

Supporting Information for “Controls on streamwater age in a saturation overland flow-dominated catchment”

[1, 2] Dana A. Lapidés

[1] W. Jesse Hahm

[3] Daniella M. Rempe

[4] William E. Dietrich

[2] David N. Dralle

¹Department of Geography, Simon Fraser University, Burnaby, BC, Canada

²Pacific Southwest Research Station, United States Forest Service, Davis, CA, USA

³University of Texas, Austin, Austin, TX, USA

⁴University of California, Berkeley, Berkeley, CA, USA

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Introduction

These supporting information include supplementary analyses and figures for “Controls on streamwater age in a saturation overland flow-dominated catchment.” These analyses consist of detailed information about StorAge Selection (SAS) parameterization (S1, Figures S1-S5), additional SAS results not shown in the main text (S2, Figures S6-S7), analysis identifying likely kinetic fractionation at low flows (S3, Figure S8), and a synthetic analysis testing the impact of sampling interval on study results (S4, Figure S9). See the main text Section 2.6 for a description of SAS methodology used in this study.

S1. Parameterization of SAS functions

The range of shapes for the streamflow SAS function is shown in Figure S1a for the median values of $k_{min_Q} = 0.45$ and $k_{max_Q} = 1.04$ among the top 95th percentile of parameter sets sampled. As shown in Figure S1a, the SAS function varies as a function of the wetness state of the catchment. Assuming a uniform storage distribution, at the

wettest state the 50th percentile of streamflow age derives from the 25th percentile of storage ages, while at the driest state the 50th percentile of streamflow age derives from the 50th percentile of storage ages.

Histograms of the top 95th percentile of parameter sets in Figure S1b-g show that a good model fit (maximum KGE = 0.83, maximum NSE = 0.66) can arise from nearly any parameter value of: i) the minimum power for the streamflow SAS function (k_{min_Q}), ii) the scaling factor for the log-dependence on wetness state in the streamflow SAS function (\logfactor_Q), iii) the power law exponent for the ET SAS function (k_{ET}), and iv) the initial isotope concentration in storage (C_{S_0}). In contrast, the model performs best (shown via a peak in the histogram of parameter distributions) for: c) maximal power for the streamflow SAS function (k_{max_Q}) near 1 and f) initial storage volume (S_0) near our estimated maximal storage volume of 200 mm. Relationships between parameters and model performance are shown via a scatterplot matrix in Supplemental Information 1.

We parameterized the StorAge Selection (SAS) function using a Monte Carlo simulation of 10,000 parameter sets. The relationship between all parameter pairs in the calibration time period (2016-2019 water years), is shown in Figure S2 colored by NSE and in Figure S3 colored by KGE. There is no pattern in the relationships among any parameters except k_{max_Q} and S_0 that indicate a preferential relationship between these parameters. Any value of k_{min_Q} , \logfactor_Q , k_{ET} , and C_{S_0} can yield a model with a high NSE and KGE, with no relationship among the values that yield high NSE/KGE between these parameters. The value of k_{max_Q} has the biggest impact on NSE, and the value of S_0 has the biggest impact on KGE. The same patterns appear in evaluation results of the top 95th percentile of parameters in the 2020 water year, shown in Figure S4 for NSE and Figure

S5 for KGE. The parameter relationships among $kmin_Q$, $logfactor_Q$, k_{ET} , and C_{S0} fill the full space, while values are preferentially excluded from the 95th percentile parameter sets for $kmax_Q$ and $S0$.

S2. SAS results across more conditions

While only WY2019 results are shown in the main text, results of StorAge Selection modeling are similar for WY 2020 (Figure S6).

We also compare the distribution of absolute error in predicted streamflow concentration during periods of rapid wet/dry state evolution versus periods of consistent wetness (Figure S7). A transition from wet to dry state is considered to happen at an instantaneous flow rate of 0.1 mm/day (as marked in Figure S7a), with the two days before and after defined as the transition period or time when the catchment is switching states. The catchment is in a wet state any other time when streamflow is above 0.1 mm/day when not switching states. Figure S7b shows histograms of absolute error in modeled streamflow concentration when the catchment is in a wet state (blue) or switching states (red). The modes of the two histograms are very similar, although the error for switching state is slightly larger. When in a wet state, error is never above 5 ‰; however, when switching states, the tail is longer.

S3. Kinetic fractionation at low flow

To confirm that evaporative enrichment occurs at flows below 0.05 mm/day, we examined one representative flow event in 2019. From April 15-March 15, flow decreases steadily with no precipitation. In Figure S8, points are colored by date, moving from white to dark blue with increasing time and decreasing streamflow, and points outlined in red fall below the 0.05 mm/day threshold used to exclude data points from the SAS

model calibration. Figure S8 demonstrates that as flow decreases, isotopic concentration increases following a slope much shallower (≈ 4) than that the local meteoric line (≈ 8), suggesting evaporative enrichment (Craig, 1961). We examined a similar end-of-season period in 2020 but did not note evaporative fractionation, indicating that evaporative enrichment may not always occur below 0.05 mm/day, but this threshold provides a conservative cutoff to prevent calibration from being impacted by evaporative fractionation.

S4. Confidence in information on daily timescale

As described in the discussion (Section 2.6), the stream sampling interval frequency (daily, in our case) may limit the ability of the model to resolve the lower bound (youngest) water transit times. To explore this, we performed a synthetic analysis to determine the potential impact of a daily sampling interval on our results. We generated a timeseries of [dD] in streamflow with about 50% of streamflow younger than 1 day. This timeseries was generated using the form of StorAge Selection (SAS) function used in this study, i.e. a time-varying power law that varies with catchment wetness state (Equation 10 in main text) with $k_{min_Q} = 0.85$, $k_{max_Q} = 1.0$, $\logfactor_Q = 45$, $k_{ET} = 1$, $S_0 = 170$ mm, and $C_{S_0} = -50$ ‰. To enhance new (< 1 day old) water production at short timescales, we set a threshold wetness value ($w_i=0.3$) above which the power in the SAS function exponent is $k = 0.1$. To explore the impact of sampling interval on the parameterization results, we simulated a range of sampling intervals using the observed rainfall timeseries and the generated streamflow timeseries with enhanced new water fraction. We explored the effect of sampling frequency on resolved age distributions by down-sampling from daily frequency to 2, 4, 8, and 16 day sampling intervals for the streamflow by dropping additional data. (Isotope concentrations in streamflow are instantaneous rather than

aggregate measurements). In contrast, for precipitation, we averaged concentrations over the previous 2, 4, 8, or 16 days to downsample. We did not examine sampling intervals shorter than daily since we do not have data on how concentrations in rainfall vary at subdaily timescales. For each sampling interval, we ran 5,000 Monte Carlo simulations with the same range of parameters and same SAS functional forms used in the study and evaluated performance using Nash-Sutcliffe Efficiency (NSE) and Kling-Gupta Efficiency (KGE). The top 95th percentile of parameter sets for each sampling interval were retained. Model performance dropped with increasing sampling interval (Figure S9a), with the median NSE dropping below 0.5 by a sampling interval of 8 days. Generally, model performance remains quite good over a range of sampling intervals, with very comparable performance at sampling intervals of 1-4 days.

Using the top 95th percentile of parameter sets for each sampling interval, we calculated the overall fraction of water younger than 1 day throughout the study period (Figure S9b). The fraction of new water calculated for sampling interval 1-4 days have overlapping 99% confidence intervals, while much more new water is predicted for longer sampling intervals. This finding of more new water with a longer sampling interval is contrary to recent findings that indicate a shorter sampling interval may reveal more young water Gallart et al. (2020). Both sites have a Mediterranean climate and high runoff coefficients with up to 90% of streamflow made up of event water. The difference in results is likely due to the very different definition of young water. In the present study, we consider water younger than 1 day, comparable to the dominant runoff generation processes at Dry Creek, whereas Gallart et al. (2020) consider water younger than 73 days, much longer than dominant runoff generation mechanisms. Given that the new water fraction

can be captured consistently with 1-4 day long sampling intervals, the new water fraction inferred from the relatively short sampling interval of 1 day used in this study should provide confidence on the fraction of water younger than 1 day at Dry Creek.

References

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- Gallart, F., Valiente, M., Llorens, P., Cayuela, C., Sprenger, M., & Latron, J. (2020). Investigating young water fractions in a small mediterranean mountain catchment: Both precipitation forcing and sampling frequency matter. *Hydrological Processes*, *34*(17), 3618–3634.
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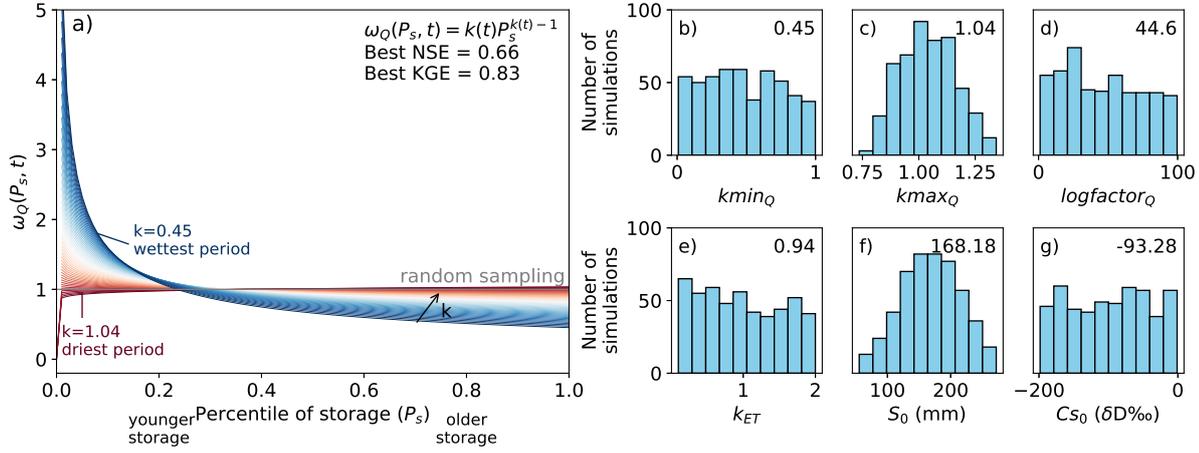


Figure S1. (a) ω_Q is the StorAge Selection (SAS) function described by the general functional form in the upper right corner of the plot. It describes the relative tendency for the stream to draw water from each age percentile of storage P_s . The displayed range of SAS functions for streamflow ω_Q is represented by the median values of k_{min} and k_{max} in the 95th percentile of parameter sets. From wettest to driest conditions assuming a uniform storage distribution, the 50th percentile of streamflow ages range from the youngest 24th-47th percentiles of storage. Histograms of parameters for the top 95th percentile of Monte Carlo simulations of 10,000 parameter sets (b-g) results in a median NSE=0.62 and maximum NSE=0.66, with the median value for each parameter shown in the upper right corner of each panel. k_{min_Q} , k_{max_Q} , and \logfactor_Q are parameters for the streamflow SAS function ω_Q . k_{ET} is a parameter for the evapotranspiration SAS function ω_{ET} . S_0 is the initial catchment storage, and C_{S_0} is the initial isotopic concentration. See Section 2.6 for full details.

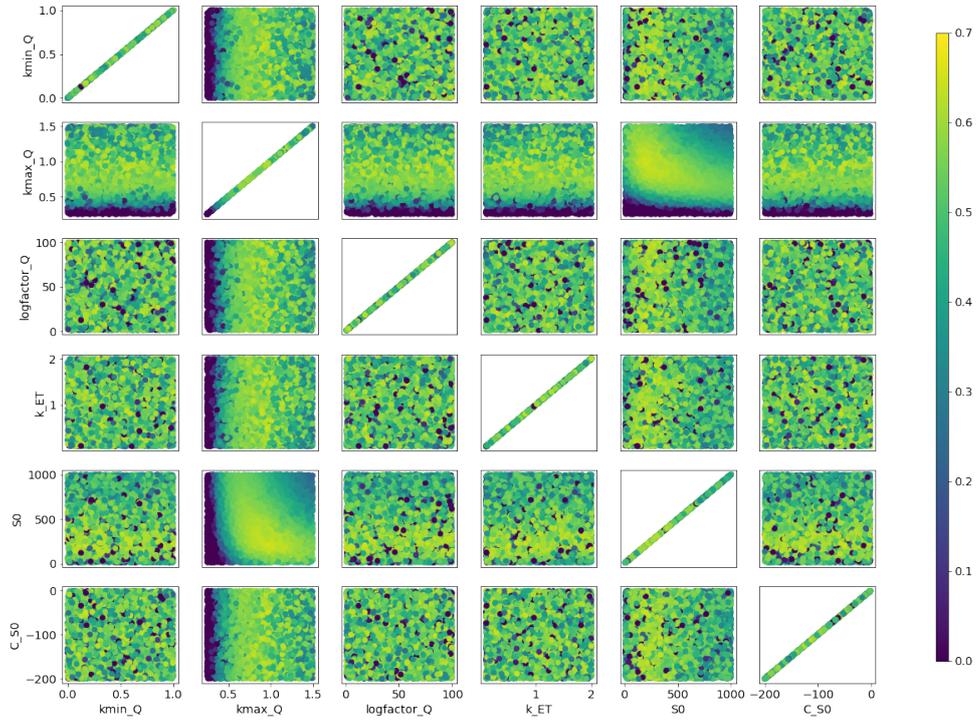


Figure S2. Covariance between parameter performance for all 10,000 parameter sets tested in Monte Carlo simulations. Points are colored by NSE.

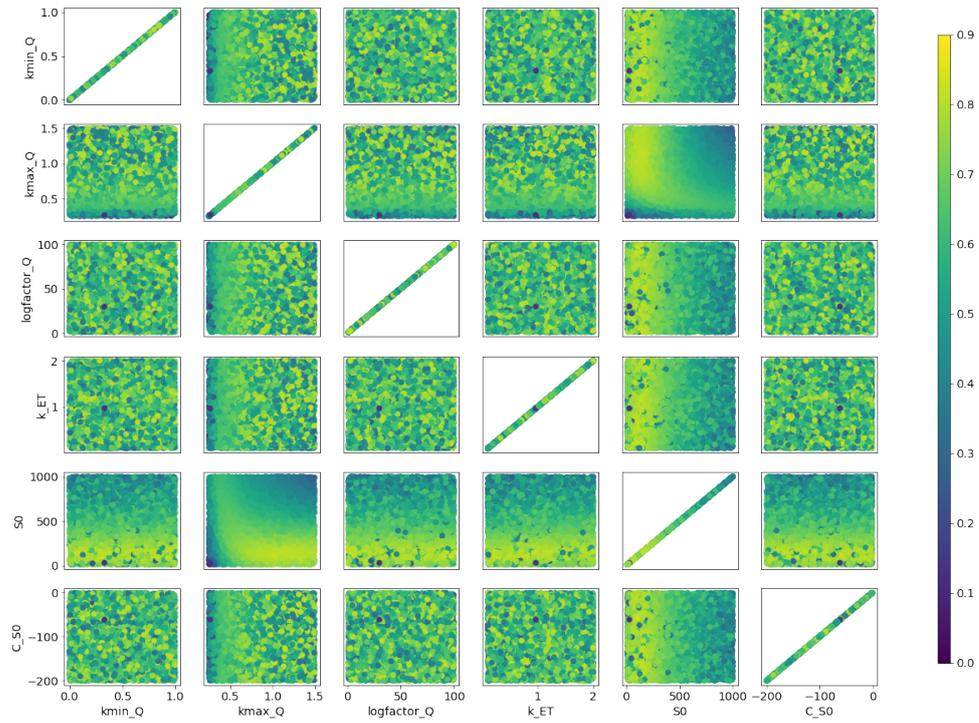


Figure S3. Covariance between parameter performance for all 10,000 parameter sets tested in Monte Carlo simulations. Points are colored by KGE.

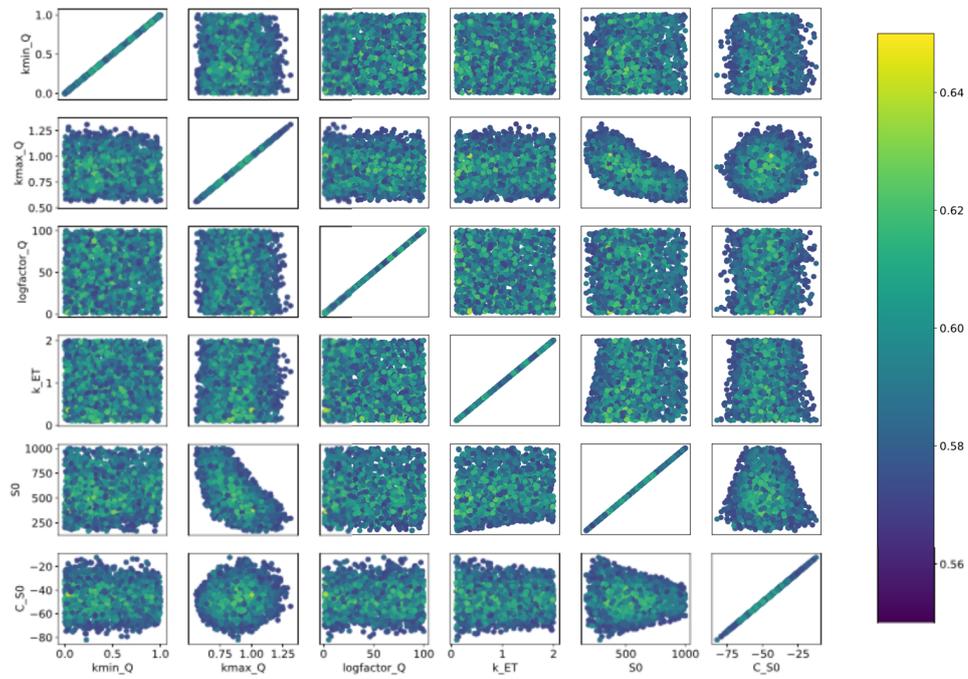


Figure S4. Covariance between parameter performance for all the 95th percentile of parameter sets tested in Monte Carlo simulations. Points are colored by NSE.

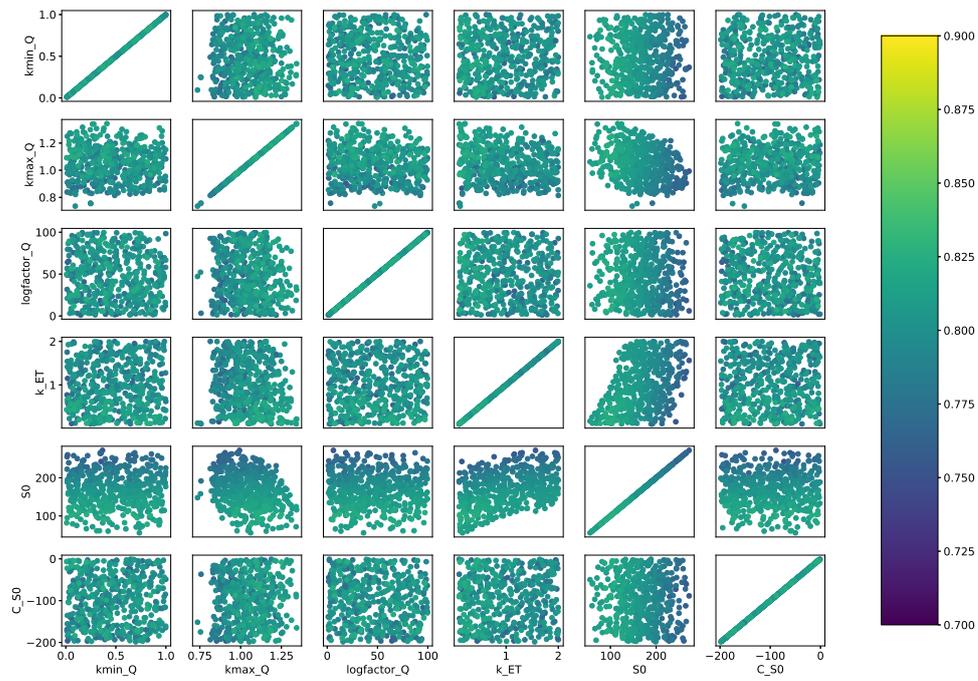


Figure S5. Covariance between parameter performance for all the 95th percentile of parameter sets tested in Monte Carlo simulations. Points are colored by KGE.

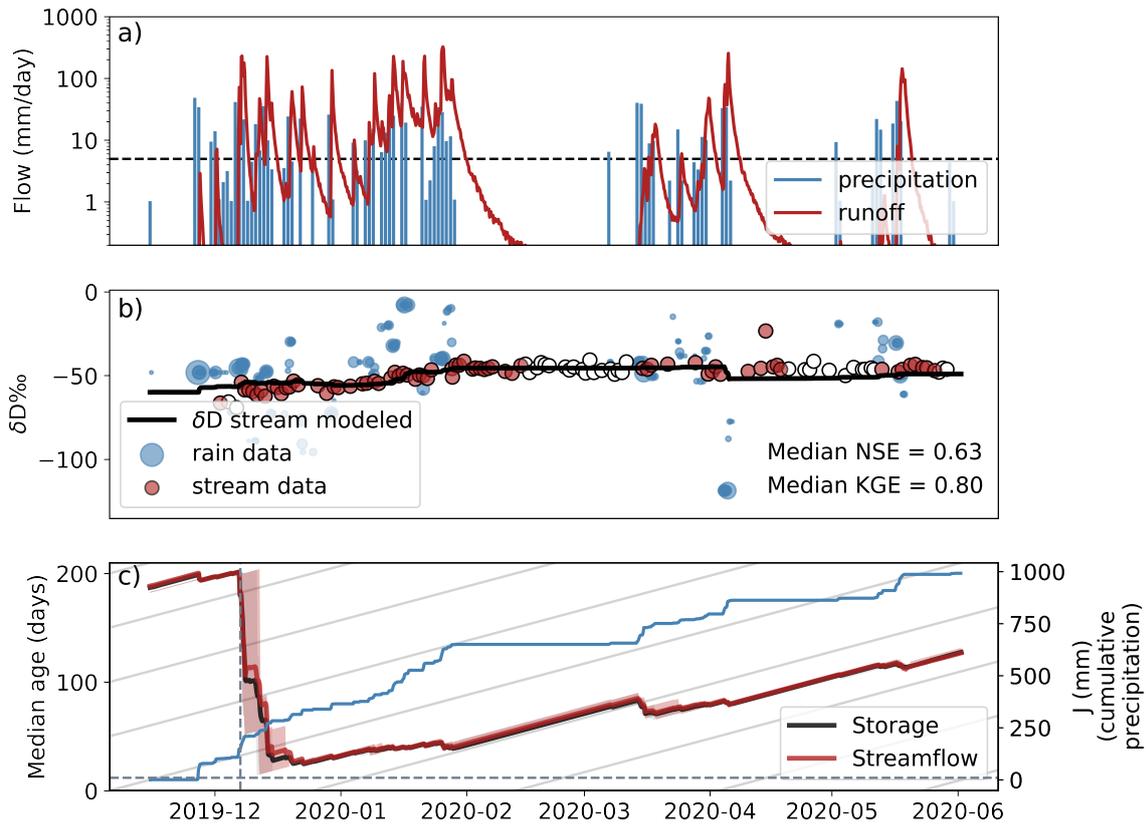


Figure S6. (a) Daily precipitation and instantaneous runoff throughout the wet season 2019-2020. Vertical dashed grey line marks the 5 mm flow threshold above which excess flow is assumed to be SOF. Horizontal dashed grey line marks a median age of 10 days. (b) Confidence bars on SAS model predictions (black line) are smaller than the width of the line. The size of plot markers for rainfall data (blue) are scaled by the volume of precipitation. Data shown in white circles are excluded from calibration of the SAS model due to in-channel evaporative enrichment (streamflow ≤ 0.05 mm/day). Marked median NSE is the median value among the top 95th percentile of parameter sets. (c) Shading around median ages indicates 25th-75th percentile of ensemble simulations, and blue line is cumulative precipitation. Vertical dashed line marks cumulative precipitation of 150 mm, and horizontal dashed line marks a median age of 10 days.

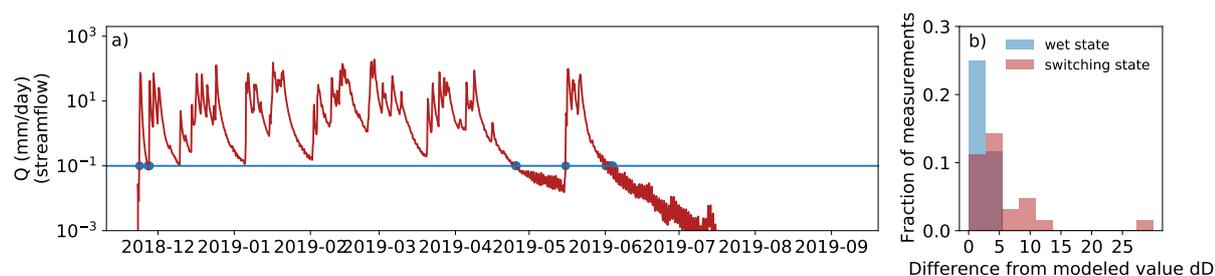


Figure S7. (a) Streamflow at Dry Creek throughout the study period with switches between wet and dry states marked as crossing the blue 0.1 mm/day threshold. Points along the hydrograph where the threshold is crossed are marked with blue dots. (b) Density histograms of absolute error in streamflow concentration between the SAS model and measured streamflow concentration. Times when the catchment is ‘switching states’ are defined by the 2 days before and after the threshold in panel a is crossed. The ‘wet state’ is all times not during a switching state when streamflow is above 0.1 mm/day.

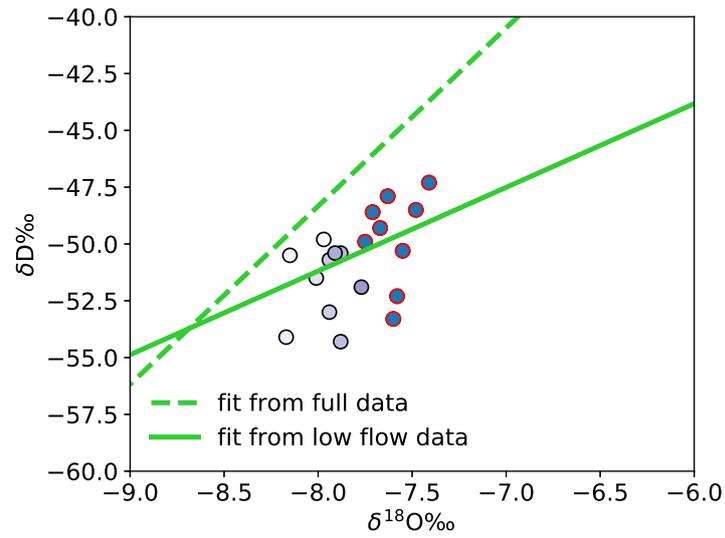


Figure S8. In dual isotope space, the isotope concentration increased from March 15-April 15, 2019 (white to dark blue) as streamflow decreased with no precipitation following a much shallower slope than that for the full set of isotope data. Red outlines indicate that streamflow falls below the 0.05 mm/day threshold for exclusion from calibration.

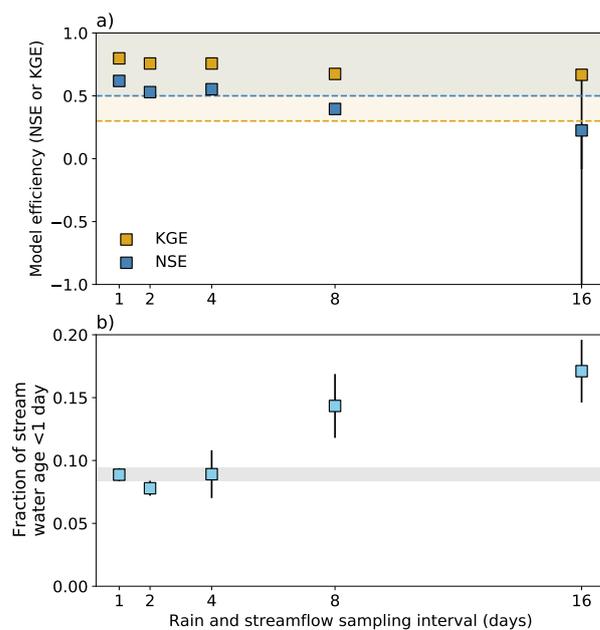


Figure S9. (a) Median model performance of parameterized SAS models as measured by NSE and KGE over a range of sampling intervals for input data. Vertical black lines show 25-75th percentile of model efficiency values. Where not visible, 25-75th percentile range is smaller than the size of the marker. The shaded gold and blue regions indicate the range of KGE and NSE values for a behavioral model (Kirchner, 2003). (b) Mean new water fraction over the full study period with vertical 99% confidence intervals. The horizontal shaded bar is the confidence interval for the 1-day sampling interval.