AGU PUBLICATIONS

Water Resources Research

RESEARCH ARTICLE

10.1002/2014WR016247

Key Points:

- Approach for time variant catchment transit time
- Modeling irregular shape of transit time distributions by time variant mixing
- Modeling catchment transit time in WS10 of HJA Forest

Correspondence to:
J. Klaus,
julian.klaus@list.lu

Citation:
Klaus, J., K. P. Chun, K. J. McGuire, and J. J. McDonnell (2015), Temporal dynamics of catchment transit times from stable isotope data, *Water Resour. Res.*, *51*, 4208–4223, doi:10.1002/2014WR016247.

Received 5 AUG 2014
Accepted 9 MAY 2015
Accepted article online 13 MAY 2015
Published online 12 JUN 2015

Temporal dynamics of catchment transit times from stable isotope data

Julian Klaus[1], Kwok P. Chun[2,3], Kevin J. McGuire[4], and Jeffrey J. McDonnell[2,5]

[1]Environmental Research and Innovation Department, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg, [2]Global Institute for Water Security, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, [3]Department of Geography, Hong Kong Baptist University, Hong Kong, [4]Department of Forest Resources and Environmental Conservation, Virginia Water Resources Research Center, Virginia Tech, Blacksburg, Virginia, USA, [5]School of Geosciences, University of Aberdeen, Aberdeen, UK

Abstract Time variant catchment transit time distributions are fundamental descriptors of catchment function but yet not fully understood, characterized, and modeled. Here we present a new approach for use with standard runoff and tracer data sets that is based on tracking of tracer and age information and time variant catchment mixing. Our new approach is able to deal with nonstationarity of flow paths and catchment mixing, and an irregular shape of the transit time distribution. The approach extracts information on catchment mixing from the stable isotope time series instead of prior assumptions of mixing or the shape of transit time distribution. We first demonstrate proof of concept of the approach with artificial data; the Nash-Sutcliffe efficiencies in tracer and instantaneous transit times were $>$0.9. The model provides very accurate estimates of time variant transit times when the boundary conditions and fluxes are fully known. We then tested the model with real rainfall-runoff flow and isotope tracer time series from the H.J. Andrews Watershed 10 (WS10) in Oregon. Model efficiencies were 0.37 for the ^{18}O modeling for a 2 year time series; the efficiencies increased to 0.86 for the second year underlying the need of long time tracer time series with a long overlap of tracer input and output. The approach was able to determine time variant transit time of WS10 with field data and showed how it follows the storage dynamics and related changes in flow paths where wet periods with high flows resulted in clearly shorter transit times compared to dry low flow periods.

1. Introduction

Understanding the velocities, celerities, and transit time distributions of the headwater hydrograph is a community challenge [*McDonnell and Beven*, 2014]. We now know that the time that it takes water particles to travel through a catchment to a stream is different to the celerity that yields the hydrograph dynamics, often observed as a fast responding hydrograph that mainly consists of old water [*Kirchner*, 2003]. Transit time, the time water particles take to travel through the catchment, is therefore a fundamental descriptor of catchment properties [*McDonnell et al.*, 2010]. Mean transit times (MTT) and the transit time distributions (TTD) (also referred to as the probability density function (pdf) of transit times) integrate catchment flow path variability, and the combined effects of water storage and fluxes as water is transported through catchments [*Broxton et al.*, 2009; *Botter et al.*, 2010; *Benettin et al.*, 2013a, 2013b]. The traditional approach for quantifying MTT and TTD of catchments is via the convolution integral that relates the input and the output of a measured conservative tracer time series with a transfer function that determines the shape of the TTD (for review see *McGuire and McDonnell* [2006]). While many studies have applied this approach since the pioneering work of *Dincer et al.* [1970] and *Maloszewski and Zuber* [1982], recent papers have commented on the assumptions and highlighted the limitations of the technique [*Hrachowitz et al.*, 2010; *Botter et al.*, 2010; *Rinaldo et al.*, 2011].

The main limitation with the standard convolution approach, as noted first by *Niemi* [1977] and restated more recently by *Hrachowitz et al.* [2013], is that convolution usually does not account for the temporal dynamics of water flow paths and their changing distributions through time, by simplifying the system to a time invariant one. Time variance in the TTD has become the focus of recent studies [e.g., *van der Velde et al.*, 2010; *Botter et al.*, 2010, 2011]—the consensus is that the assumption of time invariance will lead to unrealistic representations of MTT [*Rinaldo et al.*, 2011].

The time variant transit time (TT) and TTD vary with different wetness conditions in catchments [e.g., *Birkel et al*., 2012; *Heidbüchel et al*., 2013]. The time variance of TT and TTD can also be related to precipitation regime and storage [*Sayama and McDonnell*, 2009]. *Hrachowitz et al*. [2009] showed the impact of meteorological boundary conditions on time variant TT by using a moving window in the parameter estimation of the transfer function approach. They showed that the shape parameter of the TTD can be strongly correlated to precipitation amount and intensity [*Hrachowitz et al*., 2010]. Recent theoretical work of *Rinaldo et al*. [2011] showed that the time variant behavior of TT and TTD depends on hydrological forcing together with evapotranspiration in addition to the storage and flow path distribution of the catchment. The TTD reflects apparent mixing dynamics, variability in precipitation and evapotranspiration, and the related variability in the hydrological response [*Botter et al*., 2010, 2011]. Catchment mixing is a concept that integrates flow path variability, connectivity, and disconnectivity of different contributing storages, and "should not be viewed as analogous to a physical 'mixer' stirring the water in the catchment" [*van der Velde et al*., 2015]. The influence of various combinations of catchment mixing on TTD was recently evaluated by *van der Velde et al*. [2015]. A new concept of how catchment discharge "selects" water from within the storage (linked to catchment mixing) has emerged in the literature [*Botter et al*., 2011; *Hrachowitz et al*., 2013; *Harman*, 2015; *van der Velde et al*., 2015]. *Harman* [2015] summarized so-called "StorAge Selection" functions that control the type of water released from a catchment following the framework of *Botter et al*. [2011]. Such selection procedures are crucial to ultimately understanding how different catchments mix, store, and release water.

We now know that the time variant TTD has the potential to be highly irregular in shape [*van der Velde et al*., 2010, 2012; *Rinaldo et al*., 2011; *Botter*, 2012]. Further, there are differences between the TTDs on injection time (i.e., the time it takes for a given rainfall parcel to travel through the system) and exit time (i.e., the mean age and TTD of a water parcel leaving the system at time t). These different time perspectives are important when considering how a distinct event propagates through the system or what comprises the integrated response in catchment discharge. The different TT and TTD between water that leaves the system via streamflow and water that leaves the system via evapotranspiration is also a point that needs to be considered [*Botter et al*., 2011; *Rinaldo et al*., 2011].

So what is the way forward? It seems that advancements in developing a new theoretical foundation for MTT and TTD have outpaced the collection and interpretation of field data. New data sets and data-based approaches are needed to complement the theoretical work. Such approaches can lay the foundation of a data-driven assessment of catchment mixing and will eventually allow catchment intercomparison that is needed to understand the controls on TT and TTD.

Here we present data from the well-studied H.J. Andrews (HJA) watershed in Oregon and introduce a new approach for selecting the discharge from a catchment by accounting for temporal variability of catchment mixing. We use this approach for calculating time varying TTs and TTDs based on measured tracer input and output data and the hydrological fluxes from a catchment. Our approach is designed to account for (i) time variance in the transit time and the transit time distribution due to changing flow paths, (ii) the irregular shape of the transit time distribution, (iii) the differences between the transit time distribution conditional to injection time and exit time, and (iv) the differences between the transit time distribution and residence time distribution (RTD, the age distribution of water stored in the catchment). Here we outline this new approach. The objectives for this paper are to

1. present the new approach to quantify the time variance of TT and TTD
2. demonstrate the conceptual background and the validation of the approach using artificial data
3. demonstrate the application to field data from the well-characterized Watershed 10 (WS10) in the HJA Experimental Forest, Oregon, USA.

2. Methods

2.1. Model Development

Our new field-based approach for determining catchment transit time and its time varying distributions is shown conceptually in Figure 1. The approach is based on the conservation of mass where the components of the water cycle are either measured or calculated. By conceptualizing the observed isotope time series to be a sequence of "particles" to a system [cf. *Botter et al*., 2011], we derive the transit time distribution

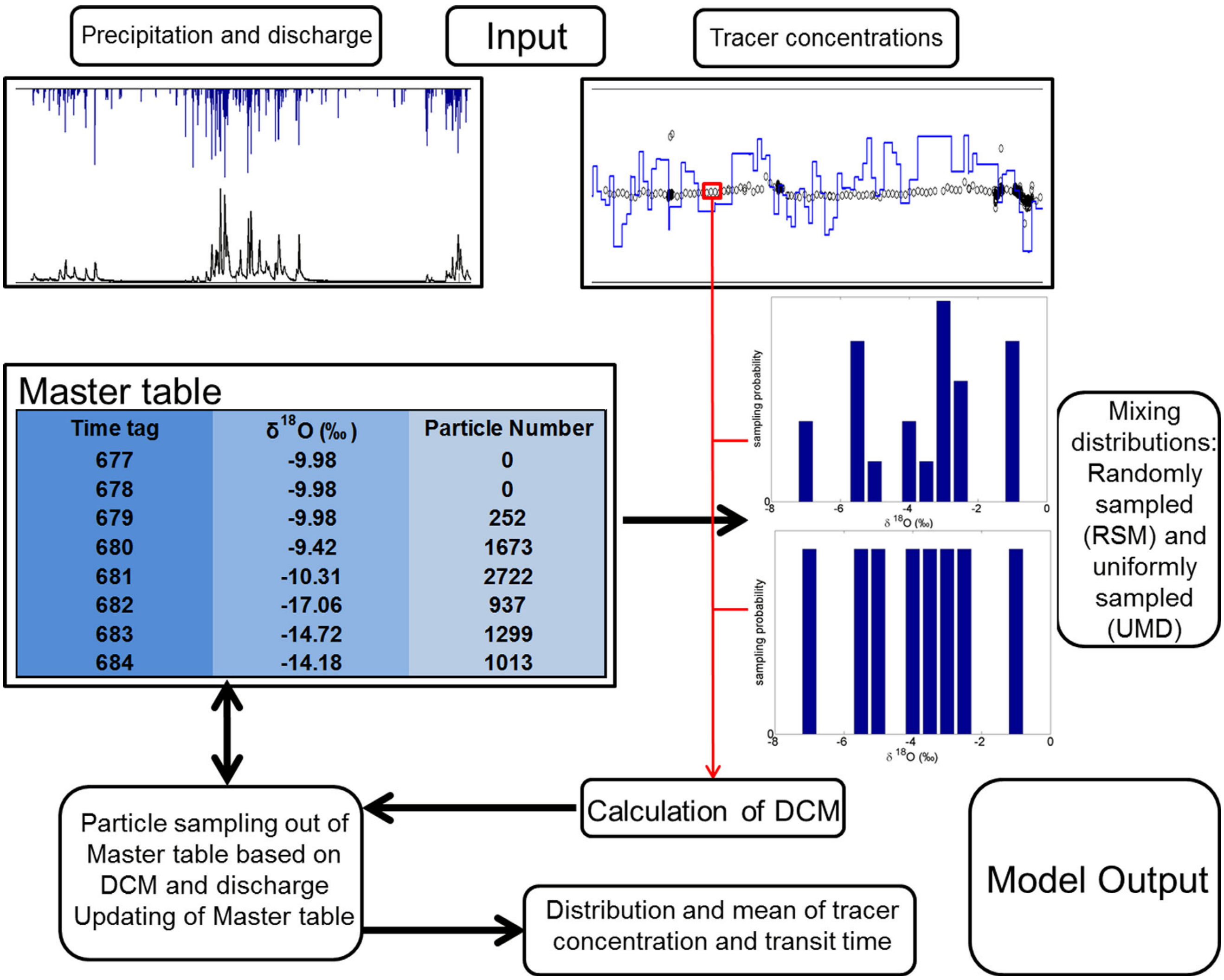

Figure 1. Conceptual diagram of the approach. The approach uses the input in form of tracer and hydrological time series and combines this with tracking of the stored tracer characteristics and ages. DCM is calculated based on the distribution of tracer concentration and the measured tracer concentration in streamflow. The RSM distribution represents a randomly sampled mixing distribution where particles have the same probability of being sampled, the UMD is a so called uniform mixed distribution, where every occurring tracer concentration has the same probability of being sampled. The value of DCM determines the ratio of sampling between RSM and UMD, and this eventually results in modeled tracer concentration, transit time, and transit time distribution of catchment discharge at every time step.

empirically. Therefore, fixed theoretical distributions such as a gamma distribution are not needed. Tracer time series of precipitation and discharge are required for using the approach. First, we assume that with every rainfall event a set of virtual particles enter the catchment with a distinct tracer concentration. The catchment is conceptualized as a single compartment. The number of particles entering the compartment per 1 mm precipitation is predefined (e.g., 100 particles per 1 mm precipitation), and the particles are mass/volume conservative for all flow and storage components. Information, such as the stable isotopic composition of the related precipitation event and the date/time of the event is attached to each individual particle. The particles enter the catchment storage and remain there (becoming progressively older with time) until they leave the system via streamflow (and potentially evapotranspiration or loss to deep groundwater). Since the number of particles entering the system is linked to the volume/mass of the corresponding precipitation event, they are volume/mass conservative and determine the volume and age of the hydrological storage (as long there are no subsurface inflows and outflows).

A master table (see example in Table 1) is used to contain the necessary information to track the particles in the approach and is updated at each model time step. This master table contains flux and tracer information. The table also keeps track of the amount of particles that are stored with a distinct time tag and its

Table 1. Snap Shot of the Master Table That Tracks the Amount of Particles That are Stored at the Time Step t, the Corresponding Tracer Value, the Number of Particles That Entered or Leave the System at Time t, and the Corresponding Tracer Concentrations[a]

Time Tag	Precipitation (mm)	Discharge (mm)	$\delta^{18}O$ (‰) in Precipitation	$\delta^{18}O$ (‰) in Discharge	Number of Particle in Precipitation Entering the System at Time t	Number of Particle in Discharge	Current Number of Stored Particles of Time Tag at Time t
677	0	0.13	n/a	−10.61	0	13	0
678	0	0.11	n/a	−10.65	0	11	0
679	3.6	0.08	−9.98	−10.65	360	8	252
680	23.9	1.31	−9.42	−10.24	2390	131	1673
681	37.8	7.21	−10.31	−10.65	3780	721	2722
682	14.2	2.30	−17.06	−10.48	1420	230	937
683	19.1	4.28	−14.72	−10.55	1910	428	1299
684	13.5	4.25	−14.18	−10.57	1350	425	1013

[a]Time information is stored by the time tag and transit time of each particle can be calculated by the difference between the current time and the time tag of the particle leaving the system.

related tracer concentration. The master table is the discretized form of the master equation similar to equation (3) in *Botter et al*. [2011]. At each time step a distinct number N of particles (proportional to the discharge, e.g., 100 particles per 1 mm flow) leaves the system. These particles are sampled out of the particles stored at time step t in the compartment (Table 1) accounting for the degree of mixing in the catchment. The degree of catchment mixing ($DCM(t)$) is calculated at time step t based on equation (1). The concentration C at time step t is:

$$C(t)=DCM(t)\times mRSM(t)+[1-DCM(t)]\times mUMD(t) \tag{1}$$

where $C(t)$ is the tracer concentration at time t as a mixture of $mRSM(t)$, the mean tracer concentration of the randomly sampled mixing distribution of all stored particles at time t, and $mUMD(t)$ the mean tracer concentration of the uniform distribution of all stored particles at time t.

RSM is a randomly sampled mixing distribution [cf. *Benettin et al*., 2013b], where every stored particle has the same probability of leaving the system. This assumption of randomly sampled mixing has a clear physical meaning and is frequently used in relation to solute transport and estimation of catchment transit times [e.g., *Hrachowitz et al*., 2013; *Benettin et al*., 2013b; *van der Velde et al*., 2015]. UMD is a uniform mixed distribution where every stored tracer concentration (i.e., assuming only one particle per tracer concentration) has the same probability of leaving the system (with repetition, as long as the distinct tracer concentration is available). The UMD implicitly gives higher weights to less frequent tracer concentrations. The UMD is the most conservative distribution choice with highest uncertainty and suited when no prior information [*MacKay*, 2003; *Park and Bera*, 2009] about flow paths and their interactions in the catchment exists. Using the proposed approach to model catchment tracer time series allows temporal dynamic considerations for catchment mixing.

$DCM(t)$ is constrained between 0 and 1, where 1 denotes randomly sampled mixing and 0 denotes incomplete mixing in the catchment (all particles are sampled out of UMD). Equation (1) is solved for $DCM(t)$ at every time step, resulting in a vector of the length t. At every time step, $DCM(t)$ times N particles are drawn from the RSM distribution and 1-$DCM(t)$ times N particles are sampled from the UMD distribution out of all stored particles. The modeled tracer concentration in the stream at time step t, $C_{mod}(t)$, is calculated as follows:

$$C_{mod}(t)=\frac{1}{N}\sum_{i=1}^{N}C_i(t) \tag{2}$$

where N is the total number of particles leaving the catchment via discharge, and $C_i(t)$ is the tracer concentration of each individual particle i that is leaving the catchment at time t.

The time variant transit time of the catchment at time, $tvTT(t)$, is:

$$tvTT(t)=\frac{1}{N}\sum_{i=1}^{N}tt_i(t) \tag{3}$$

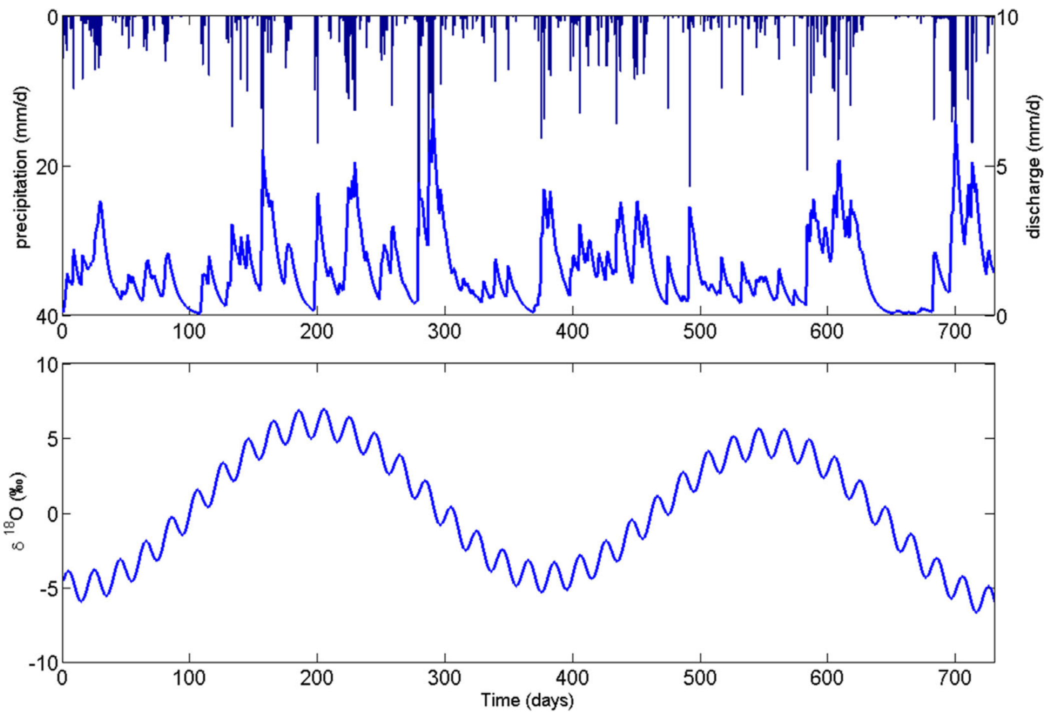

Figure 2. Artificial data used for the proof of concept with the virtual catchment. (top) Daily precipitation and daily discharge and (bottom) daily ^{18}O in precipitation.

where $tt_i(t)$ is the transit time of each individual particle i that is leaving the catchment at time step t.

The transit time distribution $ttD(t)$ is conditional on the exit time, and is the empirical probability density function of all tt_i leaving the catchment at time step t [*Rinaldo et al*., 2011]. Furthermore, the model allows calculation of the transit time distribution conditional to a recharge event at time step t, as soon as all particles of a recharge event leave the catchment. The Master Transit Time Distribution (MTTD) is also considered by following *Heidbüchel et al*. [2012]. At time step t the MTTD) (conditional on the exit time) is constructed by superimposing all individual transit time distributions $ttD(t)$, to give one empirical density function:

$$MTTD=\sum_{t=1}^{T} ttD(t) \tag{4}$$

where T is the end of the simulated period and $ttD(t)$ the observed transit time distribution at time step t.

We used a Monte Carlo approach with different seeds to account for the process that different sets of particles are sampled at each time even with the same DCM. We determine C_{mod} (t), $tvTT(t)$, $ttD(t)$, and MTTD as the mean of all individual Monte Carlo simulations. The particle selection approach is termed as DCMS (degree of catchment mixing selection).

2.2. Model Proof of Concept Approach

We used an artificial data series as an initial proof of concept of the proposed DCMS approach. We assumed a 2 year daily precipitation time series of a humid climate to drive the catchment dynamics (Figure 2). The catchment is treated as a single storage model [*Moore*, 1997], and daily discharge is calculated with an exponential storage equation initiated above a distinct storage threshold:

$$Q(t)=[storage(t-1)-Q_{thres}]\exp\left(\frac{-1}{k}\right) \tag{5}$$

where $Q(t)$ is the discharge in mm at time step t, k is the outflow constant, *storage* (t-1) the stored amount of water in mm at time step (t-1) and Q_{thres} a storage threshold that needs to be exceeded to generate discharge. We used 0.5 for k, and 5 mm for Q_{thres}.

We also assumed a skewed sine-wave input of ^{18}O with the precipitation available on a daily time step (Figure 2). These ^{18}O data were used in combination with an assumed *DCM* equaling 1 in a forward simulation of particle transport to calculate ^{18}O in the artificial catchment outflow.

Virtual particles enter the catchment storage with a distinct tracer composition and a time of recharge. For each 1 mm of effective precipitation 100 virtual particles enter the system, since initial tests showed that this is a good value that balanced calculation time and model accuracy. With the known outflow, a flow proportional number of particles leave the system. All particles have the same probability of leaving the system ($DCM = 1$) with discharge and were sampled out of the total particle population. The ^{18}O content at time t is calculated following equation (2) and $tvTT(t)$ is calculated based on equation (3). The modeled time series of ^{18}O and $tvTT(t)$ are then treated as "observed" catchment data together with the precipitation and discharge series. The initial storage of the catchment is set to 0.01 mm. To validate the developed model the approach needs to reproduce the virtual ^{18}O time series and the time series of transit time reasonably well by an inverse modeling approach.

As the last step we employed the described approach as an inverse model approach, where we minimized the difference between $C(t)$ and the observed streamflow tracer concentration and discharge is selected by DCMS. We performed a Monte Carlo simulation (10 runs in this case), and calculated the coefficient of determination (R^2) and Nash-Sutcliffe efficiency (NSE) of observation and model.

2.3. Model Testing With Field Data

2.3.1. Study Site and Data Set

The study was carried out in Watershed 10 at the H.J. Andrews Experimental Forest. Previous work there has shown that the mean transit time of the catchment streamflow is 1.2 ± 0.29 years based on a steady state, time invariant convolution approach [*McGuire et al.*, 2005]. The calculated soil water mean transit time ranges from 10 to 25 days [*McGuire and McDonnell*, 2010] and the event water transit time varies between 8 and 34 h [*McGuire and McDonnell*, 2010].

The catchment drains an area of 10.2 ha in the west central Cascade Mountains of Oregon, USA (44.2°N, 122.26°W) and elevation ranges from 473 to 680 masl (Figure 3). The catchment is currently part of the NSF Long-Term Ecological Research (LTER) program at the HJA and numerous hydrological process and modeling studies have been carried out at the site [*Harr*, 1977; *McGuire et al.*, 2005, 2007; *van Verseveld et al.*, 2009; *McGuire and McDonnell*, 2010; *Brooks et al.*, 2010; *Gabrielli et al.*, 2012]. The climate is classified as Mediterranean with wet, mild winters and dry, cool summers. Annual precipitation is 2200 mm (1979–2008) and falls mainly between October and April. Transient snow accumulation is common, but rarely persists more than 1–2 weeks and generally melts within 1–2 days [*Mazurkiewicz et al.*, 2008]. The catchment gradually wets-up from October to December and maintains the wet conditions until late spring [*McGuire and McDonnell*, 2010]. The average annual runoff ratio is 0.56 while summer low flows can fall below 0.01 mm/h and the largest peak flow reached 8.7 mm/h. Debris flows have scoured approximately the lower 60% of the stream channel to bedrock and removed the riparian zone, which led to a runoff behavior dominated by hillslope runoff with very little riparian volume or storage [*Gabrielli et al.*, 2012]. Runoff generation in the catchment shows clear thresholds, hysteresis, and event transit times varying with antecedent conditions [*McGuire and McDonnell*, 2010]. The catchment is steep (30° to over 45°) and has an average soil depth of 1.3 m. The soils are residual and colluvial well-aggregated, gravelly clay loam (*Typic Dystrocryepts*) derived from andesitic tuffs (30%) and coarse breccias (70%) comprising the Little Butte Formation formed as the result of ashfall and pyroclasitic flows from Oligocene-Early Miocene volcanic activity [*Swanson and James*, 1975; *James*, 1978]. The vegetation is second growth Douglas fir that naturally regenerated after a clearcut harvest in 1975.

Water levels at the flume were measured in 15 min intervals and transferred into discharge volume via a rating curve. Precipitation was obtained from a nearby weather station (PRIMET, 430 masl). Stable isotope data were available (δ^{18}O) from previous studies; see *McGuire et al.* [2005] and *McGuire and McDonnell* [2010] for details on sampling. We used available data from February 2001 to January 2003 (Figure 4) as model input. Daily precipitation and discharge values were calculated based on the available data set. Most periods of the isotope time series were based on weekly sampling intervals with episodes of daily precipitation and denser event based stream sampling. This time series was transferred into a daily time series of stable isotopes in precipitation and streamflow. The isotope value of a precipitation

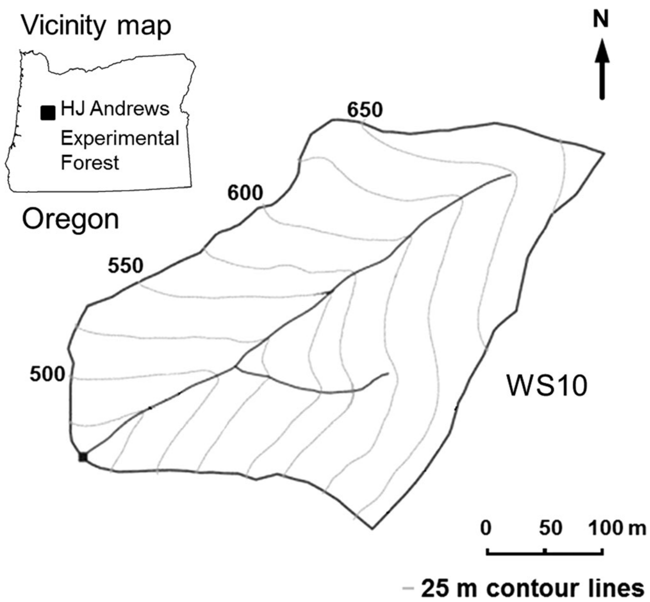

Figure 3. Map of Watershed 10 (WS10) of the H.J. Andrews Experimental forest and the location within Oregon, USA.

sample was assigned to all days between the sample and the previous precipitation isotope sample. If density of streamflow sampling was less than daily, the observed isotope value was assigned to the following days until the next stream sample was taken. When sampling frequency was subdaily a flow weighted mean value was assigned to that day. Due to the small area and elevation difference of WS10 no correction of precipitation isotopic input was applied [see also *McGuire et al.*, 2005]. The flux weighted isotopic average of precipitation ($\delta^{18}O = -11.1‰$) is consistent with the flux weighted value of discharge ($\delta^{18}O = -11.1‰$) for the period 1 February 2001 to 31 January 2003. This indicates that a constant percentage of precipitation infiltrates and contributes to groundwater recharge and runoff throughout the year. Further, these similar values of flux weighted input and output indicate that isotopic fractionation seems to be of minor importance.

2.3.2. Setup for WS10

The modeled mean transit time based on a steady state, time invariant method is 1.2 ± 0.29 years [*McGuire et al.*, 2005]. This and the rather short time series of 2 years made it necessary to repeat the available time series to determine the time variant transit time and account for spin-up time of the model. Using a repeated time series of precipitation and discharge and ^{18}O requires the same time length of all time series. Thus we did not use the available precipitation samples prior to the start of the stream sampling. A further requirement is that the catchment storage does have the same value at each beginning of the repetition of the hydrometric time series (otherwise the storage would dry out or increase continuously). Thus we used effective precipitation (P_{eff}) as a percentage of precipitation (0.596). This value is the observed mean runoff ratio of the 2 years. We used this as a constant reduction factor for precipitation (0.596) to calculate P_{eff} at every time throughout the model applications. This can be done since input

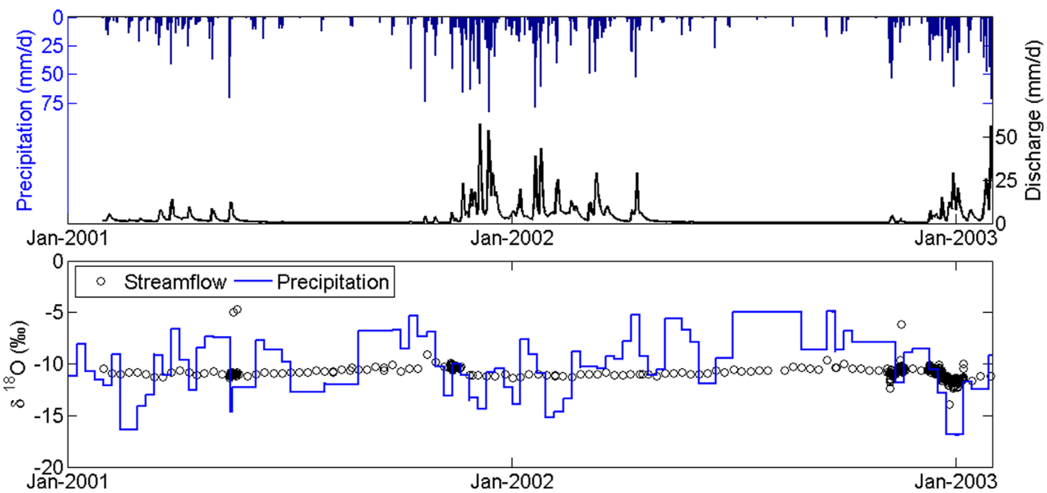

Figure 4. (top) Daily precipitation and daily discharge of WS10, and (bottom) observed streamflow and precipitation ^{18}O signal.

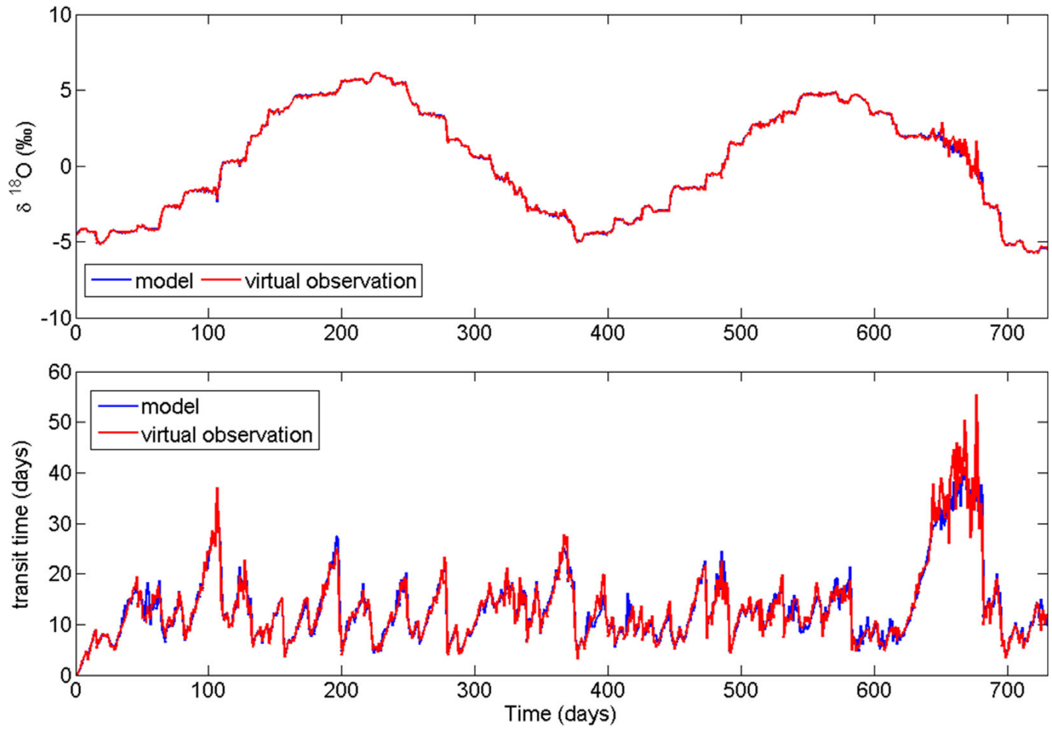

Figure 5. Results of the proof of concept. (top) Modeled and observed artificial ^{18}O time series and (bottom) model and observed/known time variant transit time.

and output flow weighted ^{18}O signal are practically the same, which means that there seems to be no preferential contribution of water from a distinct season. Thus evapotranspiration samples water randomly from precipitation at each time step. Similar assumptions were made by *Bertuzzo et al*. [2013]; they sampled evapotranspiration losses randomly out of the storage. We estimated the initial catchment storage based on the average annual precipitation of the 2 year time series (1956 mm) and the mean transit time calculated by *McGuire et al*. [2005] (1.2 years). We initialize the age distribution and ^{18}O of particles in initial storage following an exponential function with the mean residence time of 1.2 years (i.e., adding stored particles in the system for the spin-up period). The isotope signal of these stored particles copies the 2 year time series of observed precipitation, i.e., the youngest water has the isotopic signal of 31 January 2003. An appropriate initialization reduces the spin-up time in the model output but has no effect on the overall results after a few year spin-up, because particles are removed from the catchment in a year scale.

Initial tests showed that the model run yields the same transit time dynamics and modeled ^{18}O in streamflow after five repetitions of the time series. In total we run 14 years (seven repetitions) of data and analyze results based on the last 2 year period. We performed a Monte Carlo simulation of 100 model runs (with a different seed for particle sampling) to model time variant transit times *tvTT*(*t*) and their distribution as the mean of the 100 simulations, and 95%-confidence bounds of the simulations are also computed from the simulations ensembles to quantify the uncertainty of the estimated time variant transit time from particle sampling.

3. Results

3.1. Proof of Concept Results

The virtual and modeled ^{18}O time series matched exceptionally well (Figure 5). The mean value of the 10 different model runs (Figure 5, top) against the observed data showed an R^2 and a NSE of 0.998 each, with hardly any differences between the simulations. The resulting time variant transit time (Figure 5, bottom) based on 10 runs showed slightly lower model efficiencies with $R^2 = 0.94$ and NSE $= 0.94$. This confirms the choice of the mixing distributions to be sufficient.

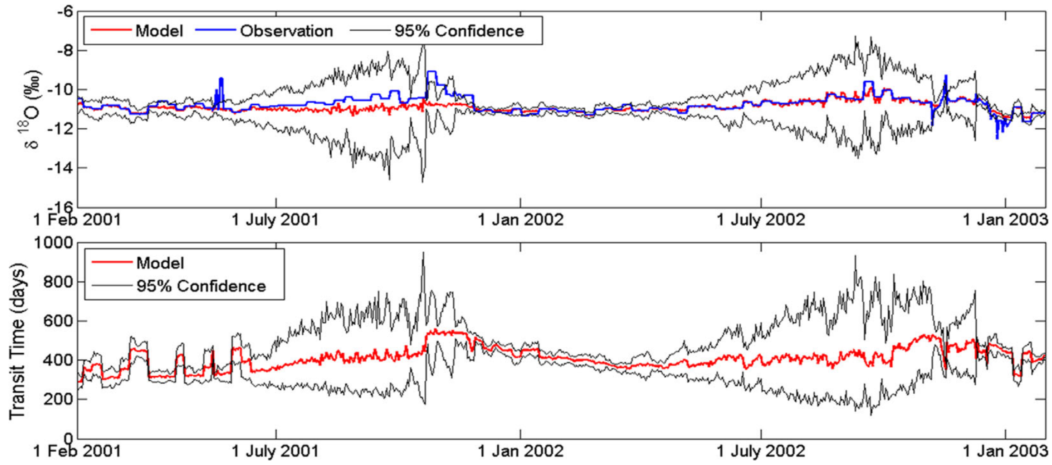

Figure 6. (top) Observed and modeled ^{18}O time series in WS10, including the 95%-confidence bounds of the model results, and (bottom) the modeled time variant catchment transit time and the 95%-confidence bounds.

3.2. Field Application Results

3.2.1. Modeling of ^{18}O

The model provided satisfactory simulations to the observed 2 year ^{18}O time series (Figure 6, top) with $R^2 = 0.45$ and NSE = 0.37. The model fit was remarkably different between the first and second year, with clearly better results in the second year ($R^2 = 0.32$ and 0.76 and NSE = -0.07 and 0.86). This was perhaps not surprising considering that the mean transit time was more than a year and the data time series length was only 2 years. While the stable isotopes leaving the catchment in the second year were observed within the precipitation time series, the ^{18}O data of the first year remain partly unaccounted in the model since the related precipitation events occurred outside the model/observation period. During the first year the model underestimated the isotopic signature especially from summer 2001 to fall 2001 (but spring 2001 was modeled rather well). The model performed very well during most of 2002 capturing the catchment isotope dynamics. In late 2002 and early 2003 the model had difficulty matching the measured ^{18}O dynamics. Here high frequency observations of several runoff events showed short-term dynamics that our single storage model (without any fast flow components and running in daily time steps) was unable to account for. The 95%-confidence bounds of the model shown in Figure 6 (top) show that the model was able to capture the observations with a few exceptions, including: runoff events in spring 2001, winter of 2002, and some data during the summer low flow of 2001 (Figure 6, top).

3.2.2. Time Variant Transit Time Modeling and Catchment Mixing

With the DCMS approach we were able to model a time variant transit time over the observation period (Figure 6, bottom). The dynamics of the modeled transit times were generally linked to the dynamics of streamflow (Figure 7). Catchment transit time increased during the long dry season in WS10, while model output was noisy during dry episodes. In fall 2001 the increase in transit time ceased after significant wet-up of the catchment and increased streamflow. Stored water was flushed out of the catchment and replaced by new water related to the main fall/winter precipitation input, thereby reducing the transit time. Mixing patterns on WS10 shows some fuzzy behavior in the first year of observation and smoother dynamics in the second year (Figure 8). WS10 is randomly sampled during most of the wet period in winter 2001/2002, at some phases

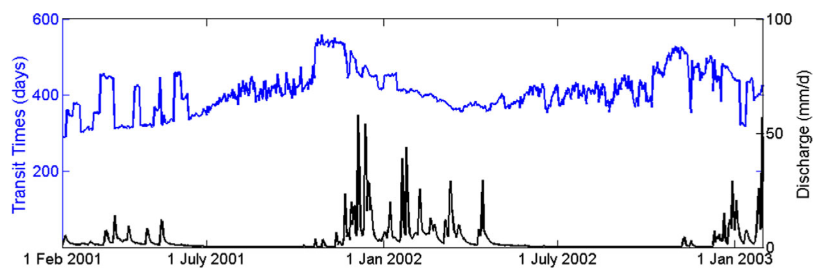

Figure 7. Discharge (black) versus catchment transit time (blue) in WS10.

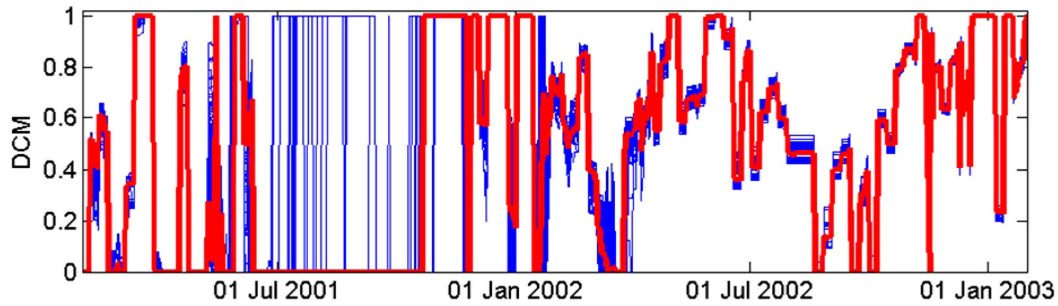

Figure 8. Mixing dynamics in WS10, expressed by the variation of DCM (1 denotes randomly sampled mixing). Red line indicates the median of all DCM, while blue lines are the DCM of the 100 Monte Carlo simulations.

during spring 2002, and approaches the state of randomly sampled mixing toward the end of 2002. During the dry phase in summer 2001 and fall 2002 DCM stays at or approaches zero.

3.2.3. Individual and Master Transit Time Distribution

Our approach allows for examination of individual transit times in the stream water sample (conditional to the exit time). It also enables examination of how an individual rain event travels through the system (transit time distribution conditional to recharge time). Figure 9 shows four individual transit time distributions conditional to the exit time at four points in time during the observation period (Figure 9). The *ttD(t)* at 14 April 2002 and 30 January 2003 represent higher flow stages, while the *ttD(t)* at 5 July 2002 and 13 October 2002 were sampled at the beginning and toward the end of the summer low flow conditions of 2002. There was no single smooth, continuous distribution that represented the shape of the *ttD(t)*. Rather there were clear age gaps in the distributions. The age gaps represented time periods without precipitation before the sampling date, e.g., if no rainfall (and particle input) occurred 300 days before the sample, no particle with the age of 300 days can be found in streamflow. The most apparent difference is that the distributions during high flow are denser in young age compared to low flow periods. The 10% percentiles are at 31 days (14 April 2002) and 29 days (30 January 2003) during the wet period, while this age is much higher for the dry period with 70 days (5 July 2002) and 139 days (13 October 2002). The difference between the wet/dry periods vanishes for the oldest components (90th percentile), with water ages of 1080 days (14 April 2002), 943 days (5 July 2002), 1050

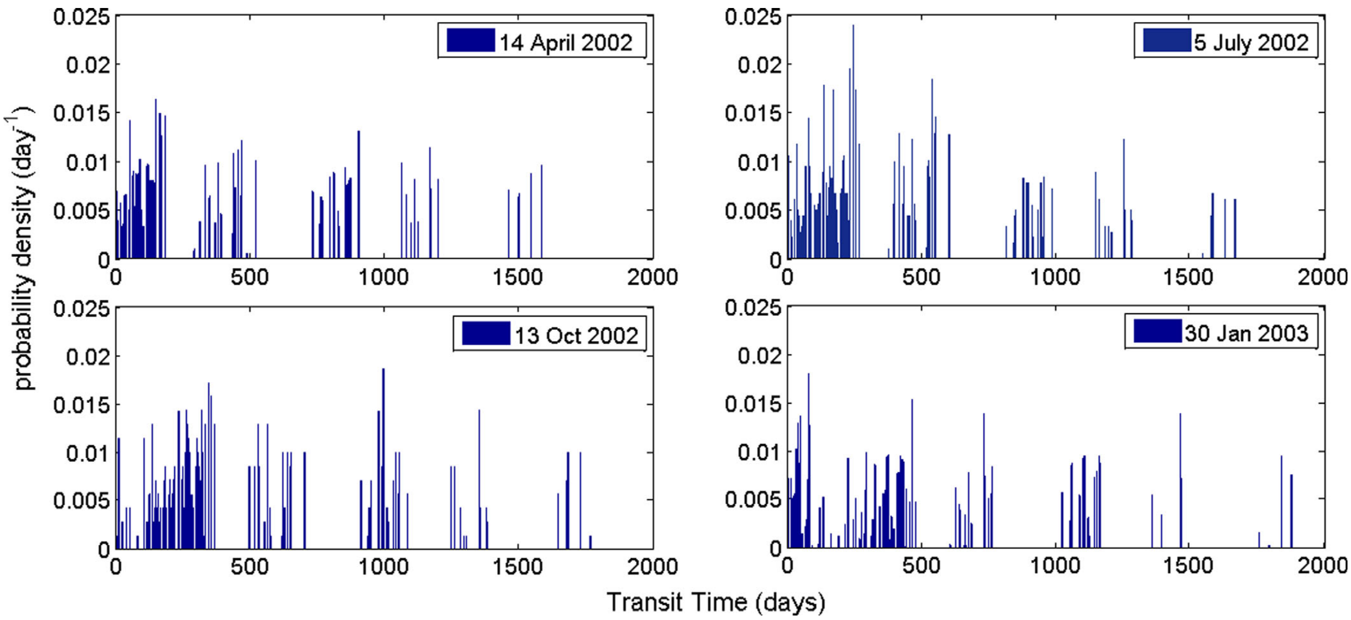

Figure 9. Transit time distribution (conditional to the exit time) at 4 days during the observation period in WS10. The probability density represents the distinct fraction of transit time in streamflow at the respective date. The four different times represent different flow stages with differences in the transit time distribution.

Table 2. Percentiles of the Transit Time Distributions *ttD(t)* of Four Different Dates[a]

	Percentiles of *ttD(t)*				
Date	10th	25th	50th	75th	90th
14 Apr 2002*	31 days	80 days	144 days	522 days	1080 days
5 Jul 2002	70 days	134 days	217 days	526 days	943 days
13 Oct 2002*	139 days	218 days	308 days	630 days	1050 days
30 Jan 2003	29 days	73 days	358 days	626 days	1101 days

[a]Dates marked with a (*) are during the wet period.

days (13 October 2002), and 1101 days (30 January 2003). Details regarding these 4 transit time distributions can be found in Table 2. These results are related to the fact that the annual climate cycle controls much of long-term behavior, while short-term behavior is mainly controlled by single rainfall-runoff events (Figure 9). The four distributions also showed no ages older than approximately 1900 days. This is consistent with the MTTD (Figure 10) that showed no particles older than 2200 days. The MTTD indicated that water was most likely to leave the catchment within one day. At higher transit times the MTTD showed strong variability. This is due to the fact that water is flushed out with subsequent precipitation events increasing the probability at these distinct times. The MTTD allows examining the water fraction leaving the system between distinct times. In this case 50% of the water had left the catchment after 329 days. This is in contrast with the mean transit time of 415 days. After 1049 days 90% of the water had left the system, while 10% of water left the catchment within 28 days. The transit time distributions conditional to injection exhibit different patterns visualized with two precipitation events on 15 September 2001 (4.6 mm) and on 6 March 2002 (48.8 mm). The large precipitation event during the wet season has a much longer transit time and some of its water remains in the system over years (Figure 11, top right), while water from the September event is flushed out as soon discharge increases after the dry season (Figure 11, top left). With this approach the discharge created by a distinct event can be tracked over time (Figure 11, bottom).

4. Discussion

4.1. How This Work Compares to Other Approaches for Time Variant TTD?

Besides convolution-based approaches [*Hrachowitz et al*., 2010; *Heidbüchel et al*., 2012] hydrological models can be used for predicting time variant transit time and transit time distributions of hydrological and hydrogeological systems (run in a forward modeling scheme). Physics-based models combined with a particle tracking scheme [e.g., *Kollet and Maxwell*, 2008; *de Rooij et al*., 2013], particle tracking approaches, like the Multiple Interacting Pathways (MIPs) model that uses particle tracking for flow and transport [*Davies et al*., 2011, 2013], and solute transport schemes in rather conceptual models [*Sayama and McDonnell*, 2009; *Hrachowitz et al*., 2013] are at hand. Physics-based models require detailed knowledge about hillslope or catchment properties such as hydraulic conductivity of the soil for their use. Further, the MIPs model requires assumptions of water velocity distribution [*Davis et al*., 2013]. Even at the hillslope scale, such detailed data (and information on their

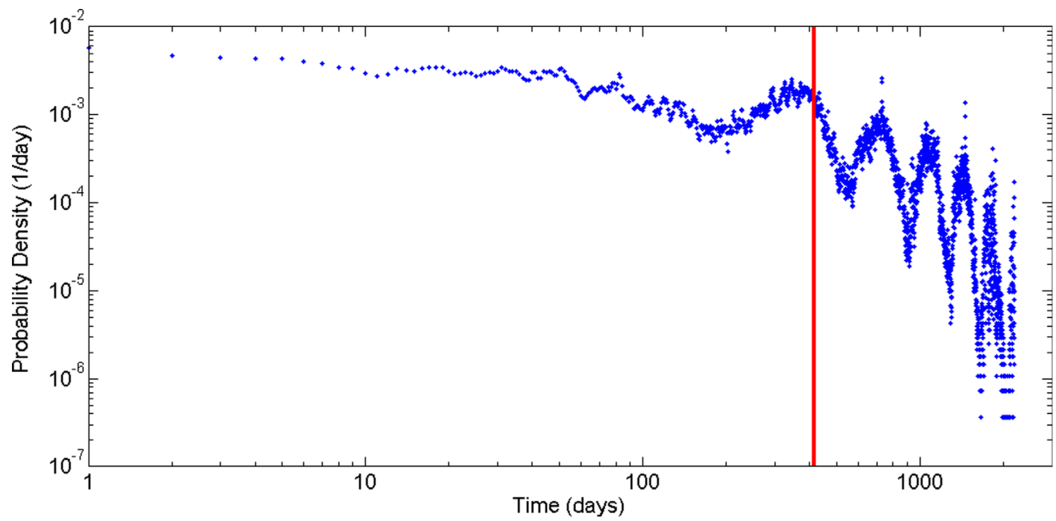

Figure 10. Master transit time distribution (conditional to the exit time) of the available data set in WS10. The red line indicates the mean transit time of WS10.

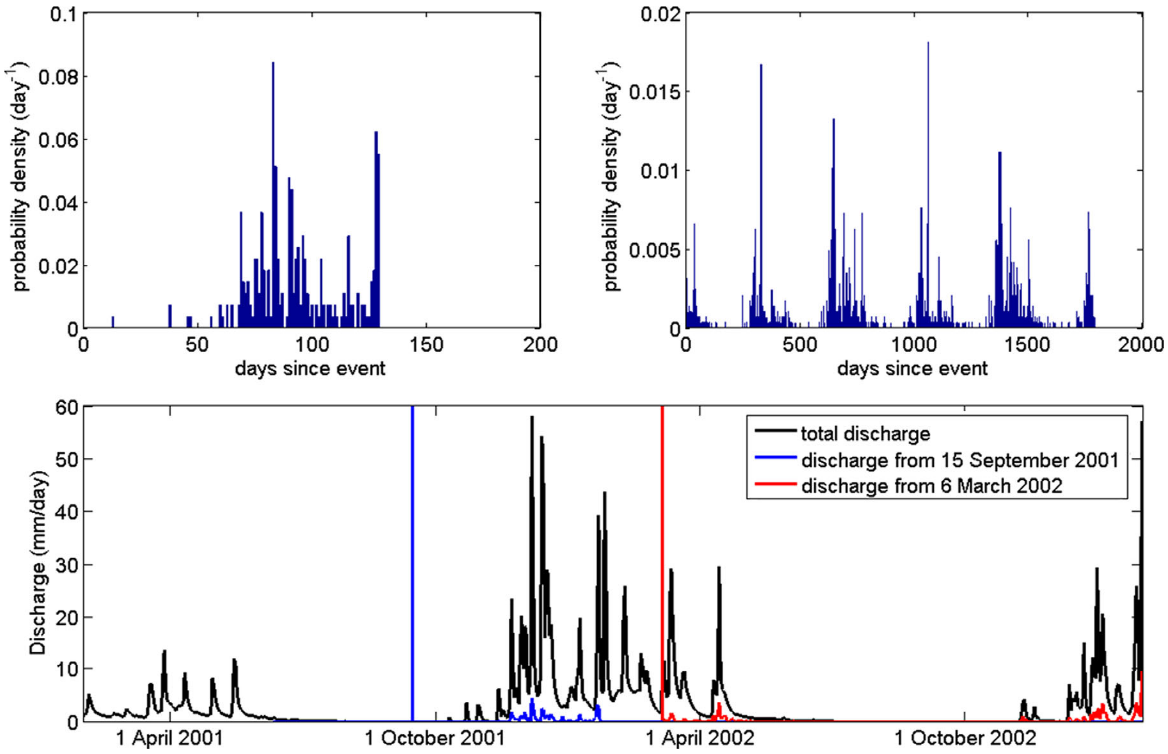

Figure 11. Transit time distributions (conditional to injection time) for two rainfall events in HJA WS10. (top) (left) The probability density function (15 September 2001) and (right) (6 March 2002). (bottom) How the two precipitation events propagate to discharge (their contribution is scaled by a factor 20) is shown. The vertical lines indicate the point in time of the individual recharge events.

spatial distribution) is currently impossible to obtain [*Harr*, 1977]; and some data exist only for limited very well studied experimental sites. The conceptual models need some assumption on the mixing within the model/catchment. The presented approach does not require such detailed data sets and makes no assumptions about the shape of the transit time distribution (they are nonparametric). Here we employ a particle-based approach to track information like tracer concentration or time information, and solve catchment mixing inversely based on the tracer data. The advantage of such an approach is that detailed catchment property information is not needed which makes the approach relatively easy to apply over various hydrological scales. The transport of the particles is solely dependent on the observed flow and by DCM, which is determined from the tracer time series for every individual time step representing the mixing in the catchment, by inverse modeling. Calculation of DCM in this way is eventually a data-driven approach to determine temporal variability in catchment mixing, if the mixing distributions cover the range of potential mixing states. Moreover, the links between mixing functions (e.g., ω in the framework outlined by *Botter et al.* [2011] and used thereafter [e.g., *Benettin et al*., 2013a] or StorAge Selection (SAS) functions [*Harman*, 2015]) and the DCM should be explored in future. A data-driven determination of these functions would be a next step in transit time research.

4.2. How Computed Time Variant TT and TTD at the HJ Andrews WS10 Compare to Other Catchments?

Transit time dynamics in WS10 followed storage dynamics, similar to model results by *Sayama and McDonnell* [2009], with longer transit times than in their work that provided no fit for the ^{18}O data. WS10 shows shorter transit times during wet catchment state and longer transit times during summer low flow. These findings are similar to *Birkel et al*. [2012], who found that the shape parameter of the TTD changed with antecedent wetness in the Wemyss catchment, Scotland. The MTTD can provide insight into the catchment response characteristics. A water parcel is most likely to leave WS10 within 1 day after it precipitated. The time it takes for 50% of the water to leave the WS10 catchment is shorter compared to the work of *Heidbüchel et al*. [2012] in the Marshall Gulch (MG) catchment, Arizona, USA, and the Rietholzbach (RHB) catchment, Switzerland. In WS10 50% of the water leaves the catchment within 329 days, in MG within 380 days, and in the RHB within 346 days. The first 10% of water of an event are leaving WS10 within 28 days and this is slightly faster than in MG (32 days) and clearly faster than in the RHB (53 days) [*Heidbüchel et al*., 2012].

However, some care needs to be taken here, because the compared results from the literature are based on different approaches, with different assumptions of catchment mixing. We need to pay more attention on the importance of how catchment mixing is implemented. For example, recent work by *van der Velde et al*. [2015] showed the impact of different mixing assumptions on the resulting TTD for the MG catchment.

The generally fast response at HJA WS10 might be explained by differences in hydro-climatology and the relation of storage, storage availability, and precipitation distribution and amount. Further studies are needed to compare different catchment characteristics and their influence on the different parts of the MTTD. The presented approach can be a valuable tool for additional catchment intercomparison even with only limited data (i.e., tracer input-output and hydrometric time series).

4.3. A New Tool for the Experimental Hydrologist?

The nonstationary, nonlinear characteristics of hydrological response require new approaches in tracer hydrology to determine the characteristics of catchment response with tracer data [*Botter et al*., 2010; *Rinaldo et al*., 2011]. The DCMS approach is able to deal with time variance and the irregular shape of the TTD and extracts information on time variant catchment mixing from the stable isotope time series instead of prior assumptions of mixing or the shape of TTD. The approach considers the time variability of water flow in the soil, crucial for transit time determination [*Rinaldo et al*., 2011], although our approach simplifies the catchment as a single storage [cf. *Harman*, 2015]. Nevertheless, this simplification in this approach brings us a step forward in describing catchment TTDs in a time variant manner and with their irregular shape without a priori assumptions about catchment mixing [*Botter et al*., 2010, 2011; *van der Velde et al*., 2010, 2012; *Benettin et al*., 2013b]. It goes beyond previous established field methods that have used a time invariant mean transit time and an assumption of the shape of the transfer function and thus the TTD. Most importantly, the approach helps the experimental hydrologists better understand the behavior of their catchment, their TT, and TTD without the requirement for demanding information about flow velocities or physical catchment properties as required in more advanced hydrological models [e.g., MIPs by *Davies et al*., 2011, 2013]. Consistent with common transport models, the approach can supply a full analysis of transit time distributions, conditional to exit or recharge time, and of the storage within the catchment based on hydrometric and tracer data.

The mixing dynamics of a catchment are regarded as key control on the shape of the TTD [*Botter et al*., 2010] and determining this a priori remains still a challenge in hydrology. Nevertheless, our choice of the mixing distributions (RSM and UMD) remains subjective, and more work on their selection is needed. We could imagine linking observed dominated flow processes with the utilized distributions. For example, when preferential flow dominates catchment response one of the distributions can account for a last in first out effect [*Hrachowitz et al*., 2013], or another example is to go beyond two mixing distributions by using several tracers. Eventually, this should allow us to better understand the controls on observed mixing dynamics (Figure 8). Further, the work can be extended in a way that the approach accounts for a more complex representation of catchment structure using several storages [*Benettin et al*., 2013b; *Hrachowitz et al*., 2013], but this will depend on the complexity of runoff generation and flow paths in the investigated catchment. In this paper, we employed a simple scheme to account for precipitation, using *Peff* as a fixed ratio of precipitation, and thus sampling the isotopic loss in evapotranspiration randomly out of precipitation at every time step. In general, the approach is flexible, and the way evapotranspiration is realized should be guided by catchment properties and available data. Nevertheless, the way evapotranspiration fluxes [see *Botter et al*., 2011] are accounted for remains challenging, although different sampling scheme exists [e.g., *Bertuzzo et al*., 2013; *Harman*, 2015]. Ideally such sampling schemes are based on data of stable isotopes in transpiration and evaporation fluxes, but such data are very limited. Moreover, growing evidence of ecohydrological separation between transpiration and groundwater recharge [*Brooks et al*., 2010; *McDonnell*, 2014] adds additional complexity. In some catchments fractionation of stable isotopes can play a role, and might require adjustment [cf. *Birkel et al*., 2011]. Furthermore, the current approach can be extended and modified to account for differences in short and long-term transit times [e.g., *Roa-Garcia and Weiler*, 2010] that would allow better representation of the short-term components of the transit time. Data sets like the one used, with a base flow sampling but also event-based hydrograph sampling [*McGuire et al*., 2005; *McGuire and McDonnell*, 2010] are a first step toward quality data sets that observe these short and long-term variations. *McDonnell and Beven* [2014] recently outlined the urgent need for additional data sets of isotope time series in precipitation and streamflow, high frequency measurements, and more contrasting catchment comparisons. This is consistent with other calls, that better understanding of short and long-term variations in catchment transit time can be achieved by measuring stable isotopes in high frequency [cf. *Kirchner et al.*, 2004]. The knowledge gain by high frequency data for hydrological process studies [*Birkel et al.*, 2012; *Klaus et al.*, 2013; *Pangle et al.*, 2013] is undebatable [*Klaus and McDonnell*, 2013] and in reach with recent technological developments [*Berman et al.*, 2009; *Herbstritt et al.*, 2012; *Stöcker et al.*, 2012; *Pangle et al.*, 2013]. We agree with *Rinaldo et al.* [2011] that the availability of high quality data sets is a prerequisite of further development and understanding of hydrological systems. With mostly weekly samples of precipitation and streamflow stable isotopes some limitations arise. Fast catchment responses and their link to fast changing transit times will be overlooked with the inverse DCMS. Further, the assumption that the measured value of ^{18}O in streamflow is constant until the next know sample can induce some high frequency noise in DCM and the resulting transit time. Notwithstanding, we show here that the use of DCMS can yield insights into the time variant transit times and their distributions when sampling densities are coarser than daily. Perhaps a key factor for future progress is the generation of long-term data sets that extend beyond the usual 2 or 3 years of sampling. Future sampling campaigns need to account for the different characteristic transit times between short-term and long-term response in their sampling, to better understand the multimodal characteristics of TTD.

5. Conclusion

The presented approach calculates time variant transit times and transit time distributions of hydrological systems based on time series of tracer input and output. The model performed very well in a virtual environment with artificial data, and reproduced known transit time with a NSE $>$ 0.9. This showed that the approach supplies very good estimates of time variant transit times when the boundary conditions and fluxes are fully known. Further the approach performs reasonable well when applied to WS10 of the HJA, with a NSE of 0.37 for the ^{18}O modeling for a 2 year time series (NSE of 0.86 for the second year), underlying the need of long tracer time series with a long overlap of tracer input and output. The approach was able to determine time variant transit time of WS10 with field data and showed how it follows the storage dynamics where wet periods with high flows resulted in clearly shorter transit times compared to dry low flow periods. The transit time distributions are highly irregular in shape and show that these distributions do not follow a predetermined distribution such as the gamma or exponential distributions that are often used to describe the TTD. The approach is able to distinguish between transit time distributions conditional to exit and recharge times and can thus account for recently developed theoretical framework of time variant TT and TTD. This new tool should usher reevaluation of hydrological transit times and their time variant characteristics in the future, allowing for the time variance in catchment mixing determined by the ^{18}O time series sampled in the catchment outlet. It can also be extended to account for flexible model structures that reflect catchment properties better than a simple one box approach.

Acknowledgments
Funding for this work by Deutsche Forschungsgemeinschaft (German Research Foundation) is gratefully acknowledged (DFG Grant KL 2529/1-1 "Development and testing of a new time variant approach for stream water transit times"). The second author was supported during this work by the Global Institute for Water Security Post-Doctoral Fellowship of the NSERC Canada Excellence Research Chair Program. Streamflow, precipitation, and GIS data sets were provided by the HJ Andrews Experimental Forest research program, funded by the National Science Foundation's Long-Term Ecological Research Program (DEB 0823380), US Forest Service Pacific Northwest Research Station, and Oregon State University. We would like to thank four anonymous reviewers for their very helpful comments. The data are freely available by contacting the corresponding author by email, from the HJ Andrews Experimental Forest research program, and from Kevin J. McGuire for the tracer data.

References

Benettin, P., A. Rinaldo, and G. Botter (2013a), Kinematics of age mixing in advection-dispersion models, *Water Resour. Res.*, *49*, 8539–8551, doi:10.1002/2013WR014708.

Benettin, P., Y. van der Velde, S. E. A. T. van der Zee, A. Rinaldo, and G. Botter (2013b), Chloride circulation in a lowland catchment and the formulation of transport by travel time distributions, *Water Resour. Res.*, *49*, 4619–4632, doi:10.1002/wrcr.20309.

Berman, E. S. F., M. Gupta, C. Gabrielli, T. Garland, and J. J. McDonnell (2009), High-frequency field-deployable isotope analyzer for hydrological applications, *Water Resour. Res.*, *45*, W10201, doi:10.1029/2009WR008265.

Bertuzzo, E., M. Thomet, G. Botter, and A. Rinaldo (2013), Catchment-scale herbicides transport: Theory and application, *Adv. Water Resour.*, *52*, 232–242, doi:10.1016/j.advwatres.2012.11.007.

Birkel, C., D. Tetzlaff, S. M. Dunn, and C. Soulsby (2011), Using lumped conceptual rainfall–runoff models to simulate daily isotope variability with fractionation in a nested mesoscale catchment, *Adv. Water Resour.*, *34*(3), 383–394, doi:10.1016/j.advwatres.2010.12.006.

Birkel, C., C. Soulsby, D. Tetzlaff, S. Dunn, and L. Spezia (2012), High-frequency storm event isotope sampling reveals time-variant transit time distributions and influence of diurnal cycles, *Hydrol. Processes*, *26*(2), 308–316, doi:10.1002/hyp.8210.

Botter, G. (2012), Catchment mixing processes and travel time distributions, *Water Resour. Res.*, *48*, W05545, doi:10.1029/2011WR011160.

Botter, G., E. Bertuzzo, and A. Rinaldo (2010), Transport in the hydrologic response: Travel time distributions, soil moisture dynamics, and the old water paradox, *Water Resour. Res.*, *46*, W03514, doi:10.1029/2009WR008371.

Botter, G., E. Bertuzzo, and A. Rinaldo (2011), Catchment residence and travel time distributions: The master equation, *Geophys. Res. Lett.*, *38*, L11403, doi:10.1029/2011GL047666.

Brooks, R. J., H. R. Barnard, R. Coulombe, and J. J. McDonnell (2010), Ecohydrologic separation of water between trees and streams in a Mediterranean climate, *Nat. Geosci.*, *3*(2), 100–104, doi:10.1038/ngeo722.

Broxton, P. D., P. A. Troch, and S. W. Lyon (2009), On the role of aspect to quantify water transit times in small mountainous catchments, *Water Resour. Res.*, *45*, W08427, doi:10.1029/2008WR007438.

Davies, J., K. Beven, L. Nyberg, and A. Rodhe (2011), A discrete particle representation of hillslope hydrology: Hypothesis testing in reproducing a tracer experiment at Gårdsjön, Sweden, *Hydrol. Processes*, *25*(23), 3602–3612, doi:10.1002/hyp.8085.

Davies, J., K. Beven, A. Rodhe, L. Nyberg, and K. Bishop (2013), Integrated modeling of flow and residence times at the catchment scale with multiple interacting pathways, *Water Resour. Res.*, *49*, 4738–4750, doi:10.1002/wrcr.20377.

de Rooij, R., W. Graham, and R. M. Maxwell (2013), A particle-tracking scheme for simulating pathlines in coupled surface-subsurface flows, *Adv. Water Resour.*, *52*, 7–18, doi:10.1016/j.advwatres.2012.07.022.

Dincer, T., B. R. Payne, T. Florkowsk, J. Martinec, and E. G. E. I. Tongiorgi (1970), Snowmelt runoff from measurements of tritium and oxygen-18, *Water Resour. Res.*, *6*(1), 110–124.

Gabrielli, C. P., J. J. McDonnell, and W. T. Jarvis (2012), The role of bedrock groundwater in rainfall-runoff response at hillslope and catchment scales, *J. Hydrol.*, *450–451*, 117–133, doi:10.1016/j.jhydrol.2012.05.023.

Harman, C. J. (2015), Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed, *Water Resour. Res.*, *51*, 1–30, doi:10.1002/2014WR015707.

Harr, R. D. (1977), Water flux in soil and subsoil on a steep forested slope, *J. Hydrol.*, *33*(1–2), 37–58, doi:10.1016/0022-1694(77)90097-X.

Heidbüchel, I., P. A. Troch, S. W. Lyon, and M. Weiler (2012), The master transit time distribution of variable flow systems, *Water Resour. Res.*, *48*, W06520, doi:10.1029/2011WR011293.

Heidbüchel, I., P. A. Troch, and S. W. Lyon (2013), Separating physical and meteorological controls of variable transit times in zero-order catchments, *Water Resour. Res.*, *49*, 7644–7657, doi:10.1002/2012WR013149.

Herbstritt, B., B. Gralher, and M. Weiler (2012), Continuous in situ measurements of stable isotopes in liquid water, *Water Resour. Res.*, *48*, W03601, doi:10.1029/2011WR011369.

Hrachowitz, M., C. Soulsby, D. Tetzlaff, J. J. C. Dawson, S. M. Dunn, and I. A. Malcolm (2009), Using long-term data sets to understand transit times in contrasting headwater catchments, *J. Hydrol.*, *367*(3–4), 237–248, doi:10.1016/j.jhydrol.2009.01.001.

Hrachowitz, M., C. Soulsby, D. Tetzlaff, I. A. Malcolm, and G. Schoups (2010), Gamma distribution models for transit time estimation in catchments: Physical interpretation of parameters and implications for time-variant transit time assessment, *Water Resour. Res.*, *46*, W10536, doi:10.1029/2010WR009148.

Hrachowitz, M., H. Savenije, T. A. Bogaard, D. Tetzlaff, and C. Soulsby (2013), What can flux tracking teach us about water age distribution patterns and their temporal dynamics?, *Hydrol. Earth Syst. Sci.*, *17*(2), 533–564, doi:10.5194/hess-17-533-2013.

James, M. E. (1978), Rock weathering in the central western Cascades, MS thesis, Univ. of Oreg. Eugene.

Kirchner, J. W. (2003), A double paradox in catchment hydrology and geochemistry, *Hydrol. Processes*, *17*(4), 871–874.

Kirchner, J. W., X. Feng, C. Neal, and A. J. Robson (2004), The fine structure of water-quality dynamics: The (high-frequency) wave of the future, *Hydrol. Processes*, *18*(7), 1353–1359, doi:10.1002/hyp.5537.

Klaus, J., and J. J. McDonnell (2013), Hydrograph separation using stable isotopes: Review and evaluation, *J. Hydrol.*, *505*, 47–64, doi:10.1016/j.jhydrol.2013.09.006.

Klaus, J., E. Zehe, M. Elsner, C. Külls, and J. J. McDonnell (2013), Macropore flow of old water revisited: Experimental insights from a tile-drained hillslope, *Hydrol. Earth Syst. Sci.*, *17*(1), 103–118, doi:10.5194/hess-17-103-2013.

Kollet, S. J., and R. M. Maxwell (2008), Demonstrating fractal scaling of baseflow residence time distributions using a fully-coupled groundwater and land surface model, *Geophys. Res. Lett.*, *35*, L07402, doi:10.1029/2008GL033215.

MacKay, D. (2003), *Information Theory, Inference, and Learning Algorithms*, Cambridge Univ. Press, Cambridge, U. K.

Maloszewski, P., and A. Zuber (1982), Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability, *J. Hydrol.*, *57*(3–4), 207–231, doi:10.1016/0022-1694(82)90147-0.

Mazurkiewicz, A. B., D. G. Callery, and J. J. McDonnell (2008), Assessing the controls of the snow energy balance and water available for runoff in a rain-on-snow environment, *J. Hydrol.*, *354*(1–4), 1–14, doi:10.1016/j.jhydrol.2007.12.027.

McDonnell, J. J. (2014), The two water worlds hypothesis: Ecohydrological separation of water between streams and trees? *WIREs Water*, *1*, 323–329. doi:10.1002/wat2.1027.

McDonnell, J. J., and K. Beven (2014), Debates—The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph, *Water Resour. Res.*, *50*, 5342–5350. doi:10.1002/2013WR015141.

McDonnell, J. J., et al. (2010), How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis, *Hydrol. Processes*, *24*(12), 1745–1754, doi:10.1002/hyp.7796.

McGuire, K. J., and J. J. McDonnell (2006), A review and evaluation of catchment transit time modeling, *J. Hydrol.*, *330*(3–4), 543–563, doi:10.1016/j.jhydrol.2006.04.020.

McGuire, K. J., and J. J. McDonnell (2010), Hydrological connectivity of hillslopes and streams: Characteristic time scales and nonlinearities, *Water Resour. Res.*, *46*, W10543, doi:10.1029/2010WR009341.

McGuire, K. J., J. J. McDonnell, M. Weiler, C. Kendall, B. L. McGlynn, J. M. Welker, and J. Seibert (2005), The role of topography on catchment-scale water residence time, *Water Resour. Res.*, *41*, W05002, doi:10.1029/2004WR003657.

McGuire, K. J., M. Weiler, and J. J. McDonnell (2007), Integrating tracer experiments with modeling to assess runoff processes and water transit times, *Adv. Water Resour.*, *30*(4), 824–837, doi:10.1016/j.advwatres.2006.07.004.

Moore, R. D. (1997), Storage-outflow modelling of streamflow recessions, with application to a shallow-soil forested catchment, *J. Hydrol.*, *198*(1–4), 260–270, doi:10.1016/S0022-1694(96)03287-8.

Niemi, A. J. (1977), Residence time distributions of variable flow processes, *Int. J. Appl. Radiat. Isot.*, *28*(10–11), 855–860, doi:10.1016/0020-708X(77)90026-6.

Pangle, L. A., J. Klaus, E. S. F. Berman, M. Gupta, and J. J. McDonnell (2013), A new multisource and high-frequency approach to measuring δ^2H and δ^{18}O in hydrological field studies, *Water Resour. Res.*, *49*, 7797–7803, doi:10.1002/2013WR013743.

Park, S. Y., and A. K. Bera (2009), Maximum entropy autoregressive conditional heteroskedasticity model, *J. Econometrics*, *150*, 219–230, doi:10.1016/j.jeconom.2008.12.014.

Rinaldo, A., K. J. Beven, E. Bertuzzo, L. Nicotina, J. Davies, A. Fiori, D. Russo, and G. Botter (2011), Catchment travel time distributions and water flow in soils, *Water Resour. Res.*, *47*, W07537, doi:10.1029/2011WR010478.

Roa-Garcia, M. C., and M. Weiler (2010), Integrated response and transit time distributions of watersheds by combining hydrograph separation and long-term transit time modeling, *Hydrol. Earth Syst. Sci.*, *14*(8), 1537–1549, doi:10.5194/hess-14-1537-2010.

Sayama, T., and J. J. McDonnell (2009), A new time-space accounting scheme to predict stream water residence time and hydrograph source components at the watershed scale, *Water Resour. Res.*, *45*, W07401, doi:10.1029/2008WR007549.

Stöcker, F., J. Klaus, L. A. Pangle, C. Garland, and J. J. McDonnell (2012), High-frequency observations of δ^2H and δ^{18}O in storm rainfall, Abstract H31B-1114 presented at 2012 Fall Meeting, AGU, San Francisco, Calif., 3–7 Dec.

Swanson, F. J., and M. E. James (1975), Geology and geomorphology of the H. J. Andrews Experimental Forest, western Cascades, Oregon, *Res. Pap. PNW-188*, 14 pp., Pac. Northwest For. and Range Exp. Stn., Portland, Oreg.

van der Velde, Y., G. H. de Rooij, J. C. Rozemeijer, F. C. van Geer, and H. P. Broers (2010), Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics, *Water Resour. Res.*, *46*, W11534, doi:10.1029/2010WR009105.
van der Velde, Y., P. J. J. F. Torfs, S. E. A. T. van der Zee, and R. Uijlenhoet (2012), Quantifying catchment-scale mixing and its effect on time-varying travel time distributions, *Water Resour. Res.*, *48*, W06536, doi:10.1029/2011WR011310.
van der Velde, Y., I. Heidbüchel, S. W. Lyon, L. Nyberg, A. Rodhe, K. Bishop, and P. A. Troch (2015), Consequences of mixing assumptions for time-variable travel time distributions, *Hydrol. Processes*, in press.
van Verseveld, W. J., J. J. McDonnell, and K. Lajtha (2009), The role of hillslope hydrology in controlling nutrient loss, *J. Hydrol.*, *367*(3–4), 177–187, doi:10.1016/j.jhydrol.2008.11.002.