Ecohydrologic separation alters interpreted hydrologic stores and fluxes in a headwater mountain catchment

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Abstract

Recent studies have demonstrated that compartmentalized pools of water favor to supply either plant transpiration (poorly mobile water) or streamflow and groundwater (highly mobile water) in some catchments, a phenomenon referred to as ecohydrologic separation. The omission of processes accounting for ecohydrologic separation in standard applications of hydrological models is expected to influence estimates of water residence times and plant water availability. However, few studies have tested this expectation or investigated how ecohydrologic separation alters interpretations of stores and fluxes of water within a catchment. In this study, we compare two rainfall-runoff models that integrate catchment-scale representations of transport, one which incorporates ecohydrologic separation and one which does not, for a second-order watershed at the H.J. Andrews Experimental Forest (Oregon, USA), the site where ecohydrologic separation was first observed. The models are calibrated against multiple years of stream discharge and chloride concentration. Model structural variations caused mixed results for differences in calibrated parameters and differences in storage between reservoirs. However, large differences in catchment storage volumes and fluxes arise when considering only mobile water. These changes influence interpreted residence times for streamflow-generating water, demonstrating the importance of ecohydrologic separation in catchment-scale water and solute transport.

Key words

two water worlds hypothesis; hydrologic connectivity; soil water; preferential flow; residence times; plant water sources; conceptual model; tracer

1. Introduction

The unsaturated root zone—the vegetation-accessible region between the earth's surface and the groundwater table (Stephens, 1995)—is the primary node where precipitation is partitioned into terrestrial storage in catchments, either directly within the unsaturated zone or via groundwater recharge, indirect drainage to the stream, and evaporative fluxes (Savenije & Hrachowitz, 2017). This partitioning ultimately determines the pathways water takes to reach the catchment outlet, residence times within various stores, and the physical and chemical processes experienced during transport and storage. Many conceptual and mathematical models either treat the unsaturated zone as completely mixed or assume transport occurs via translatory flow (i.e., infiltrating precipitation displaces water previously stored in soil in a sequential order; Hewlett & Hibbert, 1967). However, work on ecohydrologic separation (the partitioning of less-mobile water available for transpiration by plants from more-mobile water that becomes streamflow; e.g., Brooks, Barnard, Coulombe, & McDonnell, 2010; Evaristo, McDonnell, Scholl, Bruijnzeel, & Chun, 2016; Goldsmith et al., 2012; Hervé-Fernández et al., 2016) challenges the conceptual representation of translator flow. Ecohydrologic separation, also referred to as the two water worlds hypothesis (Berry et al., 2017; McDonnell, 2014), conceptualizes the existence of several pools of water that have limited mixing, effectively representing the unsaturated zone as a location of parallel storage processes. Specifically, under dry conditions some infiltrating water bypasses small pores of the unsaturated zone while other infiltrating water is bound and stored in small pores. Evidence in support of ecohydrologic separation is common in many catchments (see meta-analysis by Evaristo, Jasechko, & McDonnell, 2015) and the conceptual model of ecohydrologic separation explains empirical data. However, we have limited understanding of how including this process in hydrologic models alters our interpretations of stores and fluxes of water at the scale of catchments.

Representation of ecohydrologic separation in hydrologic models could influence estimates of residence times and fluxes of water and solutes (Phillips, 2010; Sprenger, Leistert, Gimbel, & Weiler, 2016; Sprenger et al., 2018) and thus challenge perceptions of dominant hydrologic processes operating within a catchment. For example, because the tightly bound water stored in the unsaturated zone is isolated from flow to streams, the volume of mobile water is expected to be smaller than would be expected from a one water world conceptualization in which all unsaturated water has the potential to generate streamflow. The reduced volume of mobile water should, therefore, result in more variable residence times of water and solutes in the unsaturated zone, with increased residence times for the immobile fraction of water and decreased residence times for the mobile fraction. Furthermore, hydrologic connectivity between subsurface reservoirs controls fluxes of water and solutes through the catchment, and thus stream solute and hydrologic response (e.g., Jencso, McGlynn, Gooseff, Bencala, & Wondzell, 2010; Jencso et al., 2009). Changes in residence times and fluxes of water from hillslopes to streams may alter the potential for associated biogeochemical reactions or weathering to occur within those zones. While this thought experiment suggests ecohydrologic separation will be important at the catchment scale, there are few examples which qualitatively demonstrate its impact on our understanding of stores and residence times of water.

Transport characteristics which reflect working definitions of the two water worlds hypothesis have been incorporated in a number of modeling studies, although the term has not been explicitly used. For example, some studies assume groundwater recharge via preferential flow does not mix with unsaturated zone water and retains the chemical signature of precipitation (e.g., Birkel, Soulsby, & Tetzlaff, 2014). Other have used hydrologic models to explore alternative explanations to the conceptualization of two isolated soil water pools to explain isotopic patterns, typically suggestive of a higher degree of mixing. Sprenger, Leistert, Gimbel, and Weiler (2016) invoked successive mixing of stored water with new rainwater in a soil physical model. Knighton, Saia, Morris, Archiblad, and Walter (2017) found that a combination of preferential and matrix flow best simulated unsaturated zone stable water isotopes in a lumped hydrologic model.

Recent publications have highlighted the influence mixing assumptions have on intepreting internal process dynamics and have advanced approaches for representing incomplete mixing (i.e., nonuniform sampling) associated with ecohydrologic separation. Several modeling studies use age-based methods to examine selective retention and release dynamics in catchments, in which sampling of storage for outflow is biased toward particular ages according to a SAS function or a mixing coefficient (e.g., Benettin, Rinaldo, & Botter, 2013; Benettin, Velde, Zee, Rinaldo, & Botter, 2013; Botter, Bertuzzo, & Rinaldo, 2011; Harman, 2015; Hrachowitz, Savenije, Bogaard, Tetzlaff, & Soulsby, 2013; Rinaldo et al., 2015; van der Velde et al., 2015; van der Velde, Torfs, Van der Zee, & Uijlenhoet, 2012). This transfer function technique can indirectly account for different sources of mixing, including moisture-dependent variations in flow paths and temporal mixing dynamics between mobile and less mobile storages, but does not resolve internal catchment dynamics and treats the entire catchment as a single control volume. Still, several studies demonstrate how a SAS function approach can be applied to simulate selective sampling of younger water for transpiration (Harman, 2015; van der Velde et al., 2015; Wilusz, Harman, & Ball, 2017). This is contradictory to the two water worlds hypothesis in that the youngest portion of water has the potential to bypass plant-available storage, meaning transpiration would not be selected from the youngest portion of catchment storage. Evaristo et al. (2019) observe that the ages of water taken by roots are older than seepage to groundwater recharge by a factor of two in a mesocosm water tracing experiment.

Partial mixing in the root zone is less common in process-based models, but its importance in reproducing observed tracer patterns is increasingly recognized. Using a physically-based ecohydrologic model which tracks water isotopes and assumes full mixing in each soil layer, Kuppel, Tetzlaff, Maneta, and Soulsby (2018) conclude that discrepancies between observed and modeled values reveal a need for incorporating partial mixing processes. Time-variable mixing has been represented in a small number of lumped models. For example, Hrachowitz et al. (2013) and van der Velde et al. (2015) compared model performance and water age distributions between a “complete mixing model,” used in most conceptual modeling studies, and a “dynamic partial mixing model,” in which a greater portion of new water bypasses passive (hydraulically inactive) storage under wetter conditions. Additionally, under high soil moisture conditions more water is routed to preferential flow pathways, only partially mixing with matrix water (see also Hrachowitz, Fovet, Ruiz, & Savenije, 2015). McMillan, Tetzlaff, Clark, and Soulsby (2012) investigate how mixing within the unsaturated zone can be parameterized by time-variable tracer data. They find that when separate state variables are used for tension and free storage reservoirs, the free storage becomes a very fast response store with low transit times. Here, we build upon these mixing approaches in order to explicitly represent ecohydrologic separation in a catchment-scale hydrologic model and assess its influence on water storage and residence times.

Both simple, lumped black box models (e.g., Soulsby, Tetzlaff, & Hrachowitz, 2010; Speed, Tetzlaff, Soulsby, Hrachowitz, & Waldron, 2010) and more detailed process-based and spatially explicit hydrologic models (e.g., Maxwell et al., 2016) can be used to study stores and fluxes of water in catchments. Lumped conceptual models are comparatively simple, with data requirements scaling with model complexity to offset equifinality and the number of calibrated parameters minimized through a reduced-complexity structure that isolates dominant catchment processes (Fenicia, Savenije, Matgen, & Pfister, 2008; Schoups, Van de Giesen, & Savenije, 2008; Young, Parkinson, & Lees, 1996). Physically-based distributed models allow for greater spatial resolution, but over-parameterization renders inter-model comparison impractical because the degree of dissimilarity between model structures and processes represented make it difficult to identify the individual components that result in performance differences (Clark et al., 2015a; Clark et al., 2015b). The comparative advantages of lumped models for inter-model comparison make them suitable for incorporating ecohydrologic separation and comparing internal stores and fluxes across structurally different models.

The two water worlds hypothesis refers to a proposed explanation for observed ecohydrologic patterns, typically described by isotopic data. However, there lacks a precise definition of the processes which result in a range of observations that have been described under the two water worlds hypothesis (Berry et al., 2017). This flexible, evolving definition necessitates that authors place studies within the context of definitions informed by previous studies. Here we identify key characteristics common with many descriptions of the two water worlds hypothesis, and thus use our own interpretations, to consider how dominant storages and their linkages might be organized in one possible model representation. A two water worlds model (2WW) has an architecture that incorporates two main features: 1) unsaturated storage that is hydrologically less connected to other catchment storages for at least part of the year and from which plants extract water, and 2) parallel transient storage processes by which some infiltrating precipitation bypasses tightly bound storage to generate streamflow and recharge groundwater. In contrast, in a one water world model (1WW), plants extract water from a pool that is fully connected to the catchment year-round.

The overarching goal of this study is to determine how including ecohydrologic separation in a lumped catchment model alters interpreted stores, fluxes, and residence times of water and solutes within a catchment. In reaching this goal of quantifying differences in internal dynamics, we are guided by three expectations. First, we expect the accuracy of 1WW and 2WW in predicting stream discharge will be similar because of a comparable number of free parameters and the broad success of lumped representations in predicting discharge in the literature (e.g., Beven, 2011; Duan, Sorooshian, & Gupta, 1992). Next, we expect 2WW will more accurately predict a seasonal stream chloride signal because ecohydrologic separation isolates the source of water for evapotranspiration, which generates chloride enrichment of the unsaturated zone during dry periods (Figure 1), from the source of water for stream discharge. Finally, we expect 2WW will decrease residence times for mobile, streamflow-generating water because new precipitation is able to bypass a portion of unsaturated storage while bound water remains in place. Concurrently, residence times for the bound water fraction will increase, resulting in more variable residence times overall. To investigate alterations in stores, fluxes, and residence times of water, we developed two hydrochemical lumped rainfall-runoff models which incorporate the key features of 2WW and 1WW described above, for a headwater catchment at the H.J. Andrews Experimental Forest (Oregon, USA), the site which motivated the two water worlds hypothesis (Brooks et al., 2010). Models are calibrated against stream discharge, as well as chloride concentrations to ensure adequate simulation of solute transport in addition to discharge dynamics. Previous studies at the site provide evidence in support that the ecohydrologic separation mechanism is operating in the catchment (Brooks et al., 2010). Thus, this study does not seek to identify 1WW or 2WW as a best or correct conceptual framework. Instead, we ask how our evolving conceptual model—informed by the findings of Brooks et al. (2010)—results in changes to our interpretation of the storage and transport of water and solutes at the catchment scale. Recent studies conducted in other catchments indicate that ecohydrologic separation is strongest in climates with distinct dry and wet seasons (Geris et al., 2015) and the magnitude of ecohydrologic separation is temporally variable throughout the year (Hervé-Fernández et al., 2016; McCutcheon, McNamara, Kohn, & Evans, 2017; Sprenger, Tetzlaff, & Soulsby, 2017), such that the two water worlds hypothesis holds during the dry season but not during the wet season when small and larger soil pores become hydrologically connected. Thus, in our analysis we particularly focus on alterations to water residence times and storage during the dry season when differences between 1WW and 2WW are potentially most relevant.

2. Site description and data

In this study we analyze data from Watershed 10 (WS10, 0.96 km^2), a headwater catchment of the H.J. Andrews Experimental Forest located in the western Cascade Mountains of Oregon, USA. The catchment has been extensively studied over the last several decades, resulting in detailed site descriptions (Dryness, 1969; McGuire et al., 2005; Swanson & James, 1975; Swanson & Jones, 2002). WS10 has steep hillslopes (> 50%), narrow valley bottoms, and highly conductive soils (Dryness, 1969; Harr, 1977). These features, along with the presence of significant preferential subsurface flow paths, result in fast hydrologic responses to precipitation (McGuire & McDonnell, 2010). Bedrock is volcanic in origin, including andesitic and dactic tuffs and coarse breccias as the parent materials for overlying soils, which are about 1 m thick (Swanson & James, 1975). The forest is mainly coniferous with some deciduous species in the riparian zone. Elevations range from 461 to 679 m a.m.s.l. The region has a Mediterranean climate with wet, mild winters and dry, warm summers. During the study period (1-Jan-1989 to 31-Dec-2014), mean annual precipitation was 2200 mm, about 80% of which fell between October and April. Typically, highest precipitation occurs in late November and minimum precipitation occurs in late July, coinciding with minimum streamflow. Mean annual streamflow for WS10 was 1420 mm during the study period. Therefore, annual evapotranspiration is estimated to be about 770 mm annually, or about 35% of precipitation. The catchment is at a sufficiently low elevation that major seasonal snowpack does not develop. Therefore, we do not include snow processes in our analysis, consistent with previous modeling studies of WS10 (Klaus, Chun, McGuire, & McDonnell, 2015; McGuire, Weiler, & McDonnell, 2007; Rodriguez, McGuire, & Klaus, 2018).

Daily discharge values were obtained from a fixed trapezoidal flume located at the outlet of the catchment (H.J. Andrews station GSWS10). Stream water samples for chemistry were collected proportionally to streamflow at the gauge location as composite samples typically spanning three weeks, and samples were analyzed for chloride. Daily precipitation and temperature data to estimate potential evapotranspiration were obtained from the nearby climatic station located below the outlet of WS10 (430 m a.m.s.l , H.J. Andrews station PRIMET). Precipitation samples to be analyzed for chemistry were collected weekly from a bulk collector located the same elevation (H.J. Andrews collector RCADMN) and analyzed for chloride. Precipitation chloride concentration has little systematic variation seasonally (Figure 1). However, high concentration outliers, likely due to some evaporation prior to collection, resulted in general over-estimation of stream chloride concentrations during the wet season when stream chloride concentrations are low. As such, we use the approximate chloride concentration of stream discharge during the wet season (0.1 mg L^{-1}) as a constant input concentration for precipitation. We selected the study period based on availability of data for stream discharge, stream chemistry, precipitation, and precipitation chemistry.

3. Hydrologic model development

We developed two hydrologic models with the objective of reproducing the hydrograph and chloride concentration timeseries within the stream draining WS10. One model includes ecohydrologic separation characteristics (2WW; Fig. 2A) and one does not (1WW; Fig. 2B). Both 1WW and 2WW are lumped conceptual models that comprise interconnected reservoirs that represent dominant physical processes affecting hydrologic and transport response. We began with basic model structures and applied a flexible development approach in which we progressively made modifications motivated by performance inadequacies and knowledge of catchment characteristics (after Fenicia, Kavetski, & Savenije, 2011; Fenicia, McDonnell, & Savenije, 2008).

Both the 2WW and 1WW models include four reservoirs: a plant available unsaturated storage reservoir, S_{U1} (mm); a fast flow unsaturated reservoir supplying interflow, S_{U2} (mm); a slow flow groundwater reservoir, S_{GW} (mm); and a hydrologically passive solute mixing reservoir, S_P (mm) (Table 1, Figure 2). We use a forward Euler numerical approximations at a daily timestep to solve the equation set for all simulations. The models have a similar number of calibration parameters (6 for 1WW and 7 for 2WW) in order to minimize performance effects due to differences in the number of parameters (Perrin, Michel, & Andréassian, 2001). Both models use the same underlying mathematical representations for hydrologic dynamics. Relevant state and flux equations are given in Table 2. The models differ only in how water and solutes are routed within a time step, primarily based on unsaturated storage being organized in serial (1WW) or parallel (2WW).

The 1WW model is a modified version of a model developed by Euser et al., 2013 and Hrachowitz et al., 2014. The primary adaptation is the inclusion of a passive mixing reservoir because damping and delay of the interflow solute signal was determined to be a crucial process for reproducing stream chloride concentrations in both 1WW and 2WW. In the 1WW model, all infiltrating precipitation P (mm d^{-1}) is first mixed in the plant available unsaturated zone reservoir before draining to subsequent reservoirs within the same daily time step, reflecting the sequential transport processes of translatory flow (Table 3). In contrast, in 2WW, water is partitioned in parallel between S_{U1} and preferential flow paths to S_{U2} and S_{GW} such that fast flow water does not mix with the hydrologically disconnected water stored in S_{U1}. The portion of infiltrating precipitation partitioned to S_{U1} decreases with increasing wetness conditions.

3.1 Model structure

3.1.1 Solute transport

Chloride is assumed to be fully and instantly well-mixed throughout each storage volume. In general, chloride mass is routed through each storage according to:

$$c_{out} = \frac{c_{in} * R_{in} + \mathrm{m}}{S} \qquad (2)$$

In which c_{out} (mg mm^{-1}) is the outflowing concentration, c_{in} (mg mm^{-1}) is the inflowing concentrating, R_{in} (mm d^{-1}) is the flux of water into the reservoir, m (mg) is the chloride mass in the reservoir in the previous time step, and S (mm) is the water storage after the addition of water inflows for the time step but before water outputs are subtracted for the time step.

3.1.2 Unsaturated reservoir 1

S_{U1} represents the portion of the unsaturated zone that is available to plants for transpiration, commonly considered the dynamic portion of the unsaturated zone (Savenije, 2016). Soil moisture within S_{U1} controls numerous sub-surface processes, including water partitioning between storage, evaporation, and interflow. In 2WW and 1WW, the amount of daily observed precipitation that gets stored in S_{U1} is determined by partitioning coefficient C_R which is a function of S_{U1max} (mm), a parameter that reflects the maximum slow-flow unsaturated storage capacity (Table 2). C_R is controlled by shape parameter β. For high soil moisture conditions C_R tends to 1, indicating that little precipitation P is partitioned to S_{U1}. Moisture in the unsaturated reservoir is depleted by evapotranspiration ET (mm d^{-1}), which increases linearly with soil moisture until it reaches a fractional threshold, L_P, of the maximum storage capacity, above which it is equal to potential evapotranspiration E_P. In 2WW, water fluxes to groundwater (R_{GW}) and water fluxes to unsaturated reservoir 2 (R_{U2}) are routed directly to S_{GW} and S_{U2} without mixing with water in S_{U1}. In 1WW, all precipitation is mixed with S_{U1} prior to entering subsequent storages, reflecting the sequential transport processes of translatory flow. While the difference in mixing results in differences in chloride fluxes to each reservoir, the equations describing the volume of water which is ultimately routed to each storage for each timestep (R_{U1}, R_{U2}, and R_{GW}) remain the same for both 1WW and 2WW. The characteristics of S_{U1} in 2WW are consistent with what is referred to as "bound" or "poorly mobile" water in the two water worlds conceptual model (e.g., Brooks, 2015; Evaristo et al., 2015).

Potential evaporation estimates are required to calculate daily evapotranspiration in the models. Daily reference evapotranspiration E_R (mm d^{-1}) was estimated using the Hargreave's equation (Hargreaves & Samani, 1985), which is based on differences between measured values of daily maximum and minimum air temperature:

$$E_R = 0.0023(T_{mean} + 17.8)(T_{max} - T_{min})^{0.5} R_a \quad (1)$$

in which T_{mean} is mean daily temperature, T_{max} is maximum daily temperature, T_{min} is minimum daily temperature, and R_a is extraterrestrial radiation. E_R and R_a are in units of equivalent water evaporation and temperatures are in °C. Potential evapotranspiration E_P is assumed to be equal to E_R.

3.1.3 Unsaturated reservoir 2

S_{U2} is a fast-responding reservoir representing macropores that contribute to lateral preferential flow to the stream (i.e., interflow). The portion of precipitation that is routed to preferential flow via C_R, which includes both vertical and lateral components, is further partitioned between interflow and groundwater recharge (R_{U2} and R_{GW}) according to a calibrated preferential recharge coefficient, C_P. Outflow from the mobile unsaturated reservoir is linear with storage and characterized by a calibrated storage coefficient K_{U2} (d^{-1}). In 1WW, S_{U1} is hydrologically connected to S_{U2}, thus mediating connectivity between S_{U1} and flow paths that supply streamflow. In 2WW, S_{U1} is hydrologically disconnected from S_{U2}. The characteristics of S_{U2} in 2WW are consistent with the "mobile" water described in the two water worlds hypothesis.

For 2WW, water contained within S_{U1} can only be depleted through evapotranspiration, but chloride is exchanged between S_{U1} and S_{U2} without yielding a net transport of water via mass transfer. Chloride exchange between S_{U1} and S_{U2} is modeled as:

$$\frac{dc_{U2}}{dt} = -\alpha * \frac{S_{U1}}{S_{U2}} * (c_{U2} - c_{U1}) \qquad (3)$$

in which c_{U1} (mg/mm) and c_{U2} (mg/mm) are the chloride concentrations in S_{U1} and S_{U2} respectively, t is time (d^{-1}), and α (d^{-1}) is the mobile-immobile exchange coefficient. The mass-transfer formulation used to exchange solutes between S_{U1} and S_{U2} is based on a standard first-order rate-limited mass transfer model (Haggerty & Gorelick, 1995) and enforces solute exchange proportional to the difference in concentration between the reservoirs.

3.1.4 Groundwater reservoir

The groundwater reservoir represents baseflow contributions to stream discharge. The portion of precipitation that is partitioned to S_{GW} depends on partitioning coefficients C_R and C_P. Outflow from S_{GW} is linear with storage and characterized by storage coefficient K_{GW} (d^{-1}). K_{GW} was determined to be 0.05 d^{-1} a priori through calculation of a master recession curve (MRC) that represents the baseflow recession of the catchment (Fenicia, Savenije, Matgen, & Pfister, 2006). The technique includes concatenating a set of recession segments by shifting them in time so that the curves overlap, forming an MRC. The lower portion of the MRC, which is assumed to characterize baseflow, defines a line when extrapolated and plotted semi-log. The line decreases one log cycle in time $1/K_{GW}$. In 1WW, flow paths to S_{GW} first mix with S_{U1} within the same time step. In 2WW, flow paths to S_{GW} bypass the bound unsaturated zone water represented by S_{U1} but mix with mobile unsaturated zone water of S_{U2}.

3.1.5 Passive mixing reservoir

The damped and time-lagged response of tracer time series relative to hydrologic responses to precipitation provides insight into catchment transit times and suggests the presence of hydrologically inactive mixing volumes that cannot be inferred from discharge dynamics alone (Benettin, Kirchner, Rinaldo, & Botter, 2015; Birkel, Soulsby, & Tetzlaff, 2011). These residual storages do not influence hydrologic responses but are critical to simulating chemical signatures and estimating temporal scales of solute transport and mixing. We conceptualize this passive storage to mainly represent the riparian zone and weathered bedrock below the elevation of the streambed at our study site. Outflow from S_{U2} is routed through a passive storage volume, S_P, to reproduce the observed damped and lagged chloride response.

3.3. Model architecture decisions

Models were iteratively developed to better reflect dominant catchment behavior while maintaining parsimony, closely following the procedures of Fenicia et al. (2011) and Kavetski & Fenicia (2011). An interception reservoir and snow component were tested and removed after having minimal effect on model performance. Similarly, infiltration-excess overland flow routing was incorporated in the models but did not improve model performance. This result was anticipated because soils within H. J. Andrews Experimental Forest are highly porous and infiltration rates are sufficiently high (typically > 20 cm h^{-1}) that overland flow rarely occurs (Dryness, 1969; Jones, 2000). We also tested incorporating a groundwater passive reservoir, but preliminary calibrations suggested little groundwater storage so this value was set to 0, consistent with Rodriguez, McGuire, and Klaus (2018) who found this parameter to be unidentifiable for WS10. The catchment is steep and mainly composed of thin soils (~1 m deep) over shallow bedrock (van Verseveld, McDonnell, & Lajtha, 2008), limiting saturated storage. Previous studies indicate that groundwater dynamics in WS10 are dominated by fracture flow, and a highly fractured region within the upper meter of bedrock provides a pathway for rapid lateral subsurface stormflow (Gabrielli, McDonnell, & Jarvis, 2012). A passive reservoir in series behind S_{U2}, determined to be important for damping and lagging of the chloride signal, is expected to account for most saturated riparian storage.

Evapotranspiration was initially assumed to remove water and chloride from S_{U1} with chloride removal represented as a fraction, *J*, of the reservoir concentration (Benettin et al., 2015). Chlorine is a necessary micronutrient for proper biogeochemical functioning and metabolism in plants (Hänsch & Mendel, 2009); it is taken up in small quantities by roots and can accumulate in foliage (Berger, Eagar, Likens, & Stingeder, 2001; Likens, 2013). Because *ET* represents the combined fluxes of both evaporation and transpiration, *J* was expected to be small. Preliminary calibration of *J* was close to zero, implying that evapoconcentration of chloride in pore water is more important to catchment solute dynamics than removal by plant uptake. This is in accordance with the strong seasonal chloride signal observed in the stream. To reduce the number of calibration parameters, *J* was fixed at zero for all simulations presented in this study, thereby neglecting plant uptake of chloride.

Several studies indicate seasonal transience of ecohydrologic separation in some climates (Hervé-Fernández et al., 2016; McCutcheon, McNamara, Kohn, & Evans, 2017; Sprenger, Tetzlaff, & Soulsby, 2017), such that the two water worlds hypothesis does not apply during the wet season when catchments exhibit increased hydrologic connectivity between soil pores. As such, we tested models in which we conditioned hydrologic exchange between S_{U1} and S_{U2} to be dependent upon soil moisture in the unsaturated reservoir. However, the additional complexity of moisture-dependent mixing was not adequately supported by the available data and resulted in a reduction in parameter identifiability. Therefore, we elected to present fully 1WW and 2WW models. We note here that in some catchments these models might represent seasonal endmembers in which 1WW reflects wet season dynamics and 2WW reflects dry season dynamics.

3.4. Model evaluation

Data from 1 January 1989 through 31 December 2014 were used as model input. These 26 years were identified to have all required input data for the model. The first year of data was used for model warm-up and the following 12 years for calibration. The final 13 years were used for model validation. A spin-up period was employed prior to all simulations by running the model through the first 13 years of data 10 times in order to establish appropriate initial values for state variables from meteorological data and input parameter values. Variables spanning orders of magnitude were sampled from a logarithmic parameter space to ensure equal coverage across all orders of magnitude (after Kelleher et al., 2013; Ward et al., 2017; Ward et al., 2013), and a Latin hypercube scheme was used to sample the parameter space. A total of 50,000 parameter sets were simulated for each model formulation.

We used a multi-objective calibration approach by first selecting a hydrologic behavioral set and subsequently selecting a subset of chloride transport behavioral models from this hydrologically acceptable set. Lumped conceptual models can have limited predictive power even after acceptable hydrologic calibration, suggesting poor representation of internal processes (Gupta & Sorooshian, 1983; Hrachowitz & Clark, 2017; Klemeš, 1986; McDonnell et al., 2007). Multi-objective calibration approaches using information orthogonal to stream discharge, such as solute concentrations, have been proposed to constrain subsets of models that can adequately reproduce multiple response dynamic signatures (Benettin, Kirchner, Rinaldo, & Botter, 2015; Hrachowitz et al., 2014; Kim, Jung, & Chun, 2016). Using a sequential approach of first selecting baseline models based on hydrologic behavior alone allows us to assess the influence of the additional tracer constraints. We used the Nash-Sutcliffe efficiency of discharge (NS_Q) and logarithmic values of discharge (LNS_Q) for calibrating hydrologic parameters against daily discharge. The logarithmic transformation of discharge results in increased sensitivity to systematic model under- or over- prediction relative to non-transformed Nash Sutcliffe efficiency by increasing the influence of low flow values compared to peak values (Krause, Boyle, & Bäse, 2005). Because the chloride time series is less dynamic, Nash-Sutcliffe efficiency (NS_{Cl}) was selected for transport calibration. First, we eliminated models with an NS_Q below 0.6 from the pool of potential behavioral models. Of the remaining models, the 500 models with the highest LNS_Q were retained for the hydrologic behavioral set (1% of models, 500 total parameter sets). From within the hydrologic behavioral set, models within the top 10% for NS_{Cl} were selected for the retained feasible solutions (50 total parameter sets). The best model solution was selected based on the best performance for chloride within the behavioral set.

3.5 Statistical analysis

Kruskal-Wallis tests were performed to test whether behavioral set performance, parameters, and median water storage within reservoirs differ between model structures using a significance threshold of 0.05. We take $p < 0.05$ as an indicator that differences between models are unlikely to be attributable to chance alone (i.e., 95% certainty of differences). Hereafter, we use the terminology "statistical significance at the 95% confidence interval" as a shorthand for this interpretation. Additionally, percent differences (Δ) in medians were calculated using:

$$\Delta_{1,2} = \frac{X_{1WW} - X_{2WW}}{(X_{1WW} + X_{2WW})/2} * 100 \qquad (4)$$

in which 1WW and 2WW subscripts indicate values of interest for 1WW and 2WW, respectively, and *X* represents a parameter of interest. Subscripts for Δ indicate differences between 1WW and 2WW (1,2), 1WW and 2WW mobile water only (1,2M), or 2WW and 2WW immobile water only (2,2IM).

The hydrologic residence time distributions for all time steps and storages were determined by tracking individual parcels of water of a given age through the models. Daily mean water residence time distributions for individual reservoirs were created using the storage-weighted mean residence time for each day of all models, with a total of 9,131 days of simulation for each of the 50 behavioral models for both 2WW and 1WW. Kruskal-Wallis tests were performed to test whether median daily mean residence times for each storage differ between model structures using a significance threshold of 0.05. However, because sample sizes are so large, there is high power to detect small differences. As such, we take particular care to place the results in the context of the magnitude of those differences by calculating the percent difference between median residence times. Probabilities and cumulative probabilities of water parcels of given ages in the unsaturated zone on each day of the year were determined by summing the water in storage on a particular day of the year over all years and all model runs (1300 samples used to construct each daily probability distribution) and normalizing by the total amount of water in storage on a particular day of the year over all years and all model runs.

4. Results

4.1 Parameter calibration and model performance

For model parameters to provide useful information, it is important that they are unique, optimal, robust solutions (Kelleher et al., 2013; Wagener, McIntyre, Lees, Wheater, & Gupta, 2003; Ward et al., 2017). Model calibration resulted in identifiable values for calibrated parameters for both 1WW and 2WW (steepest portions of cumulative distributions, Fig. 3). The levels of identifiability for the feasible solutions (post-selection based on chloride criteria) are higher than the initial hydrologic behavioral set, as indicated by a narrowing of the steep portion of the distributions. The identifiability range for some parameters, such as the maximum plant available unsaturated storage capacity S_{U1max} and transpiration threshold L_P, are wider for 2WW than 1WW (Figure 3).

Both models reproduce the features of the hydrograph well despite reduced-complexity structures (median LNS_Q = 0.83 and 0.82 for 1WW and 2WW calibration, FigureS1a-b; median LNS_Q = 0.80 for validation of both models, Figure 4a-b). The difference in median LNS_Q between models for the calibration period is unlikely to be attributable to chance alone (p = 0.01), but the difference is not significant at the 95% confidence level and is small (0.01). This does not hold for the difference in median LNS_Q over the evaluation period (p = 0.93), suggesting a higher degree of similarity. We also calculated NS_Q (median NS_Q = 0.73 and 0.69 for 1WW and 2WW calibration period; median NS_Q = 0.69 and 0.67 for 1WW and 2WW validation). Reported values of NS_Q are not significantly different at the 95% confidence level for either calibration ($p < 0.01$) or validation (p = 0.01). Both models under-estimate peak flows. It is not surprising that the models reproduce the time series of flow similarly because they have the same underlying hydrologic equations. The small difference between the hydrologic performance range of 1WW and 2WW is due to the second calibration step, which eliminates models based on stream chloride performance.

The chloride objective function NS_{Cl} shows acceptable model performance for 1WW and 2WW (median NS_{Cl} = 0.78 and 0.77 for 1WW and 2WW calibration, respectively; Figure 4c-d; median NS_{Cl} = 0.77 and 0.75 for validation, Figure S1c-d). Both models reproduce the pattern of seasonal chloride enrichment, including the timing and magnitude of oscillations. Similar to LNS_Q, the difference in median NS_{Cl} over the calibration period is unlikely due to chance ($p < 0.01$), but the difference is small (0.02). The difference in median NS_{Cl} is not significantly different at the 95% confidence interval between models for validation ($p = 0.31$). Overall, although there are some statistical differences between model evaluation criteria for discharge and chloride concentration for the calibration period, the magnitude of p-values relative to the significance threshold vary and median differences tend to be small, thus limiting their meaning in the context of this study. This could suggest that observed streamflow chloride concentration is not a strong predictor of unsaturated zone processes, such as ecohydrologic separation, in the catchment. Similarly, Knighton et al. (2017) observe minimal effects of unsaturated-zone percolation mixing on stream water isotopic signature and postulate that tracers in streamflow may not always be a strong feedback on internal catchment processes. Kuppel et al. (2018) observe some sensitivity of isotope tracers to unsaturated zone mixing processes, attributing the difference between the studies to a larger groundwater contribution at their site. Baseflow contributions in WS10 are relatively small, similar to the intermittent catchment studied by Knighton et al. (2017).

4.2 Comparing one- and two- water worlds parameters, storages, and residence times

Of the six calibration parameters common to both models, only two differ significantly between models at the 95% confidence level, S_{U1max} and C_P ($p < 0.01$, Figure 5).

The magnitudes of percent differences are about 30% for both parameters. While the parameter range of C_P is similar between models, the range of S_{U1max} values in the 2WW behavioral set is about three times that of 1WW. The magnitudes of percent differences for the parameters that are not significantly different (K_{U2}, S_P, L_P, and β) range from 1% to 18%. When put in the context of calibration ranges, differences in parameters are not large.

Still, differences in parameters and solute routing result in variations in the simulated hydrologic function of the catchment (fluxes and stores of water within the catchment). The medians of the average simulated water storages for individual reservoirs S_{U1} and S_{GW} are unlikely due to chance ($p < 0.01$, Figure 6a and c), with differences of 21% and -29%, respectively. Groundwater heights above bedrock during stormflow have been observed to be shallow in WS10 (10-15 cm, van Verseveld et al., 2008) and lie within the range of modeled groundwater storage during stormflow for both models when soil porosity is taken into account. Storage in fast-flow reservoir S_{U2} does not differ significantly between models ($p = 0.14$, Figure 6b). At the catchment scale we can compare differences between water storage regardless of mobility, as well as compare mobile water volumes exclusively, which influence residence times of streamflow-generating water. Because all water is mobile in 1WW, these values stay constant for total and mobile storage. For 2WW, mobile water storage ($2WW_M$) excludes S_{U1} immobile storage ($2WW_{IM}$) and unsaturated zone mobile water storage is equal to S_{U2}. Unsaturated zone storage (S_{U1} and S_{U2}) differs significantly between 1WW and 2WW for all water but is not highly significant at the 95% confidence level ($p = 0.04$, Figure 6d). Differences between 1WW and $2WW_M$ are also unlikely to be attributable to chance ($p < 0.01$). While unsaturated zone storage for all water is larger for 2WW ($\Delta_{1,2} = 21\%, 53\text{ mm}$), mobile water unsaturated zone storage is smaller and the magnitude of the difference is much larger ($\Delta_{1,2M} = -198\%, -220\text{ mm}$). S_{U1} is two orders of magnitude larger than S_{U2} for both 2WW and 1WW (Figure 6a-b). Thus, exclusion of S_{U1} from the mobile unsaturated storage volume for 2WW could be expected to result in a large negative difference in unsaturated zone mobile storage compared to 1WW. For total catchment storage, the volumes of all water for 1WW (S_{U1}, S_{U2}, S_{GW}, and S_P)

and 2WW (S_{U1}, S_{U2}, S_{GW}, and S_P) do not differ significantly ($p = 0.10$, Figure 6e). Mobile water volumes (S_{U2}, S_{GW}, and S_P for 2WW) differ significantly at the 95% confidence interval ($p < 0.01$) and the magnitude of the difference is large ($\Delta_{1,2M} = -137\%, -233$ mm).

Due to large sample sizes, even small differences between distributions of daily mean residence times for behavioral model sets result in statistically significant differences ($p < 0.01$ for all reservoirs considered). Therefore, we proceed with interpreting only the magnitude of these differences when evaluating their importance. When considering all water stored in the unsaturated zone regardless of mobility, the 2WW median daily residence time is 102% (81 days) larger than 1WW (Figure 7a). However, in line with our expectations, when accounting for water mobility, the 2WW median residence time for mobile water ($2WW_M$) is smaller than 1WW and the difference is -168% (-35 days). This is largely due to a smaller pool of mobile water in the 2WW unsaturated zone compared to 1WW. Furthermore, median residence time for 2WW immobile water is larger than 2WW total water but the difference is small ($\Delta_{2,2IM} = 2\%$, 3 days). On average, immobile water makes up a larger portion of unsaturated zone storage for 2WW compared to mobile water (Figure 6); thus, the total unsaturated zone residence time distribution for 2WW is similar to that of the immobile fraction. The range of daily mean residence times for the total unsaturated zone is about four times larger for 2WW than 1WW.

Similar to unsaturated storage, the median residence time for all water stored in the catchment for 2WW is larger than 1WW (74%, 55 days), consistent with observations of similar total water storage and modeled hydrographs. When considering only mobile water storage, 2WW median residence time is smaller than 1WW (-75%, -25 days); Figure 7b) and shows a bimodal distribution. This bimodal distribution is due to seasonal differences in residence times. During the wet season, a greater fraction of new precipitation is routed to S_{U2}, S_{GW}, and S_P. This decreases residence times for the wet season relative to the dry season (Figure S2) when a smaller fraction of new precipitation is routed to these reservoirs; instead, most new precipitation is stored in S_{U1} under dry conditions. This moisture-dependent storage results in less seasonally-variable median residence times for S_{U1}. While seasonal differences in residence times hold for both 2WW and 1WW, the bimodal distribution is most apparent when considering only mobile water for 2WW because it excludes the more constant residence times of S_{U1} and thus the seasonal shift makes up a larger percent difference (110% for $2WW_M$ vs 83% for 1WW and 43% for 2WW; Figure S2). Kuppel et al. (2018) found similar seasonal age variations in a small headwater montane catchment in Scotland using a fully distributed ecohydrologic model which incorporates tracking of water isotopes and age: hillslopes, which make up the majority of our study catchment, had median ages ranging from a week old during the winter to several months old during the growing season. The magnitude of these values are comparable to median residence times for total catchment $2WW_M$ during the wet season (~ 2 weeks) and 2WW or $2WW_M$ during the dry season (several months). The range of daily mean residence times for the total catchment water is about twice as large for 2WW than 1WW.

In addition to comparing summary statistics for residence time distributions, we also calculated time-variable residence time distributions for each day of the year (Figure 8a-c). Residence times which correspond to precipitation during the wet season have high probabilities of being observed in storage, and residence times which correspond to the dry season inputs have low probabilities. A rapid decrease in residence time probabilities is observed for water which originates during the late dry season (i.e., July-September; Figure 8d-f). This decrease is greater for 1WW than 2WW, and largest for $2WW_M$. Water parcels originating on different days during the wet season for a particular year have more constant probabilities, particularly for 2WW. There is a slight decrease in probabilities with increasing residence for 1WW during this time and a more rapid decrease in residence times for $2WW_M$. Diagonal bands appear in Figure 8a-c due to aging of water parcels.

Overall, probabilities tend to decrease as residence times increase due to addition of younger water and continual depletion of water in storage. 1WW probability distributions have higher probabilities for shorter unsaturated zone water residence times (< ~50 days) relative to 2WW (XXXX), in agreement with the difference between distributions of daily mean residence times (Figure 6a). Likewise, when considering water mobility, this pattern is reversed and 2WW mobile water distributions are shifted towards higher probabilities for even younger water relative to 1WW (XXXX). Similarly, the cumulative probability that a parcel of water is less than particular residence times (e.g., 5 days, 50 days, and 120 days; Figure 9) is larger for 1WW than 2WW on all days of the water year when considering all water but is the opposite when considering only mobile water. For larger residence times, cumulative probabilities converge to 1 for both models (Figure 9f). During the wet season, cumulative distributions converge to 1 at lower residence times compared to the dry season when differences in cumulative probabilities are greatest and water tends to be older (Figure 9e-f).

5. Discussion

5.1 Representation of ecohydrologic separation

In this study, chloride transport through the unsaturated zone is conceptualized by assuming advective transport is limited to macropores, and transport between mobile and immobile zones is modeled using rate-limited mass transfer. The 2WW model architecture we present is one realization of how ecohydrologic separation can be incorporated in a catchment-scale lumped model, and is consistent with the conceptual models of ecohydrologic separation. Although the precise modes of mass transfer of solutes (e.g., dispersion, kinetic diffusion) have rarely been considered in isotopic studies, the isolated nature of water in 2WW necessitates a non-advective mechanism to mobilize concentrated chloride in S_{U1} to mobile pathways to the stream, while not yielding a net transport of water. The incomplete displacement of preexisting water in soils by incoming water has long been recognized and represented in physically-based pore-scale models. For example, the mobile-immobile model of transport through heterogeneous porous media (e.g., Gerke & van Genuchten, 1993; Van Genuchten & Wierenga, 1976) assumes that water in small pores is not directly connected to preferential flow paths to the stream, but is transported by first order diffusion between small and large pores. Similar conceptualizations have been applied to flow through porous media in fully saturated systems, commonly referred to as dual domain porosity (Goltz & Roberts, 1986; Haggerty & Gorelick, 1995; Singha, Day-Lewis, & Lane, 2007).

Although our model is not a mechanistic representation of pore-scale processes, we aim to represent the resultant behavior of similar processes at the catchment scale. The simplified representation linking S_{U1} and S_{U2} in our model is consistent with mechanistic models of bound storage at smaller scales.

In this study, for the 2WW model we assume that chloride transport between the mobile and immobile zones is independent of hydrologic forcing. However, we recognize that partial mixing of water between the mobile and immobile zones may be present under some hydrologic forcing conditions and soil textures. This is supported by studies showing that in some catchments ecohydrologic separation mechanisms are seasonal (Hervé-Fernández et al., 2016; McCutcheon, McNamara, Kohn, & Evans, 2017; Sprenger, Tetzlaff, & Soulsby, 2017). Furthermore, it is expected that some portion of water is transported along the pressure head gradient between immobile and mobile pores to replace bound water taken up by plants (Berry et al., 2017; Gerke & van Genuchten, 1993) in addition to some solute transport via kinetic diffusion. Furthermore, Sprenger et al. (2018) found that accounting for isotopic exchange via water vapor in a two-pore domain model improved simulations of stable water isotopes in soils. Transport due to pressure head gradients between bound and mobile pores in the unsaturated zone is not represented in the 2WW model due to a lack of data to support representation of both chloride mass transfer and partial water exchange as a function of wetness conditions. Likewise, chloride transport via hydrologic exchange between S_{U1} and S_{U2} is represented in 1WW but mechanisms of chloride mass transfer are not. The addition of mechanisms must be balanced with the available data required to constrain models. In the future, calibration of 2WW lumped conceptual models using soil isotopic data (e.g., Birkel, Dunn, Tetzlaff, & Soulsby, 2010) could help to distinguish the balance between advective and diffusive/dispersive transport processes, as well as the potential for moisture-dependent intermittent hydrologic connectivity between bound and mobile pores. Indeed, we expect that both mechanisms of solute mass transfer and water mixing would need to be incorporated to optimally model both chloride and isotopes in the catchment. The 2WW model we present represents the upper limit of differences we might observe if ecohydrologic separation were present year-round. In light of increasing data which supports seasonal transience of the two water worlds hypothesis, it is plausible that both models hold for a single catchment during different times of the year; in such catchments, we would expect the 2WW model to better represent dry season dynamics whereas the 1WW model would better represent conditions under high antecedent rainfall when different sized soil pores become connected. However, we did test a 2WW model with a moisture-sensitive α and did not find improved performance, indicating that additional empirical data will be necessary to constrain the system.

The role of passive storage in ecohydrologic separation representation remains unclear. Passive storage has been conceptualized as the unsaturated storage below field capacity that is hydraulically inactive but available for mixing (Birkel et al., 2011). In some ways, the immobile portion of the unsaturated zone (S_{U1}) in 2WW represents the opposite: water that is hydraulically active, in that it comprises dynamic water storage and provides evapotranspiration fluxes, but which is not available for mixing with mobile water. Hrachowitz et al., (2013) implements time-variable partial mixing between active and passive unsaturated storage, considering the potential importance of moisture-dependent mixing between mobile and immobile storage on internal transport dynamics. Others have defined dual catchment storage conceptualizations which consist of direct storage, the fraction of the seasonally dynamic water volume which stream discharge is sensitive to, and indirect storage, which varies without directly influencing discharge (Carrer, Klaus, & Pfister, 2019; Dralle et al., 2018). Dralle et al. (2018) interpret indirect storage volumes to consist of unsaturated storage held under tension in soils, moisture in weathered bedrock, and near-surface saturated storage which is eventually evapotranspired. These descriptions reflect some conceptualizations of passive storage, as well as incorporate aspects of the immobile storage volume S_{U1}; whereas immobile water comprises the majority of catchment storage in our study, Dralle et al. (2018) likewise determines that indirect storage comprises the majority of dynamic catchment storage. It has also been postulated that the distinction between passive and active storage in conceptual rainfall-runoff models may have implications for plant water availability (Birkel et al., 2011). In our study system, we conceptualize passive storage to mainly comprise the riparian zone and groundwater storage in weathered bedrock below the streambed elevation, resulting in placement of passive storage in serial arrangement with unsaturated reservoirs. As such, the passive storage reservoir lags and damps solute responses but does not interact with the plant water available reservoir or directly influence evapotranspiration rates. However, shallow groundwater table dynamics have been shown to strongly influence evapotranspiration in riparian zones and lead to discrepancies in modeled evapotranspiration (Kollet, 2009; Soylu, Istanbulluoglu, Lenters, & Wang, 2011). Consideration of the role of passive storage placement and mixing dynamics could have important implications for interpreted water storage and residence times, as well as approaches for incorporating ecohydrologic separation in conceptual models. Furthermore, resolving distinctions between passive, indirect, and immobile storage volumes could inform mechanistic assessments of storage-discharge relationships and catchment-scale solute transport.

5.2. Identifiability and realism of the maximum plant available unsaturated storage capacity

Despite demonstrating adequate performance relative to the hydrologic objective function, the 2WW architecture reduced certainty in the estimation of S_{U1max}, as well as L_P. This indicates that additional calibration targets may be needed to reduce parameter identifiability issues when using a 2WW approach. Several methods have been used to independently estimate maximum root zone storage capacity, including (1) the mass curve technique (Gao et al., 2014), based on an engineering application for designing reservoirs; (2) soil-derived estimates based on the available storage between wilting point and field capacity (de Boer-Euser, McMillan, Hrachowitz, Winsemius, & Savenije, 2016); and (3) a climate-based method which relies on the assumption that vegetation reserves a storage large enough to overcome drought conditions of a certain return period (de Boer-Euser et al., 2016). Furthermore, it is useful to consider the correspondence of parameter calibration to values estimated from other methods to assess confidence in a model's correspondence to reality (Gharari, Hrachowitz, Fenicia, Gao, & Savenije, 2014; Kelleher, McGlynn, & Wagener, 2017). To investigate this, we used the climate-based method to estimate S_{U1max} for comparison to the calibrated range for each model. This technique uses a simplified water balance model to estimate the required annual storages. Root zone storage has zero moisture deficit during the wet period at the beginning of the simulation. Water deficit increases when transpiration exceeds net precipitation and excess precipitation is assumed to run off. A distribution of the yearly maximum deficits were used to determine the root zone storage capacity required for vegetation to bridge a drought of a 10 year return period, following Gao et al. (2014). Using the same 26 year dataset of discharge and meteorological data for model calibration and validation, we estimated a root zone storage capacity of 480 mm. This value lies between the third quartile and upper limit for 2WW, but lies above the behavioral set range for 1WW (Figure 5a). This could indicate that 2WW model sets with S_{U1max} close to this value better correspond to reality.

5.3 Ecohydrologic separation alters residence times and storages of water and solutes

Transport timescales are broadly recognized as a key control on biogeochemical function (Hill, 1990; Hrachowitz et al., 2016; Triska, Kennedy, Avanzino, Zellweger, & Bencala, 1989), because longer timescales allow more time for contact with biogeochemically active substrates in the landscape. Therefore, differences in residence times have implications for interpretations of reactive transport. As an example, we consider nitrification, an aerobic process that occurs in the unsaturated zone. The nitrification reaction rate constant in sandy loam soils has been reported to be on the order 1 d^{-1} (McLaren, 1976) which corresponds to 99% removal by 5 days, assuming first-order kinetics. The probability that a parcel of water in the unsaturated zone is less than 5 days old is greater for 1WW than 2WW for all days of the year (Figure 9d), with the probability for 1WW being about 2 times larger than 2WW on average and about 3 times larger on average during the late dry season (July-September). If using a 2WW model, we would interpret more complete nitrification occurs in the unsaturated zone as a whole compared to 1WW. 2WW mobile water, though, is about 4 times more likely on average to be less than 5 days old compared to 1WW. Consequently, using a 2WW model would result in the interpretation of lower total nitrification for the portion of water which supplies streamflow compared to 1WW. Thus, the differences in residence times for 2WW can substantially alter our expectations about biogeochemical processes operating in the watershed, and more generally how we would expect reactive transport to occur for many solutes or pollutants.

In addition to influencing water and solute transport, differences in where water is stored in the catchment alter interpretations of plant water availability. Although the difference in total catchment water storage is not significant between models (Figure 6e), the difference in storage is significant for the plant available reservoir S_{U1} (21%, 52 mm, Figure 5a). Moreover, dry periods are of particular importance, not only because that is when ecohydrologic separation has been observed to be strongest, but dry periods also impart drought stress on plants. The percent difference in water storage in S_{U1} is also greatest during the dry summer season (72%, 50 mm, Figure S3). To further demonstrate potential differences in plant water availability during dry periods, we compared cumulative distributions of plant available water storage (Figure 10). 2WW predicts more plant available water storage for all but the lowest 6.3% of days. The lower 25th percentile of S_{U1} water storage is about twice as large for 2WW than 1WW (120.0 mm for 2WW versus 65.0 mm for 1WW). However, the lower 1st percentile of S_{U1} is about three times larger for 1WW than 2WW (2.4 mm for 2WW versus 7.5 mm for 1WW). This indicates that although 2WW results in more plant available water storage for the driest 25% of days, this model results in more extreme low storage than 1WW. Alterations in dry period water storage within the plant available water pool for 2WW could have important implications for the expected resilience of ecosystems to environmental change.

6. Conclusions

In this study we demonstrated how incorporating ecohydrologic separation into a catchment-scale hydrologic model alters interpretations of the transport of water and solutes. In our goal of quantifying differences in interpretations of internal functioning, we were guided by three expectations. First, we expected that the 2WW and 1WW models would predict stream discharge comparably well, but 2WW would more accurately predict seasonal enrichment in chloride. In line with expectations, the model formulations have similar performance metrics for stream discharge. However, both models also simulated the chloride timeseries similarly well. It is perhaps unsurprising that bulk water chemistry – which has been broadly reported and simulated for many years – did not necessitate adding the 2WW mechanism to improve model performance. Only with isotopic data did we update our conceptual model for storage and transport in the unsaturated zone, which we show here has important consequences for how we understand catchments to store and release water and solutes.

We also expected that 2WW would result in an increased range of residence times in the unsaturated zone, with decreased residence times for mobile storage and increased residence time for immobile storage. In line with our expectations, 2WW increased the range of daily mean residence times in the unsaturated zone overall, with decreased daily residence times for mobile water. This is primarily due to a smaller mobile water volume compared to 1WW, and increased daily residence times for 2WW immobile water relative to 1WW. Immobile storage makes up the majority of unsaturated storage for 2WW; therefore daily mean residence times for the total unsaturated storage are larger than 1WW overall. Despite mixed results for differences in calibrated parameters and water storages, meaningful differences in residence times and water availability emerge due to a combination of these small differences and variations in 2WW and 1WW mobile water conceptualizations. Differences in unsaturated water storages and residence times between 2WW and 1WW also tend to be largest during the dry season, when ecohydrologic separation has been observed to be strongest.

Rather than identify a best model, the goal of this study was to inform how the two water worlds hypothesis presented in isotopic studies has the potential to change interpretations of stores and fluxes of water at the catchment scale. In fact, these models might reflect seasonal endmembers of wet and dry condition dynamics in some catchments. Although we used simple models and calculations, we showed that accounting for this small-scale process alters internal catchment dynamics. We used estimates to relate these differences in internal catchment functioning to timescales for nitrification and the availability of water for vegetation, demonstrating the relevance these changes to conceptual hydrologic models have on ecological processes. There remains uncertainty about the conditions under which representation of ecohydrologic separation is necessary in hydrologic models and how it should be conceptualized. We provide a hypothesis of how ecohydrologic separation can be incorporated in a lumped conceptual model, but expect appropriate representation will vary by model type and catchment and evolve as our understanding of ecohydrologic processes increases. These questions provide opportunities for further conceptual and quantitative investigations to address catchment-scale water and solute transport under ecohydrologic separation and to test representations of ecohydrologic separation in hydrologic models of contrasting systems.

Notation

P	Precipitation, $mm\ d^{-1}$
ET	Evapotranspiration, $mm\ d^{-1}$
E_P	Potential evapotranspiration, $mm\ d^{-1}$
S_{U1}	Storage in slow unsaturated reservoir, mm
S_{U2}	Storage in fast unsaturated reservoir, mm
S_{GW}	Storage in groundwater reservoir, mm
S_P	Passive storage for fast unsaturated reservoir, mm
S_{U1max}	Maximum slow unsaturated storage
R_{U1}	Recharge of slow unsaturated reservoir
R_{U2}	Recharge of fast unsaturated reservoir
R_{GW}	Recharge of groundwater reservoir

Q_U	Runoff from fast unsaturated reservoir, *mm* d^{-1}
Q_P	Runoff from passive reservoir, *mm* d^{-1}
Q_{GW}	Runoff from groundwater reservoir, *mm* d^{-1}
Q_{Tot}	Total runoff, *mm* d^{-1}
C_R	Runoff generation coefficient
C_P	Preferential recharge coefficient
L_P	Transpiration threshold
K_{U2}	Storage coefficient of slow unsaturated reservoir, d^{-1}
K_{GW}	Storage coefficient of groundwater reservoir, d^{-1}
β	Shape parameter for C_R

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SUPPORTING INFORMATION

Additional Supporting Information may. Be found online in the supporting information tab for this article.

Tables

Table 1. Reservoir conceptualizations consistent between models

Reservoir	Conceptualization
Unsaturated Reservoir 1 (S_{U1})	Slow-flow unsaturated storage; plant available
Unsaturated Reservoir 2 (S_{U2})	Fast-flow unsaturated storage; preferential macropore flow
Groundwater Reservoir (S_{GW})	Slow-flow saturated storage
Passive Mixing Reservoir (S_P)	Storage available for mixing but hydrologically inactive; riparian zone and weathered groundwater below streambed elevation

Table 2. Water balance and flux equations for the models

Reservoirs	Storage Water Balance	Fluxes and State Equations
Unsaturated Reservoir 1 (S_{U1})	$\frac{dS_{U1}}{dt} = R_{U1} - ET$ (E1)	$C_R = \frac{1}{1+\exp\left(\frac{-S_{U1}/S_{U1max}+0.5}{\beta}\right)}$ (E5) $R_{U1} = (1 - C_R)P$ (E6)
Unsaturated Reservoir 2 (S_{U2})	$\frac{dS_{U2}}{dt} = R_{U2} - Q_U$ (E2)	$R_{U2} = C_R(1 - C_P)P$ (E7) $R_{GW} = C_R C_P\ P$ (E8) $ET = E_P \min\left(1, \left(\frac{S_{U1}}{S_{U1max}}\right)\frac{1}{L_P}\right)$ (E9)
Groundwater Reservoir (S_{GW})	$\frac{dS_{GW}}{dt} = R_{GW} - Q_{GW}$ (E3)	$S_{U2,in} = S_{U2} + R_{U2}dt$ (E10) $Q_U = S_{U2,in}(1 - e^{-K_{U2}t})dt^{-1}$ (E11) $S_{GW,in} = S_{GW} + R_{GW}dt$ (E12)
Passive Mixing Reservoir (S_P)	$\frac{dS_P}{dt} = Q_U - Q_P$ (E4)	$Q_{GW} = S_{GW,in}(1 - e^{-K_{GW}})dt^{-1}$ (E13) $Q_{Tot} = Q_P + Q_{GW}$ (E14)

Table 3. Comparison of key behaviors of unsaturated reservoir 1 (S_{U1}) for 2WW and 1WW models.

	Two Water Worlds	One Water World
Hydrologic connectivity	Protected storage, hydrologically disconnected; plants extract different water than enters the stream	Hydrologically connected to other reservoirs; plants extract same water that enters the stream
Adherence to translatory flow	When catchment wetness is high, some precipitation bypasses S_{U1} and does not participate in translatory flow	All precipitation flows through S_{U1} and is displaced by newer water, as stated by translatory flow concept
Solute tracer transport between S_{U1} and S_{U2}	Chloride transported via solute mass transfer between S_{U1} and S_{U2}	Chloride transported to S_{U2} from S_{U1} with water via advection
Moisture dependence	Greater portion of precipitation routed to storage when dry	
Solute tracer concentration effects	Where chloride is enriched via evapotranspiration	

Figure Legends

Figure 1. Input time series of observed precipitation and estimated potential evapotranspiration (E_P) for the validation period (a). Chloride concentrations observed in precipitation and the stream over the validation period and average wet season stream chloride concentration over the study period (b). The blue shaded region highlights late dry season (Jul-Sep) trends.

Figure 2. Model structures for (a) one water world (1WW) and (b) two water worlds (2WW). All water is mobile for 1WW, but plant available reservoir S_{U1} in 2WW is isolated from outflow to the stream. The red line indicates chloride mass transfer between unsaturated reservoirs S_{U1} and S_{U2} in 2WW.

Figure 3. Identifiability of model parameters toward the objective functions. (a) maximum plant available unsaturated storage capacity S_{U1max}, (b) unsaturated reservoir 2 storage coefficient K_{U2}, (c) preferential recharge coefficient C_P, (d) transpiration threshold L_P, (e) runoff generation shape parameter β, (f) passive storage S_P, (g) mobile-immobile exchange coefficient α. The black line is the preliminary hydrologic behavioral set and the blue and red lines are the retained feasible solutions for 2WW and 1WW, after implementing the selection procedure based on chloride concentration.

Figure 4. Observed (red) and modeled (blue) stream discharge (a and b) and stream chloride concentrations (c and d) with 95% confidence intervals over the validation time period. Objective function values (LNS and NS) are for the solution with the best chloride performance (blue line) and 5/50 (bold)/95th percentiles of the retained feasible solutions. Asterisks indicate objective functions used for calibration (LNS_Q and NS_{Cl}).

Figure 5. Evaluation of model set parameters (a) maximum plant available unsaturated storage capacity S_{U1max}, (b) unsaturated reservoir 2 storage coefficient K_{U2}, (c) preferential recharge coefficient C_P, (d) transpiration threshold L_P, (e) runoff generation shape parameter β, (f) passive storage S_P, and (g) mobile-immobile exchange coefficient α. Of the comparable parameters, only S_{U1max} and C_P differ significantly between models ($p < 0.05$, Kruskal-Wallis test). Δ = difference between the median values. The black line on (a) indicates an independent estimate of S_{U1max} based on climate data.

Figure 6. Evaluation of behavioral set average water storage. Subplots (a-c) compare storage between individual model reservoirs S_{U1} (a), S_{U2} (b), and S_{GW} (c). Subplots (d-e) compare storage between one water world (1WW), combined mobile and immobile water of two water worlds (2WW), and mobile water of two water worlds ($2WW_M$) for unsaturated storage S_U (d) and total catchment storage S_{Tot} (e). $\Delta_{1,2}$ = the difference between 1WW and 2WW storage and $\Delta_{1,2M}$ = the difference between 1WW and 2WW mobile water storage.

Figure 7. Daily mean water residence time distributions for the behavioral model set for unsaturated storage S_U (a) and total storage S_{Tot} (b). Both plots show distributions for 1WW, 2WW (2WW all water), and $2WW_M$ (2WW mobile water). Plot (a) shows $2WW_{IM}$ (2WW immobile water). $\Delta_{1,2}$ = the difference between 1WW and 2WW median daily residence times for all water, $\Delta_{1,2M}$ = the difference between 1WW and 2WW median daily residence times for mobile water, and $\Delta_{2,2IM}$ = the difference between 2WW all water and 2WW immobile water median daily residence times.

Figure 8. Color denotes the probability a parcel of water in unsaturated storage has a particular residence time on a particular day of the water year (Day 1 = October 1) for 1WW (a), 2WW (b), and $2WW_M$ (mobile water); dark blue diagonals represent ages corresponding to precipitation during the driest portion of the year (probability ≈ 0). Red vertical lines on a-c correspond to residence time probability distributions on Day 30 (d), Day 120 (e), and Day 210 (f). Distributions for 1WW and $2WW_M$ continue beyond the y-axis limit. The blue shaded regions indicate water which originated during the late dry season (Jul-Sep).

Figure 9. Color denotes the probability a parcel of water in unsaturated storage is younger than a particular residence time (i.e., cumulative probability) on a particular day of the water year (Day 1 = October 1) for 1WW (a), 2WW (b), and $2WW_M$ (mobile water). Red horizontal lines on a-c correspond to cumulative probabilities for residence times of 5 days (d), 50 days (e), and 200 days (f) throughout the water year. The blue shaded region indicates the late dry season (Jul-Sep).

Figure 10. Cumulative distribution of water storage in plant available reservoir S_{U1}. 2WW predicts more plant available water storage for all but the lowest 6.3% of days.