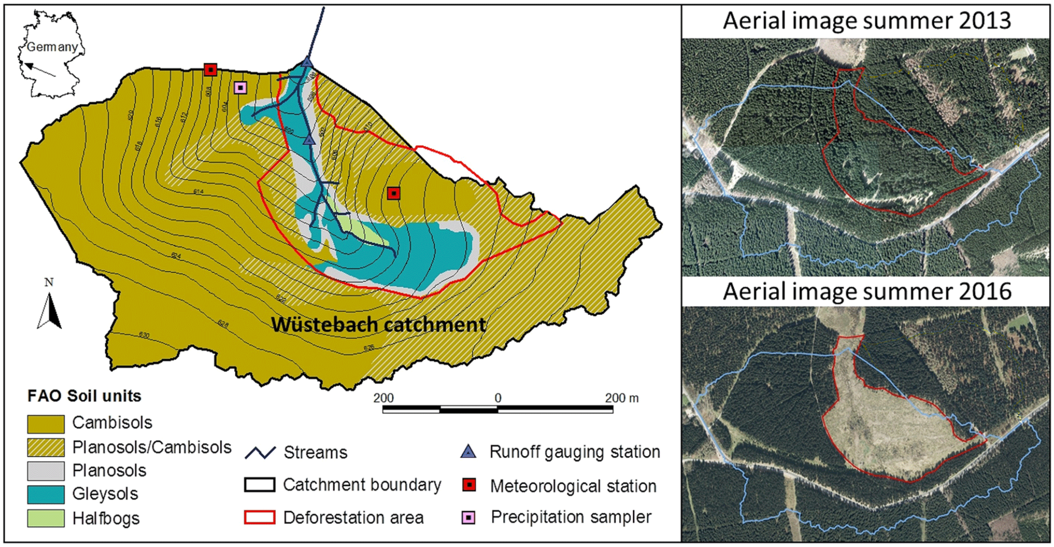

Figure S 1. Map of the Wüstebach study catchment located in Germany's Eifel National Park (adapted from Hrachowitz et al. (2021). The map shows major soil types, instrumentation of the Wüstebach experimental catchment, and the deforestation area before and after the clear-cut, the aerial images (© Google Earth, Maxar Technologies 2020).

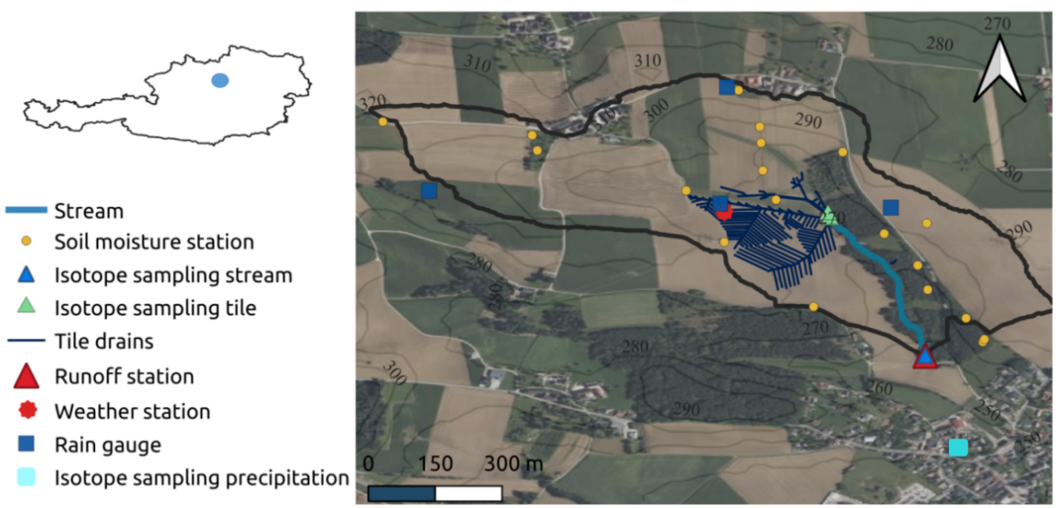

Figure S 2. Map of the HOAL catchment located in Lower Austria (adapted from Türk et al. (2024)). The map shows the location of rain gauges, a weather station, soil moisture stations, isotope sampling of streamwater and isotope sampling of precipitation (located approximately 300m south of the catchment, light blue circle) (map image from © Microsoft, Bing Maps via Virtual Earth)

Table S 1. Water balance, state and flux equations used in the transport model.Model parameter definitions are listed in Table S 2

Storage Component	Eq.	Constitutive equations	Eq.
Snow bucket			
$\frac{dS_{\text{snow}}}{dt} = P_s - P_m$	(1)	$P_s = \begin{cases} P, & T < T_T, \\ 0, & T \geq T_T \end{cases}$	(6)
	–	$P_m = \begin{cases} 0, & T < T_T, \\ \min\left(F_{\text{melt}}(T - T_T), \frac{S_{\text{snow}}}{dt}\right), & T \geq T_T \end{cases}$	(7)
Interception storage			
$\frac{dS_i}{dt} = P_r + P_m - P_e - E_i$	(2)	$P_r = \begin{cases} 0, & T < T_T, \\ P, & T \geq T_T \end{cases}$	(8)
	–	$P_e = \max\left(0, \frac{S_i - I_{\max}}{dt}\right)$	(9)
	–	$E_i = \min\left(E_p, \frac{S_i - I_{\max}}{dt}\right)$	(10)
Soil storage			
$\frac{dS_r}{dt} = P_e - R_f - R_s - E_a$	(3)	$\text{Cap} = (1+\gamma)\, S_{r,\max}\left(1 - \max\left(0, (1 - \frac{S_r}{S_{r,\max}})\right)^{\frac{1}{1+\gamma}}\right)$	(11)
	–	$R_f = P_e - S_{r,\max} + S_r + S_{r,\max}\left(1 - \frac{P_e + \text{Cap}}{(1+\gamma)\, S_{r,\max}}\right)^{1+\gamma}$	(12)
	–	$R_s = \min\left(R_{s,\max}\frac{S_r}{S_{r,\max}}, \frac{S_r}{dt}\right)$	(13)
	–	$E_a = \min\left((E_p - E_i)\min(\frac{S_r}{S_{r,\max} L_p}, 1), \frac{S_r}{dt}\right)$	(14)
Division, fast flow & overland flow	–	$R_{ff} = C_p\, R_f \quad R_{fs} = (1 - C_p)\, R_f$	(15)
	–	$Q_o = \begin{cases} 0, & P_r < P_{\text{tresh}}, \\ C_n\, R_{ff}, & P_r \geq P_{\text{tresh}} \end{cases}$	(17)
	–	$R_{fn} = (1 - C_n)\, R_{ff}$	(18)
Fast-responding bucket			–
$\frac{dS_f}{dt} = R_{fn} - Q_{of} - Q_f$	(4)	$Q_{of} = \max\left((S_f(\frac{S_f}{S_{f,\max}})^{B_f} - S_{f,\max}), 0\right)$	(19)
	–	$Q_f = \max\left(0, \left(S_f\left(1 - e^{-k_f t}\right)\right)\right)$	(20)
Groundwater storage			–
$\frac{dS_{s,\text{tot}}}{dt} = R_s + R_{fs} - Q_s - Q_l$	(5)	$S_{s,\text{tot}} = S_{s,a} + S_{s,p} + R_s + R_{fs}$	(21)
	–	$Q_{s,\text{tot}} = \frac{S_{s,\text{tot}} - S_{s,\text{tot,out}}}{dt}$	(22)
	–	$\frac{Q_s}{Q_l} = \max\left(0, \frac{k_a(S_{s,\text{tot}} - S_{s,p})}{k_p\, S_{s,\text{tot}}}\right)$	(23)
	–	$Q_s = \frac{\frac{Q_s}{Q_l} Q_{s,\text{tot}}}{(\frac{Q_s}{Q_l} + 1)}$	(24)
	–	$Q_l = \frac{Q_{s,\text{tot}}}{(\frac{Q_s}{Q_l} + 1)}$	(25)

In the Table S 1 P (mm d^{-1}) is total precipitation, P_s (mm d^{-1}) is solid precipitation (snow), P_r (mm d^{-1}) is liquid precipitation (rain), P_m (mm d^{-1}) is snowmelt, P_e (mm d^{-1}) is throughfall, E_i (mm d^{-1}) is interception evaporation, E_a (mm d^{-1}) is evaporation from the root zone, R_f (mm d^{-1}) is total preferential fast response, R_{fs} (mm d^{-1}) is fast recharge to the slow-responding reservoir, R_{ff} (mm d^{-1}) is preferential fast response, Q_o (mm d^{-1}) is infiltration-excess overland flow, R_{fn} (mm d^{-1}) is preferential fast response to the fast-responding reservoir, Q_f (mm d^{-1}) is flow from the fast-responding reservoir, Q_{of} (mm d^{-1}) is saturation-excess overland flow from the fast-responding reservoir, R_s (mm d^{-1}) is slow recharge to the slow-responding reservoir, Q_s (mm d^{-1}) is flow from the slow-responding reservoir, Q_l (mm d^{-1}) is deep infiltration loss, and Q_{tot} (mm d^{-1}) is total discharge.

Table S 2. Definitions and uniform prior distributions of the parameters of the solute-transport model (Fig. 2).

Parameter	Unit	Definition	Lower, Upper Bound
Hydrological			
T_T	(°C)	Threshold temperature for snow melt	[-4.0, 5.0]
γ	(–)	Shape factor	[0.0, 5.0]
B_f	(–)	Saturation excess overland flow coefficient	[0.0, 0.00001]
C_n	(–)	Division parameter for fraction of overland flow	[0.0, 1.0]
C_p	(–)	Division parameter for fast groundwater recharge	[0.0, 1.0]
F_{melt}	(mm d^{-1} °C^{-1})	Melt factor	[1.0, 5.0]
I_{max}	(mm)	Interception capacity	[1.2, 5.0]
K_a	(d^{-1})	Storage coefficient of the slow-responding reservoir	[0.01, 1.2]
K_f	(d^{-1})	Storage coefficient of the fast-responding reservoir	[0.01, 2.0]
K_p	(d^{-1})	Storage coefficient of deep infiltration losses	[0.0, 0.00001]
L_p	(–)	Transpiration water stress factor	[0.0, 1.0]
P_{tresh}	(mm d^{-1})	Threshold precipitation for overland flow	[2.0, 20.0]
$R_{\mathrm{s,max}}$	(mm d^{-1})	Maximum percolation rate	[0.0, 1.2]
$S_{\mathrm{f,max}}$	(mm)	Fast response storage capacity	[0.0, 20.0]
$S_{\mathrm{r,max}}$	(mm)	Root-zone storage capacity	[100, 500]
Tracer			
$S_{s,p}$	(mm)	Passive storage capacity	[1000, 10000]
$S_{U,\mathrm{Alpha}}$	(–)	SAS alpha shape parameter for root zone	[0.0, 1.0]
$S_{Gw,\mathrm{Alpha}}$	(–)	SAS alpha shape parameter for Groundwater	[0.98, 1.0]

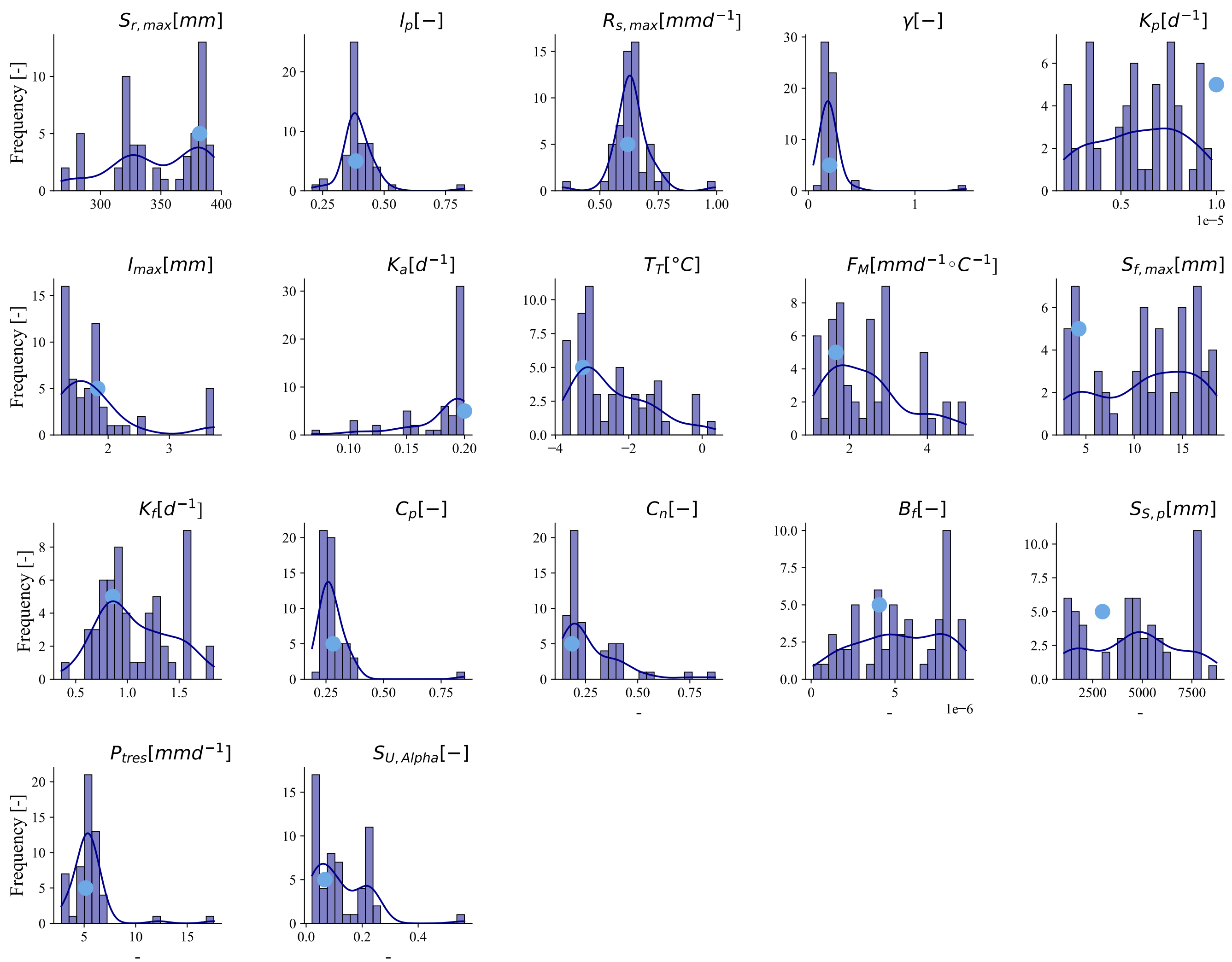

Figure S 3. Pareto optimal distributions of selected 55 parameters for the HOAL catchment. The model calibration results are shown as a frequency histogram. The dots indicate the parameter values associated with the best-balanced solution with the lowest DE.

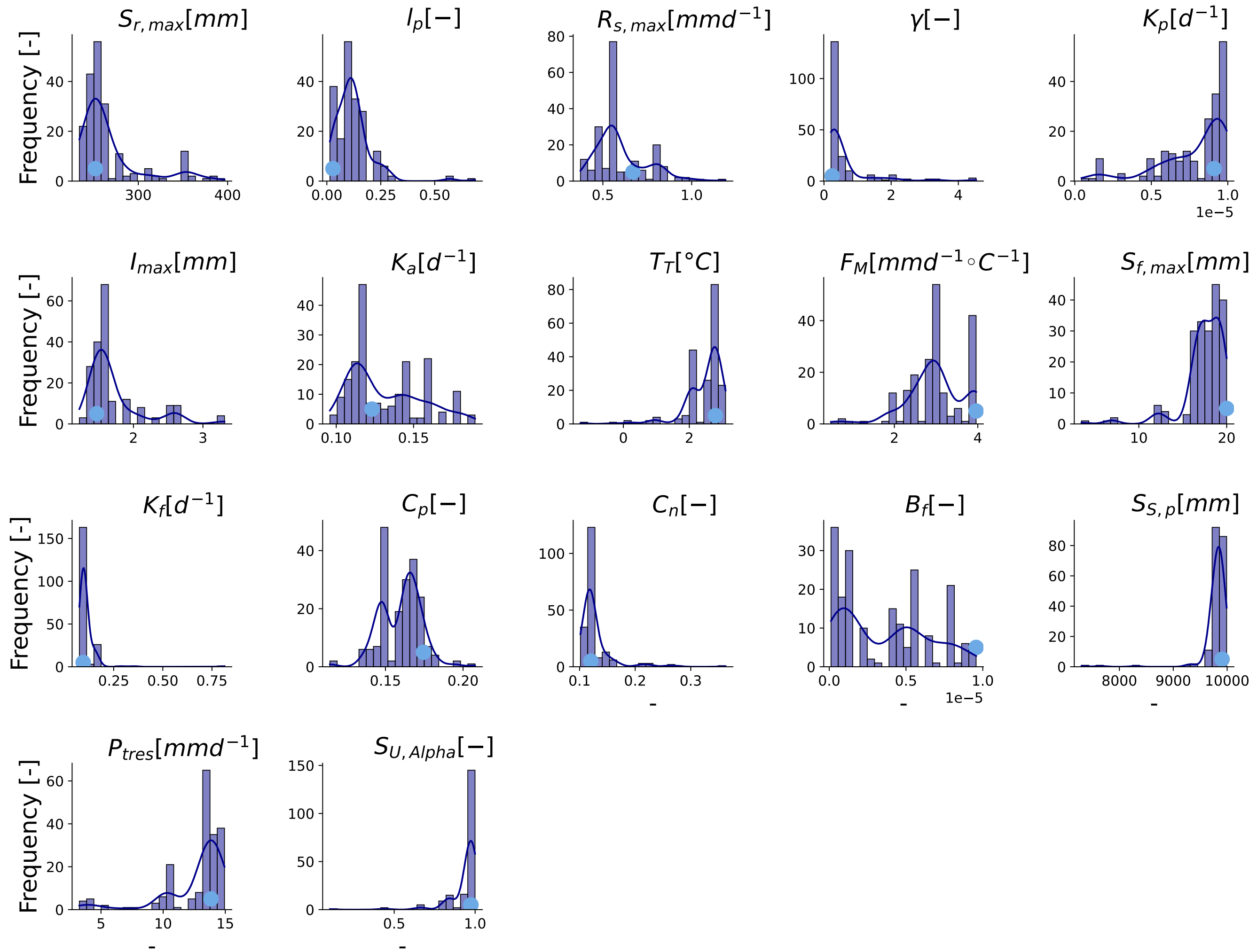

Figure S 4. Pareto optimal distributions of selected 190 parameters for the Wüstebach catchment. The model calibration results are shown as a frequency histogram. The dots indicate the parameter values associated with the best-balanced solution with the lowest DE.

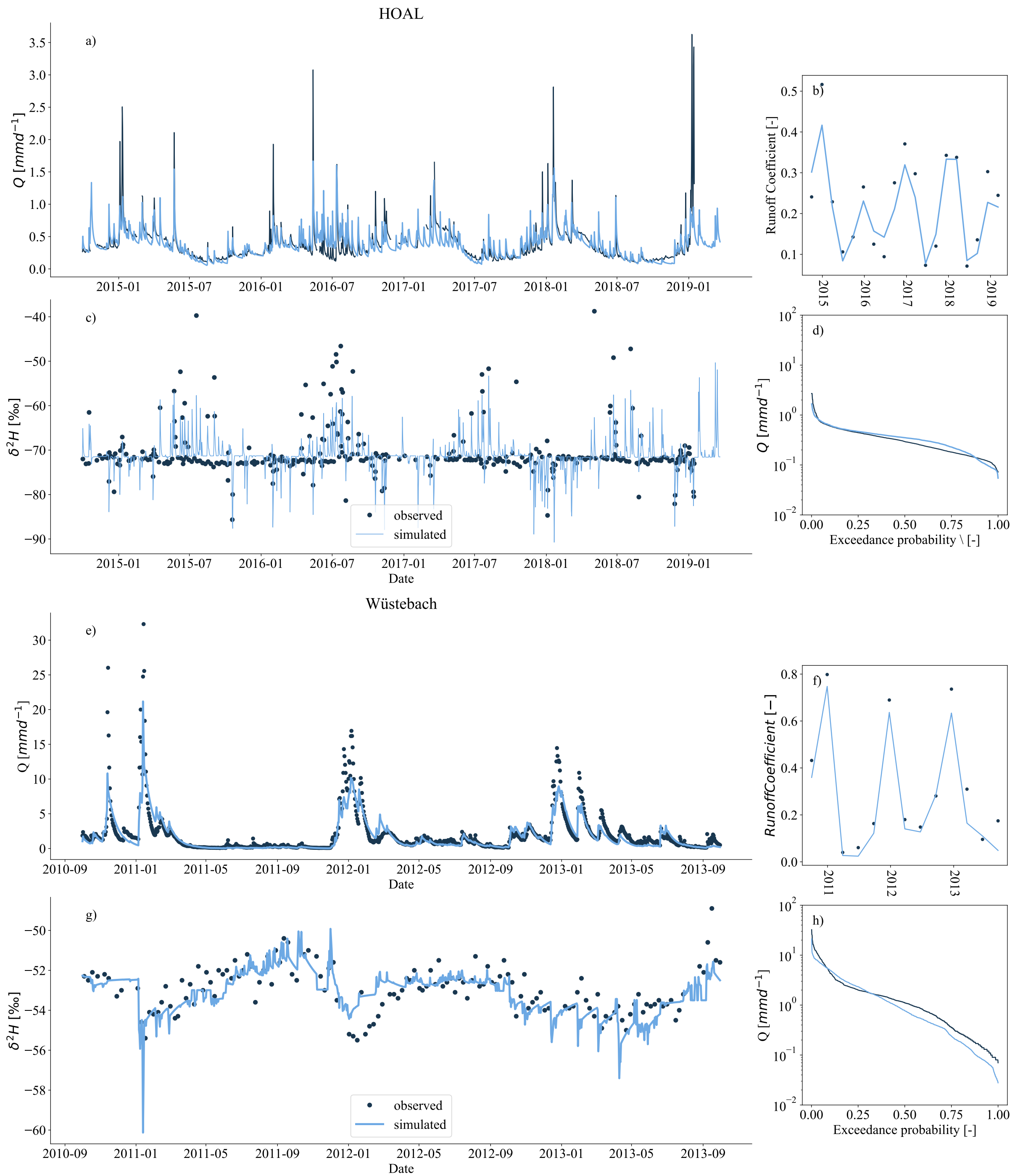

Figure S 5. Modelling results for streamflow, the signature of streamflow, and δ^2H ratios in the stream for HOAL (a-d) and Wüstebach (e-h). Observed values are presented as black lines and dots, while simulations based on the best optimal solution are shown as blue lines for all panels. (a, e) observed and modelled daily streamflow Q (mm-1). (b, f) observed and modelled a three-month averaged runoff coefficient (RC). (c, g) observed and modelled δ^2H signals in streamflow. (d, h) Observed and modelled flow duration curves for HOAL and Wüstebach, respectively.

Table S 3. Signatures for streamflow, δ^2Hsignal and the associated performance metrics used for model calibration scenarios and efficiency evaluation. The performance metrics included the Nash-Sutcliffe efficiencies of streamflow (NSE_Q), of logarithmic streamflow (NSE_{logQ}), the flow duration curve (NSE_{FDC}),the runoff coefficient averaged over three months (NSE_{RC}) as well as the NSE of the δ^2H signal in streamflow $NSE_{\delta^2\mathrm{H}}$

Signatures	**Abbreviation**	**Performance Metric**	**Reference**
Time series of streamflow		NSE_Q	(Nash and Sutcliffe, 1970)
	Q	$\mathrm{NSE}_{\log Q}$	
Flow duration curve	FDC	$\mathrm{NSE}_{\mathrm{FDC}}$	(Jothityangkoon et al., 2001)
Seasonal runoff ratio	RC	$\mathrm{NSE}_{\mathrm{RC}}$	(Yadav et al., 2007)
Time series δ^2H in streamflow	δ^2H	$\mathrm{NSE}_{\delta^2\mathrm{H}}$	(Birkel et al., 2011b)

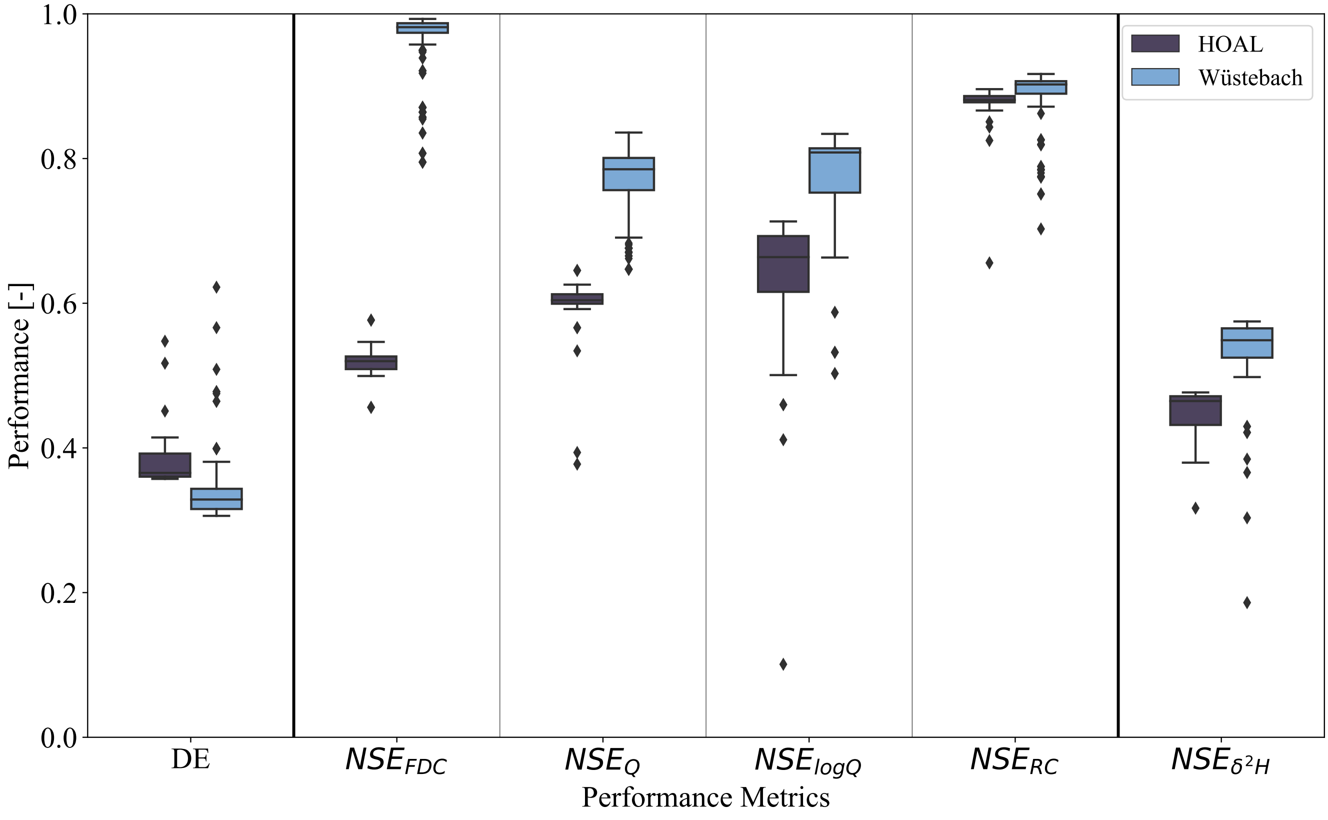

Figure S 6. Boxplots of performance metrics of the 190 best-performing parameter sets. The performance metrics included the Nash-Sutcliffe efficiencies of the flow duration curve (NSE_{FDC}), streamflow (NSE_Q), of logarithmic streamflow (NSE_{logQ}), the runoff coefficient averaged over three months (NSE_{RC}) as well as the NSE of the δ^2H signal in streamflow $NSE_{\delta^2\mathrm{H}}$

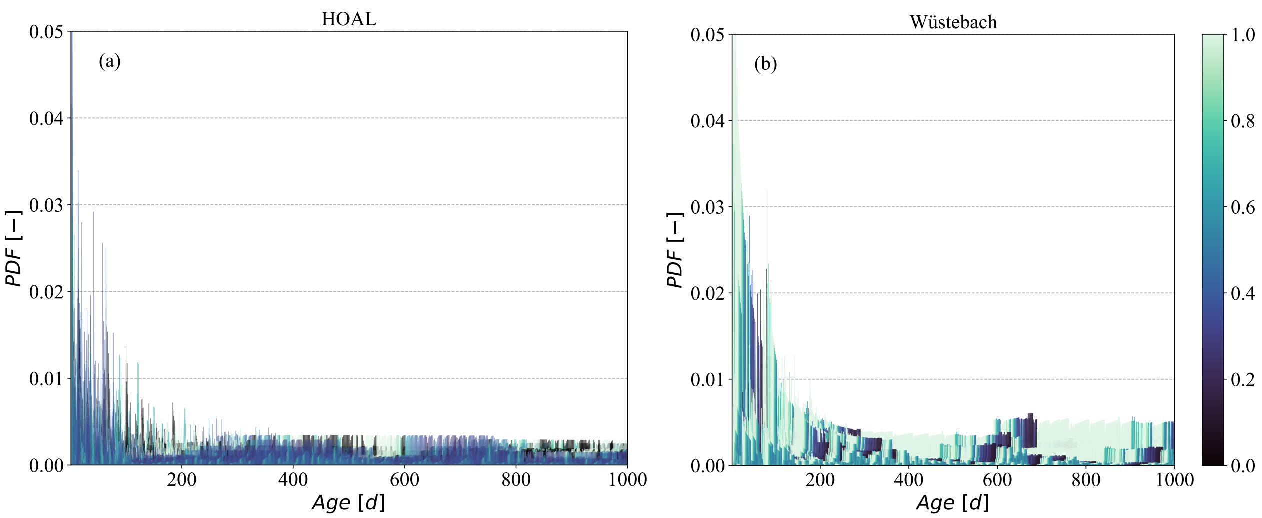

Figure S 7. Probability distribution of the transit times of streamflow for HOAL (a) and Wüstebach (b) catchments, respectively. The color of the lines corresponds to normalized streamflow, where blue indicates high flow and light green indicates low flow.

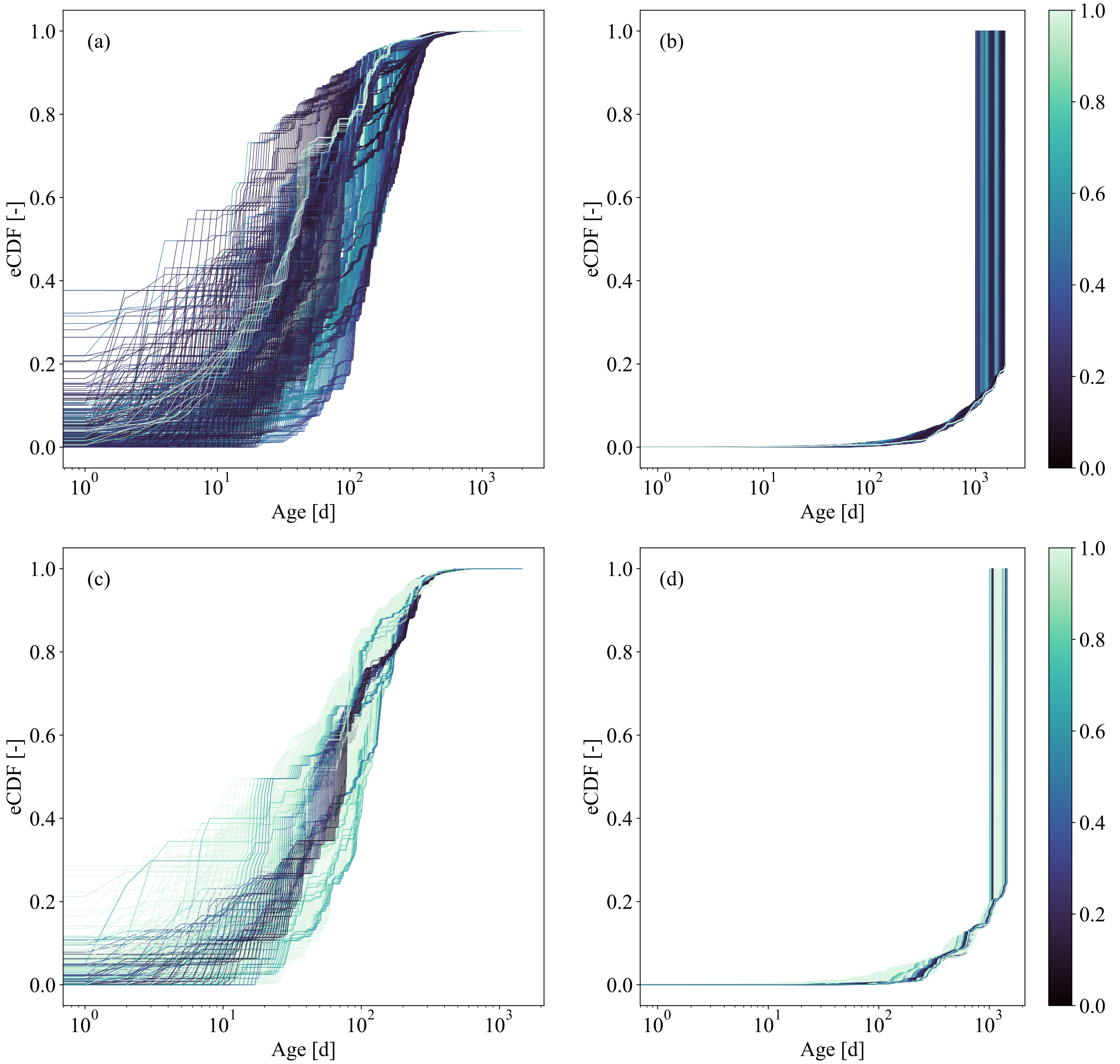

Figure S 8. Residence time distribution of the root zone (a, c) and groundwater (b, d) for the HOAL (top) and Wüstebach (bottom) catchments, respectively. The color of the lines corresponds to normalized streamflow, where light green indicates high flow and dark blue indicates low flow.

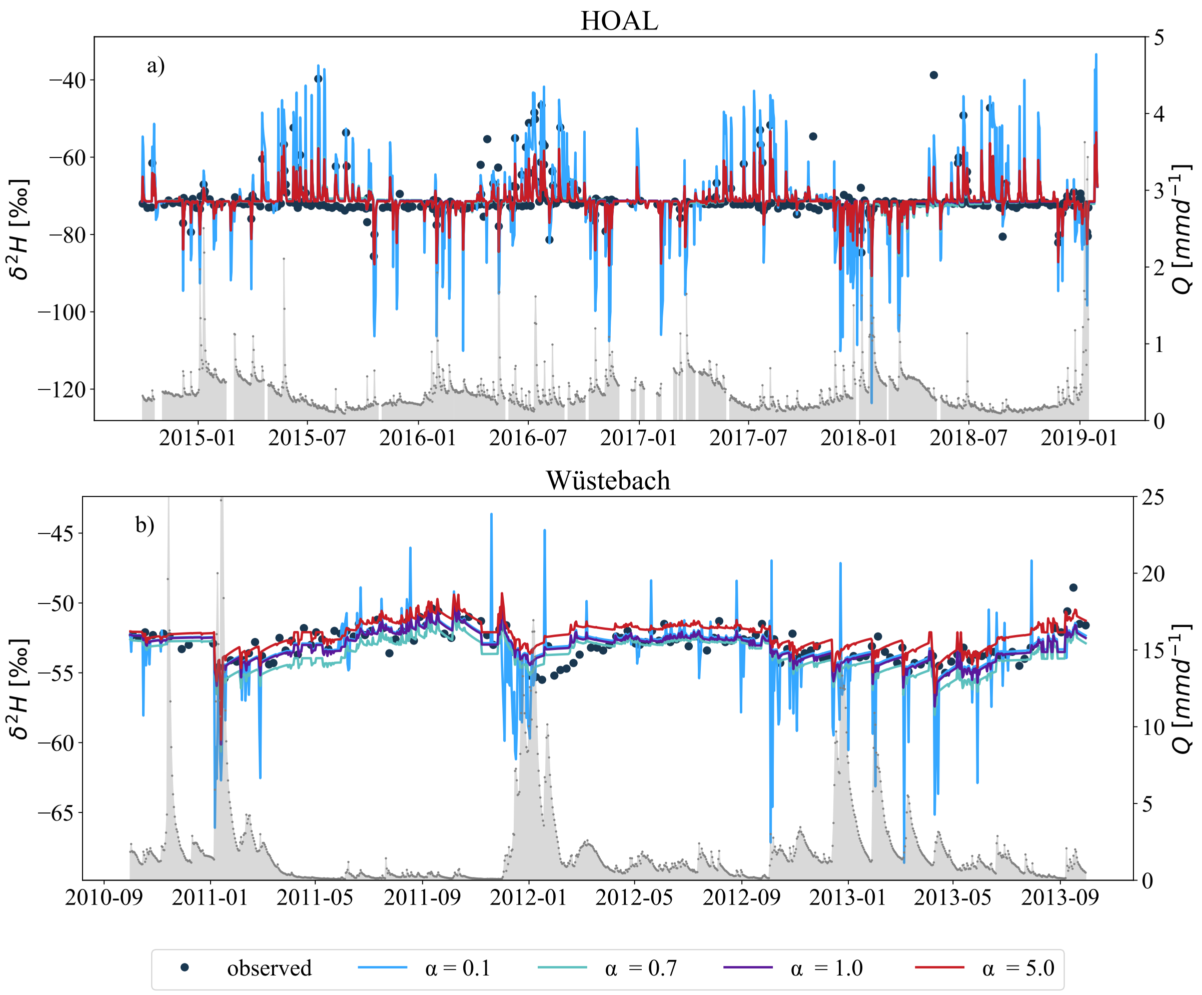

Figure S 9. Simulation of δ^2H in streamflow based on varying SAS shape parameter α [-] in groundwater for (a) HOAL and (b) Wüstebach. The simulations ranged from very young water preference (α = 0.1) to old water preference (α = 5) for the groundwater, while for the root zone compartment, a calibrated value was used (α = 0.14, for HOAL and 0.98 for Wüstebach). Line colours correspond to the simulation based on α values: blue for 0.1, turquoise for 0.7, purple for 1.0, and red for 5.0. The grey-shaded area shows the measured streamflow (Q, mm d^{-1}) for both catchments.

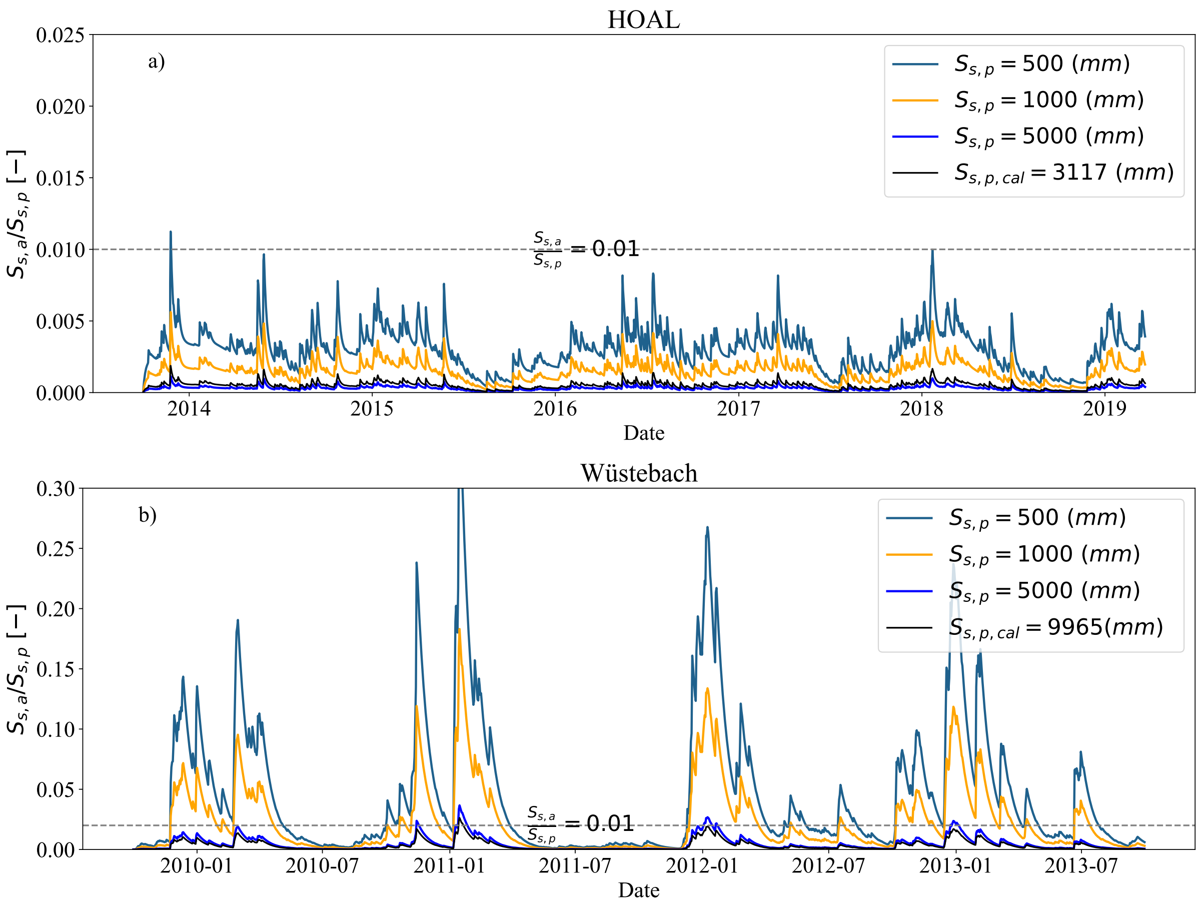

Figure S 10. Time series of the ratio of active to passive groundwater storage volumes ($S_{s,a}/S_{s,p}$) for (a) the HOAL catchment and (b) the Wüstebach catchment under varying passive storage volumes ($S_{s,p}$). Lines represent different scenarios of passive storage volumes: 500 mm (blue), 1000 mm (orange), 5000 mm (dark blue), and the calibrated passive storage volume ($S_{s,p,\text{cal}}$) of 3117 mm for HOAL and 9965 mm for Wüstebach (black). The dashed line indicates $S_{s,a}/S_{s,p} = 0.01$, representing a threshold for significant active storage contribution. The results highlight the impact of the passive storage volume on the temporal dynamics of groundwater storage partitioning in both catchments.

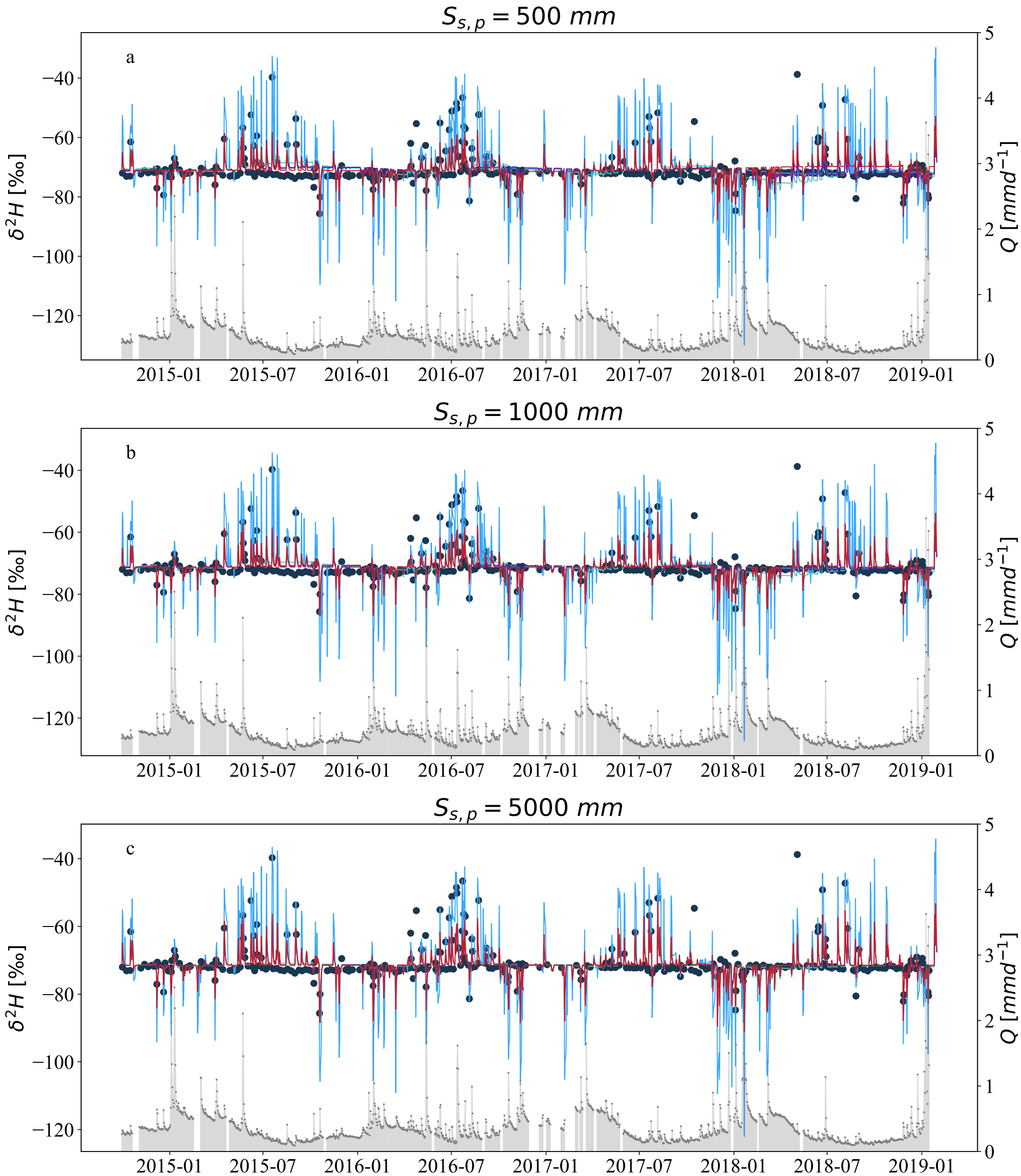

Figure S 11. The simulation results for δ^2H signals from streamflow (Q mm d^{-1}) based on varying passive groundwater storage volumes ($S_{S,p}$ = 50 mm, $S_{S,p}$ = 500 mm, 1000 mm, and 5000 mm) and different mixing assumptions determined by SAS function shape factors (α = 0.1, 0.7, 1.0, and 5.0) for the HOAL catchment (a-c). (a-c), black dots represent grab samples of δ^2H from streamflow. Line colours correspond to the simulation based on α values: blue for 0.1, turquoise for 0.7, purple for 1.0, and red for 5.0.

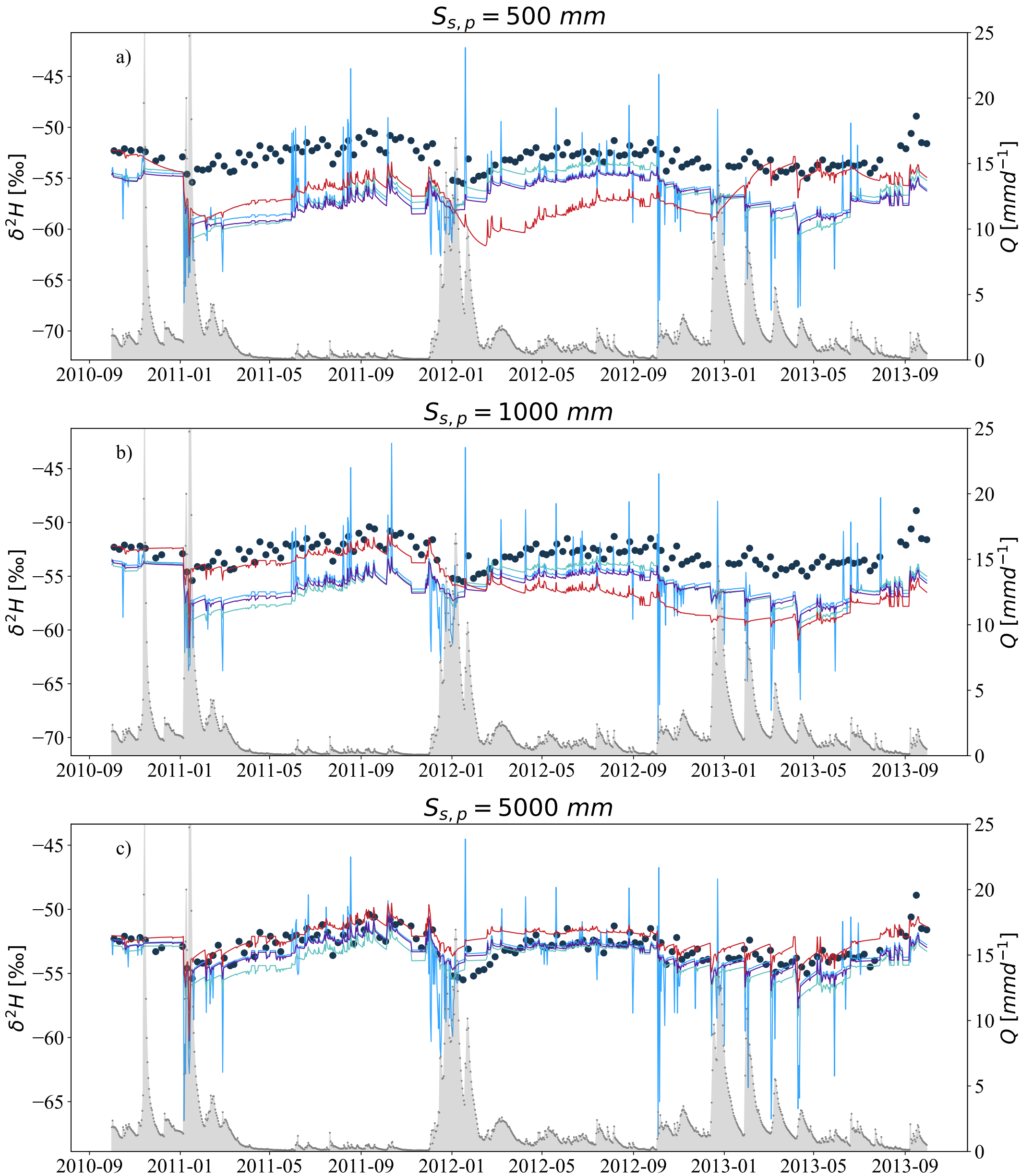

Figure S 12. The simulation results for δ^2H signals from streamflow (Q mm d^{-1}) based on varying passive groundwater storage volumes ($S_{S,p}$ = 500 mm, 1000 mm, and 5000 mm) and different mixing assumptions determined by SAS function shape factors (α = 0.1, 0.7, 1.0, and 5.0) for the Wüstebach catchment (e-f). (e-f) black dots represent weekly grab samples of δ^2H from streamflow. Line colours correspond to the simulation based on α values: blue for 0.1, turquoise for 0.7, purple for 1.0, and red for 5.0.