RESEARCH ARTICLE

10.1002/2016WR018620

Key Points:

- Observations of tracer transport in a 1 m³ sloping lysimeter with a fluctuating water table were used to investigate lumped transport modeling
- Time variability of transit times was decomposed into two components: internal (flow pathways) and external (total flow) variability
- Internal variability arising from the fluctuating water table can be captured by rank StorAge Selection functions

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Citation:

Kim, M., L. A. Pangle, C. Cardoso, M. Lora, T. H. M. Volkmann, Y. Wang, C. J. Harman, and P. A. Troch (2016), Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability, *Water Resour. Res.*, 52, 7105–7129, doi:10.1002/2016WR018620.

Received 26 JAN 2016

Accepted 19 JUL 2016

Accepted article online 22 JUL 2016

Published online 22 SEP 2016

Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability

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Abstract Transit times through hydrologic systems vary in time, but the nature of that variability is not well understood. Transit times variability was investigated in a 1 m³ sloping lysimeter, representing a simplified model of a hillslope receiving periodic rainfall events for 28 days. Tracer tests were conducted using an experimental protocol that allows time-variable transit time distributions (TTDs) to be calculated from data. Observed TTDs varied with the storage state of the system, and the history of inflows and outflows. We propose that the observed time variability of the TTDs can be decomposed into two parts: “internal” variability associated with changes in the arrangement of, and partitioning between, flow pathways; and “external” variability driven by fluctuations in the flow rate along all flow pathways. These concepts can be defined quantitatively in terms of rank StorAge Selection (rSAS) functions, which is a theory describing lumped transport dynamics. Internal variability is associated with temporal variability in the rSAS function, while external is not. The rSAS function variability was characterized by an “inverse storage effect,” whereby younger water is released in greater proportion under wetter conditions than drier. We hypothesize that this effect is caused by the rapid mobilization of water in the unsaturated zone by the rising water table. Common approximations used to model transport dynamics that neglect internal variability were unable to reproduce the observed breakthrough curves accurately. This suggests that internal variability can play an important role in hydrologic transport dynamics, with implications for field data interpretation and modeling.

1. Introduction

Transit time distributions (TTDs) have been widely used to model the transport of conservative and certain nonconservative tracers through hydrologic systems [McGuire and McDonnell, 2006; McDonnell et al., 2010; Rinaldo et al., 2011]. A TTD is a probability distribution of water transit time, which is defined here as the interval between the time a parcel of water is injected into a system (or a control volume) to the time it exits [McGuire and McDonnell, 2006]. Thus the distribution characterizes the spatially integrated hydrologic kinematics of a system and encapsulates the transport controls on conservative solute dynamics and first-order reactions (though solute transit times may be insufficient for nonlinear reactive-transport predictions [Ginn, 1999; Luo and Cirpka, 2011]). TTDs are distinct from, but related to, the residence time distribution (RTD). Residence time is the time since a parcel of water entered the system, given that it has not yet exited, and remains in storage.

TTDs have been studied extensively under steady state in porous media [Cox and Miller, 1972; Jury, 1982; Maloszewski and Zuber, 1982; Scher et al., 2002; Cvetkovic, 2011], where they provide a mathematically robust framework to model spatially integrated hydrologic transport [Botter et al., 2010]. This approach to modeling is “parsimonious” in the sense that all the (typically highly uncertain) nonlinearities and heterogeneities controlling transport are blended into a parameterization of the TTD that may have only a few

parameters [Dagan, 1989]. In some idealized cases, the functional form and parameters of these transit time distributions can be related to the geometry of the flow domain and the properties of the porous media [e.g., Małoszewski and Zuber, 1982]. These idealized cases provide a basis for interpreting parameters drawn from real systems in a physically meaningful way, and potentially inferring them a priori from measurements of the physical system, without calibration to tracer data.

However, in many hydrologic systems of interest, TTDs are not steady state—TTDs are in general time-varying if a system is forced by transient fluxes [Niemi, 1977; Lewis and Nir, 1978; Jury *et al.*, 1986]. The temporal variability of TTDs has been observed at the scale of soil columns, hillslopes, and catchments [Roth *et al.*, 1991; Rodhe *et al.*, 1996; Heidebüchel *et al.*, 2012, 2013; Kim, 2014; Quéloz *et al.*, 2015], and the temporal variability has often been attributed to the time-varying hydrologic connectivity of a system forced by transient boundary fluxes [e.g., Rodhe *et al.*, 1996; McGuire *et al.*, 2007; Botter *et al.*, 2010; Hrachowitz *et al.*, 2010; Roa-García and Weiler, 2010; Birkel *et al.*, 2012; Segura *et al.*, 2012; Hrachowitz *et al.*, 2013; van der Velde *et al.*, 2014; Harman, 2015; Birkel *et al.*, 2015]. The theory of StorAge Selection (SAS) functions [Botter *et al.*, 2011; van der Velde *et al.*, 2012; Harman, 2015; Rinaldo *et al.*, 2015; Porporato and Calabrese, 2015] has recently been developed to account for this variability in a rigorous way. The time-variable TTDs are not parameterized directly in the SAS approach. They are determined by combining parameterized SAS function with the time series of fluxes in and out of a system constituting the water balance. Similar to the use of TTDs in steady flow systems, SAS function approaches are general theories of spatially integrated transport dynamics in time-variable flow systems that can in principle be applied to any system, though their usefulness in any particular application must be demonstrated.

This paper combines a theoretical examination of TTD variability with direct observations of time-variable transit times through a 1 m³ sloping soil lysimeter (with a perched, sloping water table) forced by intermittent irrigation. Similar experimental lysimeters have been used in past studies; however, those studies often limited their attention to study flow processes exclusively [Vauclin *et al.*, 1979; Phi *et al.*, 2013], to study transport processes under steady state [Silliman *et al.*, 2002; Simpson *et al.*, 2003; Persson *et al.*, 2015], and to validate numerical models [Jinzhong, 1988]. Laboratory studies of transient flow have been done using soil columns and—thus—limited their attention to vadose zone where transport is mainly vertical [e.g., Quéloz *et al.*, 2015]. In this study, the experimental system is constructed and forced in a way that generates significantly time-varying internal flow patterns, such as changing flow paths in the unsaturated zone and a time-varying water table. This leads to variations in the spatial extent of the unsaturated (where mainly vertical transport is expected) and the saturated zone (where lateral transport is expected to be dominant). The two zones are often treated as distinct landscape units in hillslope and catchment hydrology [Weyman, 1973; Reggiani *et al.*, 1998, 2000]. Our purpose here is, in part, to examine their two-way interaction. The PERiodic Tracer Hierarchy (PERTH) method [Harman and Kim, 2014] permits direct observation of the time-variable transit time distributions with only a few distinct conservative tracers by driving the system to a time-periodic steady state. Our objective is to understand the structure of the resulting time variability, its origins in the physical system, and the ability of the SAS approaches to decompose its controls, and to represent their effects accurately. The emphasis of the presentation here is on the experimental and theoretical aspects of the work. A detailed analysis of the mechanistic origins of the observed rSAS behavior is reserved for future publications.

We postulate that the time variability of any system's TTD arises in part from the temporal variability of flow in and out of the system, and in part from variability in the configuration of flow pathways within the system. For example, if the steady flow rate through a continuously stirred tank of water instantaneously doubles, the mean transit time will halve, but the basic character of the transport does not change—the system remains well-mixed and has the same storage before and after the change. On the other hand, if flow is held constant but half the tank is suddenly isolated by a partition from the part exchanging with the fluxes, the mean transit time will also halve. There is no change in flow through the inlet and outlets, but the character of the system internally has changed, with a consequent change in the transit times. It is important to note that this example for a truly “well-mixed” system would also apply in any system in which an age distribution of the outflux throughout a system is identical to an age distribution of water within the system—whether it is physically well-mixed or not. That situation is sometimes referred to as “uniform selection” [Harman, 2015] or “random sampling” [Benettin *et al.*, 2013], to avoid the implicit assumptions about micro-mixing implied by “well-mixed.” A continuously stirred tank reactor can be physically well-mixed and have a

transit time distribution that reflects uniform selection. An idealized ground water system may have a TTD that is identical to that of the physically well-mixed case despite limited mixing between water of distinct ages [Eriksson, 1958; Bredenkamp and Vogel, 1970; Vogel, 1970; Haitjema, 1995; van der velde et al., 2014]. To avoid confusion, we will prefer the term “uniform selection” over “well-mixed.”

The two components of transport variability (the temporal variability of in-and-out flux, and the time-varying flow pathways) will be referred to here as “external” and “internal,” respectively. They are different from one another, but both, in general, contribute simultaneously to the temporal variability of transport through a hydrologic system of interest. Indeed, they may be causatively linked—an increase in precipitation and discharge in a watershed may increase the velocity of flow along existing subsurface flow pathways, and rearrange them, while also activating new pathways such as newly created flow pathways in the unsaturated zone and the overland flow. This internal rearrangement will alter the transit times, as will the increase in flow velocity along the flow pathways.

The presence of temporal variability poses a serious challenge to our ability to use transit time distributions to characterize controls on transport through an unsteady hydrologic system. Previous approaches to adapt transit time theory to deal with temporal variability do not fully or explicitly account for these types of variability. For example, the use of *flow-weighted time* [Niemi, 1977; Rodhe et al., 1996], which has been used widely to model hydrologic transport [McDonnell et al., 2010], might seem to account for the effect of external variability, but neglects the effect of internal variability. (Flow-weighted time will be discussed in detail in section 2.2.) How can these different types of variability be disentangled from each other in the breakthrough curve of an active tracer injection? How are they represented in the various transit-time-based solute transport models currently being developed? How exactly is internal variability related to the physical configuration of flow pathways in a system? At present there is not a clear definition of many of these terms in the literature, let alone answers to these questions.

The analysis presented here suggests formal definition for internal and external variability in terms of flow-weighted time and the StorAge Selection functions. The theory developed is used to shed light on the time-variable transit time distributions observed experimentally, allowing us to examine the roles of internal and external variability, their relationship to the physical system, and their representation by SAS functions.

2. Background: TTD-Based Hydrologic Transport Theories

In this section, several spatially lumped hydrologic transport theories that use transit time distributions under time-variable conditions are introduced, along with notation. For brevity, we restrict discussion to a system which has only one source zone (the irrigated upper surface in this experiment; the influx rate through the area normalized by the surface area is denoted by J) and sink zone (the lateral seepage face; the outflux rate through the face normalized by the source zone area is denoted by Q). Generalization to multiple fluxes is of course possible.

The transit time distribution is sometimes referred to as a transfer function [Jury et al., 1986], a weighting function [Małoszewski and Zuber, 1982], or a first passage time distribution [Cox and Miller, 1972]. Under steady state (real or assumed), mass outflux $M_Q(t)$ of an idealized tracer from a system can be modeled by a convolution of a mass influx time series $M_J(t)$ and a time-invariant transit time distribution [Niemi, 1977]:

$$M_Q(t) = \int_{-\infty}^t M_J(\tau) p_Q(t-\tau) d\tau \quad (1)$$

where $p_Q(T)$ is the density form (pdf) of a transit time distribution, and T is transit time. Also, an equation describing the outflow concentration time series $C_Q(t) = M_Q(t)/Q(t)$ can be readily obtained from (1) as follows [Niemi, 1977; Małoszewski and Zuber, 1982; Jury, 1982]:

$$C_Q(t) = \int_{-\infty}^t C_J(\tau) p_Q(t-\tau) d\tau \quad (2)$$

where $C_J(t) = M_J(t)/J(t)$ is inflow concentration. Note that $J(t) = Q(t) = \text{const.}$ when steady state is assumed. In this case, the kernel of both convolutions is the same time-invariant transit time distribution p_Q . Theoretical time-invariant transit time distributions have been derived extensively for a range of idealized systems

[Kaufman and Libby, 1954; Eriksson, 1958; Cox and Miller, 1972; Kreft and Zuber, 1978; Małozewski and Zuber, 1982; Logan and Zlotnik, 1995; Kirchner et al., 2001; Scher et al., 2002; Cvetkovic, 2011]. For example, an exponential distribution can be derived from the assumption of “uniform selection” [Eriksson, 1958; Bredenkamp and Vogel, 1970; Vogel, 1970; Małozewski and Zuber, 1982; Haitjema, 1995; Harman, 2015]. Moreover, if the transport behavior of a system can be characterized by the Fickian advection-dispersion mechanism, the TTD between a point injection and an adsorption boundary is an inverse Gaussian distribution [Cox and Miller, 1972; Rinaldo et al., 1985].

2.1. Time-Variable Transit Time Distributions

Under *unsteady* state, mass outflux time series can be modeled by [Niemi, 1977]:

$$Q(t)C_Q(t) = \int_{-\infty}^t J(\tau)C_J(\tau)\bar{p}_Q(t-\tau, \tau)d\tau \quad (3)$$

Unlike the steady state equations, the above equation has a time-varying kernel which depends on its injection time [Niemi, 1977; Lewis and Nir, 1978]. The time-varying kernel, $\bar{p}_Q(t-t_i, t_i)$ where t_i is an injection time, is called the forward transit time distribution (fTTD) in contrast to the backward transit time distribution $\bar{p}_Q$ (bTTD) [Niemi, 1977; Harman and Kim, 2014]. The forward TTD describes the distribution of transit times $T=t-t_i$ of infinitesimal water parcels that were injected into a system at time t_i . This is mathematically identical (isomorphic) to the distribution of “life expectancies at birth” in an age-structured population model [Benettin et al., 2015a; Porporato and Calabrese, 2015]. The bTTD describes the distribution of transit time T of water parcels that are leaving a system at time t , and is isomorphic to the distribution of “ages at death” in an age-structured population model [McKendrick, 1926; von Foerster, 1959; Niemi, 1977; Lewis and Nir, 1978; Harman and Kim, 2014; Rinaldo et al., 2015; Porporato and Calabrese, 2015].

One can express the above equation in terms of bTTDs using Niemi’s theorem $J(t_i)\bar{p}_Q(t-t_i, t_i)dt_i = Q(t)\bar{p}_Q(t-t_i, t)dt_i$ [Niemi, 1977; Botter et al., 2011], which is an expression of the equivalence of a water parcel’s life-expectancy at birth and age at death. An equation for an outflux concentration is readily obtainable as [Niemi, 1977; Lewis and Nir, 1978; Rinaldo et al., 2011; Harman and Kim, 2014]:

$$C_Q(t) = \int_{-\infty}^t C_J(\tau)\bar{p}_Q(t-\tau, t)d\tau \quad (4)$$

In contrast to the steady state model (2), this equation has the time-variable bTTD as a kernel, rather than a time-invariant distribution.

While this model is mathematically robust, the time-variability of the TTD means that general functional forms cannot be used to parameterize $\bar{p}_Q$ [Heidbüchel et al., 2012].

2.2. Flow-Weighted Time

The use of *flow-weighted time* was proposed to allow transit time distributions $\bar{p}_Q$ to be parameterized directly, despite time-variability of the flow through the system [Niemi, 1977]. This method has been applied in many studies [Roth et al., 1991; Rodhe et al., 1996; Simic and Destouni, 1999; Kirchner et al., 2000; Fiori et al., 2009; Ali et al., 2014; Harman, 2015]. The core of the approach is the transformation of the time axis into a flow-weighted time in which fluxes in and out of a system become constant. While it is originally suggested for a system which has identical transient influx and outflux [Niemi, 1977] so that $J(t)=Q(t)$ and storage is invariant, it has been applied to other systems where this is not true [Rodhe et al., 1996; Ali et al., 2014]. The transformation from calendar time space to the flow-weighted time space can be conducted separately for the inflows and outflows:

– for outflows up to time t ,

$$t_Q(t) = \frac{1}{\beta} \int_{t_0}^t Q(\tau)d\tau \quad (5)$$

– for inflows up to time t_i ,

$$\tau_Q(t_i) = \frac{1}{\alpha} \int_{t_0}^{t_i} J(\tau) d\tau \quad (6)$$

where α and β are scaling constants with the same units as Q and J , and t_0 is a reference time, which could be the time modeling or tracer injections are begun. As mentioned above, the fluxes are constant in its associated transformed time space, i.e., $Q^*(t_Q) = Q(t) dt/dt_Q = \beta$ and $J^*(\tau_Q) = J(t_i) dt_i/d\tau_Q = \alpha$. To match the scale of time with clock time, α and β can be set as $\bar{J}$ and $\bar{Q}$, respectively, where $\bar{J}$ and $\bar{Q}$ are the average of each flux during the period of interest. However, as we will see, mass balance can be ensured by requiring that $\alpha = \beta$.

If one transforms the transport model for an outflux concentration (4) into the flow-weighted time space, the following equation can be obtained:

$$C_Q^*(t_Q) = \int_{-\infty}^{\tau_Q = \tau_Q(t)} C_J^*(\tau_Q) \bar{p}_Q^*(t_Q - \tau_Q, t_Q) d\tau_Q \quad (7)$$

where $C_Q^*(t_Q(t)) = C_Q(t)$ is an outflux concentration, $C_J^*(\tau_Q(\tau)) = C_J(\tau)$ is an influx concentration, and $\bar{p}_Q^*(t_Q - \tau_Q, t_Q)$ is a bTTD at t_Q . Note that all quantities are defined in terms of flow-weighted time. The transformed bTTD is defined such that its cumulative distribution function equals that of the original, so that:

$$\bar{P}_Q(t - t_i, t) = \bar{P}_Q^*(t_Q(t) - \tau_Q(t_i), t_Q(t)) \quad (8)$$

The transit time distributions are still time-varying—they depend on t_Q . Although the TTDs may still vary in the transformed time, in practice the flow-weighted transit time distributions are typically assumed to be invariant. This assumption has been referred to as a time-invariant flow pattern [Niemi, 1977] or flow pathways [Ali et al., 2014], or, more specifically, time-invariant flow paths and storage [Rodhe et al., 1996]. Its origins are examined more rigorously below. Based on this assumption, equation (7) can be rewritten as:

$$C_Q^*(t_Q) = \int_{-\infty}^{t_Q} C_J^*(\tau_Q) p_Q^*(t_Q - \tau_Q) d\tau_Q \quad (9)$$

where $p_Q^*(T_Q) = p_Q^*(t_Q - \tau_Q)$ is a TTD that is time-invariant in the flow-weighted time space. Since it is invariant, functional forms to parameterize $p_Q^*(T_Q)$ can be chosen from the many discussed previously (exponential, inverse Gaussian, etc.). Sometimes, the flow-weighted time method has been used without considering the transformation of $\tau_Q(t_i)$ [e.g., Rodhe et al., 1996; Kirchner et al., 2000; McGuire et al., 2005]. In this case, the variability caused by an unsteady influx is neglected, degrading the ability of the fitted TTD to conserve mass and reproduce tracer dynamics. The flow-weighted time method is sometimes applied by replacing $Q(\tau)$ with $J(\tau)$ in equation (5); this has been used frequently in vadose zone hydrology [e.g., Roth et al., 1991]. In this case, the variability caused by an unsteady outflux is neglected. This approach will degrade the applicability of the fitted TTD when influx and outflux time-series differ significantly.

The time-invariant kernel $p_Q^*(T_Q)$ can be transformed back into calendar time space, yielding time-variable bTTDs $\bar{p}_Q(t - t_i, t)$. These are obtained by differentiating (8) with respect to t_i to obtain:

$$\begin{aligned} \bar{p}_Q(t - t_i, t) &= p_Q^*(t_Q(t) - \tau_Q(t_i)) \frac{d\tau_Q}{dt_i} \\ &= p_Q^*(t_Q(t) - \tau_Q(t_i)) \frac{J(t_i)}{\beta} \end{aligned} \quad (10)$$

This time-variable bTTDs can be used in the equation (4) directly. Forward transit time distributions are also obtainable from $p_Q^*(T_Q)$ by noting that:

$$\bar{P}_Q(t - t_i, t) = P_Q^*(t_Q(t) - \tau_Q(t_i)) \quad (11)$$

Differentiating with respect to t to obtain:

$$\begin{aligned} \bar{p}_Q(t - t_i, t) &= p_Q^*(t_Q(t) - \tau_Q(t)) \frac{dt_Q}{dt} \\ &= p_Q^*(t_Q(t) - \tau_Q(t)) \frac{Q(t)}{\alpha} \end{aligned} \quad (12)$$

Equations (10) and (12) will be consistent with Niemi's theorem only when $\alpha = \beta$. Thus it is imperative that the same scaling constant be used for the flow-weighted inflow and outflow times. While it is derived differently in this study, the same result is presented in Ali et al. [2014].

2.3. StorAge Selection Functions

The flow-weighted time approaches account for the effect of the time-varying inflows and outflows, but do not account for changes in the internal states of the system. Thus it would seem that (under a suitable definition of the terms) they account for the effects of *external* variability, but not *internal*. The theory of storage selection function was developed to provide a general framework for time-variable transit time distributions that accounted for all sources of variability.

Three different forms of SAS function have been developed—the *absolute* (aSAS) [Botter et al., 2011], *fractional* (fSAS) [van der Velde et al., 2012], and *rank* (rSAS) [Harman, 2015]. Recently, the similarity between the governing equations of the SAS approaches and the McKendrick-von Foerster (MKVF) model for age-structured population model [McKendrick, 1926; von Foerster, 1959] has been pointed out [Porporato and Calabrese, 2015]. It should be emphasized that these do not represent four different theories, but rather four different ways to express the same theoretical framework (some more convenient than others). In this paper, we focus our analysis on the rSAS function theory.

The rSAS theory introduces a state variable called the “age-ranked storage,” S_T , representing the volume of water in storage at time t that is younger than age T . The governing equation of the rSAS function theory is a conservation law describing the evolution of $S_T(T, t)$ over time, and can be written as follows for a system which has only one influx (J) and one outflux (Q) [Harman, 2015]:

$$\frac{d}{dt} S_T(T, t) = \frac{\partial S_T}{\partial t} + \frac{\partial S_T}{\partial T} = J(t) - Q_T(T, t) \quad (13)$$

where $T = t - t_i$. The boundary condition is $S_T(0, t) = 0$. In this governing equation, the evolution of the age-ranked storage S_T is determined by three mechanisms: the influx of zero-aged water $J(t)$, the age-ranked flux out $Q_T(T, t)$, and the aging of stored water in a system $\partial S_T / \partial T$. The age-ranked flux Q_T is the rate that water younger than T is leaving the system.

The conservation law has two unknowns: S_T and Q_T . One can imagine a (likely time-varying) function f that parameterizes the relationship between them: $Q_T = f(S_T, t)$. This function describes the rate that water in storage younger than some age T is being removed as discharge, and so maps volumes of storage S_T onto rates of discharge of Q_T , something like a storage-discharge relationship. The rSAS function Ω_Q is a normalized form of this relationship ($\Omega_Q = f/Q$). Since Q_T can be written as the product $Q_T(T, t) = Q(t) \bar{P}_Q(T, t)$, this function maps values of S_T to fractions of discharge $\bar{P}_Q$ as follows:

$$\Omega_Q(S_T(T, t), t) = \bar{P}_Q(T, t) \quad (14)$$

The rSAS function is a probability distribution supported by S_T . As a pdf it can be written:

$$\omega_Q(S_T(T, t), t) \frac{\partial S_T}{\partial T} = \bar{p}_Q(T, t) \quad (15)$$

The rSAS function is a property of a specific system and explains how different aged-water in the system is “selected” to comprise the outflux. For example, the function is a uniform distribution if the selection shows no preference by age, and is appropriate for several idealized groundwater systems [Eriksson, 1958; Bredenkamp and Vogel, 1970; Vogel, 1970; Małoszewski and Zuber, 1982; Haitjema, 1995]. Consequently this case is referred to as “uniform selection” [Harman, 2015]. While the function only describes the selection of differently aged water particle (or parcels) in a system by the outflux, this selection is the result of the hydrodynamics of a system [Harman, 2015; Rinaldo et al., 2015]. The internal flows are not captured by the rSAS function—only the emergent result that the water delivered to the outlet of the control volume is some sample of the water inside it, with some biases toward younger or older water. Once the rSAS function is specified, solving the above equations numerically for a given time series of J and Q yields a bTTDs that varies each moment in time.

3. Experimental Observation of Time-Varying TTD

Experiments in a sloping soil lysimeter under a controlled environment were conducted to examine the temporal variability of TTDs in light of the concepts presented above. Observation of the time-variable transport requires multiple breakthrough curves (BTCs) of conservative tracers injected at different times

[Lewis and Nir, 1978; Zuber, 1986; Harman and Kim, 2014; Quelo et al., 2015]. Moreover, the amount of information that can be extracted from the BTCs about the RTDs, bTTDs, and SAS functions is related to the portion of water “tagged” by each tracer; thus, it requires enough distinct tracers to be injected that useful details can be resolved. However, a number of applicable conservative tracer is very limited [Harman and Kim, 2014; Quelo et al., 2015].

To observe the time-varying functions experimentally, we applied the PERiodic Tracer Hierarchy (PERTH) method [Harman and Kim, 2014] which enables measurement of the time-varying functions with a limited number of conservative tracers. The key requirement for doing so is the ability to drive the system hydrodynamics to a periodic steady state (PSS). The methods below describe the procedure used to obtain a series of breakthrough curves (BTC), and from these extract forward and backward transit time distributions, age-ranked storage, and the rSAS function.

3.1. Experimental Setup

The sloping soil lysimeter, which is located at Biosphere 2, University of Arizona, USA, is shown in Figure 1. It is filled with packed 0.05 m^3 gravel and 0.95 m^3 loamy sand. The gravel and loamy sand are the same type of soils that fill the Landscape Evolution Observatory (LEO) hillslopes. The gravel is emplaced at the downstream boundary to mimic conditions in the larger experimental hillslopes at the facility [Pangle et al., 2015]. The loamy sand is crushed late Pleistocene basaltic tephra extracted from near Merriam Crater in northern Arizona, USA (more details about LEO and the soil properties such as mineral composition, particle size distribution, and hydraulic properties can be found in Pangle et al. [2015]). The lysimeter was filled with soil incrementally; 0.32 m thick wetted soil layers were added to the lysimeter and compacted to a 0.25 m deep increment using a tamping device (with an intention to pack as homogeneous as possible). Four iterations of this procedure resulted in a 1 m deep soil with an estimated dry bulk density of 1480 kg/m^3 . This experimental setup was selected to allow the control volume to be variably saturated in space and in time. When irrigated from above, transport is expected to be mainly vertical through the vadose zone, and laterally along the incline in the saturated zone (and capillary fringe).

Figure 1. Schematic of the sloping soil lysimeter. The dark blue colored volume indicates where it is filled with gravel, and the remaining volume is filled with loamy sand. The locations of each Frequency-Domain Reflectometry (FDR) sensor are depicted by the yellow circles, and the light blue colored area illustrates the surface where the sensors are in transverse dimension. The irrigation system is indicated by the bold black lines, and the location of the magnetic flow-meter is depicted by the green circle. A probable water table profile at a specific time is depicted by the solid dark blue line, and probable flow pathways are indicated by dotted blue lines with arrows.

Figure 2. Overall time series of several key measurements of this experiment. The timing of tracer injections are illustrated by colored-irrigation in the top plot.

The soil lysimeter was equipped with a tipping bucket (Onset RG3) at the outlet to measure discharge, an electronic conductivity probe (Microelectrodes MI-905) to estimate outflow chloride concentration continuously, and an autosampler (customized with a single channel peristaltic pump and a stepper motor (Adafruit Industries) controlled by the Arduino Uno microcontroller board) to collect outflow water samples every hour. Four sprinklers on the top of the lysimeter irrigated the top of the soil with water with and without tracers. A magnetic flow meter (Seametrics PE102), installed between sprinklers and the diaphragm pump (Flojet G575215) delivering water to the irrigation system, measured the amount of supplied water to the irrigation system continuously. Fifteen Frequency-Domain Reflectometry (FDR) probes (Decagon 5TM) were installed inside the soil lysimeter to measure volumetric water content continuously. Four load cells (Honeywell Model 41) were installed in the lysimeter base to measure overall mass change continuously over time. The initial mass of dry soil and gravel in the lysimeter was corrected to ensure that the average storage measured by the mass loads matched the average storage estimated by the spatially integrated volumetric water content measurement from the FDR probes.

A periodic steady state condition was generated by applying an identical irrigation sequence in each consecutive 24 h period. ($t_c = 24$ h—the notation of Harman and Kim [2014] will be used throughout this section). The irrigation sequence was designed to deliver an identical volume of irrigation under four distinct conditions, and generate large variations in the soil lysimeter hydraulics. On each day, the four irrigation

pulses were applied with two different intensities and durations (3 h at 13.1 mm/h, and 1.5 h at 26.1 mm/h on average). The pulses were timed such that two were delivered under wet antecedent conditions, and two after the lysimeter had drained for 7.5 h (see Figure 2). The irrigation durations and intensities were carefully determined to avoid overland flow. Each day's irrigation corresponded with approximately 36% of the total pore volume of the lysimeter. Prior to introducing tracers, seven irrigation cycles were applied to drive the lysimeter to the periodic steady state. (At least three cycles were required for this purpose).

Five tracer injections were used to probe the system with two conservative tracers—deuterium (^2H) and chloride (Cl^- ; dissolved NaCl in irrigation water). ^2H was used as the reference tracer and was injected during an entire day's irrigation sequence ($\Delta_R = 9$ h). Cl^- was used as the probe tracer (since it could be monitored continuously from the EC probe), injected four times ($m = 4$), once during each of the four pulses ($\Delta_i = 3$ h for $i = 0, 3$, and 1.5 h for $i = 1, 2$). The probe tracer injection periods covered the reference tracer injection period without overlapping ($\cup_i \Delta_i = \Delta_R$). This conforms to a requirement of the PERTH method and ensures that BTC of the reference tracer (C_R) can be compared with the (appropriately normalized) sum of the BTCs of probe tracers. This is useful for examining the effect of overlap between the BTC of consecutive probe tracer BTC, and if necessary correcting for this overlap to obtain a better estimate of the true probe tracer BTC (C_i).

The number of days between probe tracer injections (n) was chosen so that the breakthrough curve was well into the tail period at time nt_C , and would therefore likely not differ greatly between each injection period [Harman and Kim, 2014]. However, we did not have a priori information about hydrologic transport behavior of the soil lysimeter prior to this experiment. Thus the reference tracer was injected first and the shape of the BTC was examined over 8 days of PSS irrigation, corresponding to about 2.5 pore volumes of water following tracer injection. While ^2H was used as the reference tracer, chloride was also injected so that we could see the response of voltage directly and continuously from the EC probe to facilitate this decision making. This procedure required one assumption that the two widely known as a conservative tracer behave in the same way so that we could get the overlapped probe tracer BTC (C) by subtracting the ^2H BTC from the Cl^- BTC (because both are not in the same unit, it required normalization). Analysis of the correlation between their concentrations during the reference tracer breakthrough suggested that this assumption was valid, except at high concentrations (greater than 20% of the input concentration). The deviation might be caused by electrostatic exclusion of the chloride anions from small pores, which can cause the chloride to move faster (on average) than the solvent water in soils [Flury and Wai, 2003]. However, concentrations were found to be highly correlated at low concentrations, where correspondence is most critical for correcting the probe tracer BTC overlap.

Eight days after injection of the tracers, we determined that the n should be larger than 4 because the voltage time series showed only small fluctuation around the decreasing signal (see the last plot of Figure 2). We set n to 5, which also fixed the maximum transit time could be resolved in this experiment at $T_{\max} = nt_C = 120$ hrs. Chloride was injected as a probe tracers with the first, second, third, and fourth pulses on (respectively) day 9, 14, 19, and 24 of the experiment.

The reference tracer $\delta^2\text{H}$ (C_R^*) was chosen to be 750‰ (VMSOW) and the reference and probe tracer chloride concentration (C_i^*) was 6900 $\mu\text{mol/L}$. These were much higher than its background values of -60 ‰ and 7.6 $\mu\text{mol/L}$, respectively. During the injection periods, irrigation water samples were regularly collected to examine the consistency of the injected tracer concentration. The average observed injection chloride concentration was 6915.0 ± 71.0 $\mu\text{mol/L}$ and $\delta^2\text{H}$ was 743.3 ± 12.3 ‰. Outflow was collected hourly. Collected samples were analyzed using a Los Gatos Research DLT-100 Laser Spectrometer for $\delta^2\text{H}$ relative to Vienna Standard Mean Ocean Water (VSMOW). The precision of the $\delta^2\text{H}$ measurement is estimated to be ± 0.38 ‰ in this device with the analysis protocol used. Cl^- concentration of each sample was analyzed by Thermo Scientific Dionex Ion Chromatography (IC) DX-600 with AG and AS-11 anion exchange column set and NaOH eluent. A smoothly connected piecewise function was used to convert the voltage signal V (with units of volt V) from the conductivity probe at the outlet to a time series of chloride concentration in $\mu\text{mol/L}$: $C(V) = \alpha e^{\beta V}$ for voltage $V < \theta$ and $\alpha \beta e^{\beta \theta} V + \alpha(1 - \beta \theta) e^{\beta \theta}$ for voltage $V \geq \theta$. Parameters $\alpha = 1.59$ $\mu\text{mol/L}$, $1/\beta = 0.032$ V, and $\theta = 0.15$ V were calibrated to minimize RMSE against the chloride concentration samples taken from the output. The RMSE of this relationship was 10.3 $\mu\text{mol/L}$.

3.2. Breakthrough Curve Correction

Following the PERTH method [Harman and Kim, 2014], the probe tracer breakthrough curves (C , see the sixth plot of Figure 2) were corrected to remove the effects of overlap between the tail of one breakthrough, and the start of the next, yielding corrected breakthrough curves (C_0, C_1, C_2 , and C_3). The PERTH method consists of two correction steps, but only the first step was applied in this study. The first correction step of the PERTH method assumes that the overlapped portions are well-represented by the shape of the reference tracer breakthrough. The reference tracer BTC (C_R) was therefore scaled and shifted in time, and subtracted from the probe tracer BTC.

$$C_i(t) = \begin{cases} C(t) & i=0 \\ C(t) - \sum_{j=0}^{i-1} \frac{C_j^* \Delta_j}{C_R^* \Delta_R} C_R(t - jnt_c - dt_c) & i > 0 \end{cases} \quad (16)$$

where $d = 3$ is the difference in the number of cycles prior to the first probe tracer (probe 0) injection (8 cycles) and the number of cycles between probe tracer injections ($n = 5$).

The second correction step was not used. Imperfect tracer mass recovery in the experiments, while small, was large enough to prevent the correction from being applied. The sum of shifted probe tracer BTCs prior to any correction step of the PERTH method ($\sum_i C(t + int_c + (d+n)t_c)$) should have been higher than the reference BTC because the sum contains overlapped signals. However, the summed BTC was a slightly lower than the reference tracer BTC (red line in the figure), especially from 28–60 h. Tracer mass balance analysis suggests that this error was most significant during the third and fourth probe tracer injections. About 92% of reference tracer was recovered during the first 5 days following injection, as was 95% of the first probe tracer (probe tracer 0). While the amount of error was not large, it prevents the second correction step from being applied. It also limits our ability to resimulate the reference tracer BTC from models extracted from the observed TTDs.

3.3. Forward and Backward Transit Time Distributions

The forward transit time distribution $\bar{p}_Q$ (fTTDs) obtained from the BTC is not a true fTTD since the injection is not instantaneous at a single injection time t_i . Rather it represents a time-averaged fTTD for injection over the intervals Δ_i . This time-averaging is represented by the notation $\bar{t}_i$ below. The fTTD can be estimated from the BTC by [Harman and Kim, 2014]:

$$\bar{p}_Q(t - \bar{t}_i, \bar{t}_i) = \frac{M_{Q,i}(t)}{M_J(t_i) \Delta_i} = \frac{C_i(t) Q(t)}{C_i^* J(t_i) \Delta_i} \quad (17)$$

where $M_{Q,i}$ is the mass outflux of i th probe tracer, $\overline{M_J(t_i)}$ is the total mass of injected probe tracer i , and $\overline{J(t_i)}$ is the average irrigation rate over the irrigation duration Δ_i .

Particular values on the backward transit time distribution pdf $\bar{p}_Q$ (bTTDs), can be estimated by [Harman and Kim, 2014]:

$$\bar{p}_Q(t - \bar{t}_i, t) = \frac{C_i(t)}{C_i^* \Delta_i} \quad (18)$$

When compared to the equation (17), bTTDs are related to fTTDs as $Q(t) \bar{p}_Q(t - \bar{t}_i, t) = \overline{J(t_i)} \bar{p}_Q(t - \bar{t}_i, \bar{t}_i)$. This is merely a restatement of the Niemi's theorem for the injection time averaged fTTDs and bTTDs over Δ_i .

However, no single BTC provides a complete picture of a single bTTD—rather the periodic steady state condition must be exploited, and information from multiple points on each of the four BTC must be combined to provide the complete distribution. Unlike BTCs and fTTDs, which are functions of injection time $\bar{t}_i$, the bTTDs are functions of exit time (or more specifically in this experimental context, sampling time) t . If one imagines a set of axes with time at outflow on the horizontal axis, and transit time on the vertical axis (Figure 3), the estimated bTTDs run along vertical “slices” of this domain (which contain a range of transit times at a single, fixed outflow time). The shifted BTCs $C_i(t - t_i)$ and fTTDs follow diagonal “slices” through the domain (which contain a range of outflow and transit times, linked by the rule that $T = t - t_i$, and t_i is fixed for each slice). Because four BTCs are obtained for injections at different times, only four discrete intervals of backward transit time are observed for each sampling time, and not the full distribution. However, due to the hydrologic periodicity we generated on the soil lysimeter, it is possible to assume that the diagonal

Figure 3. Illustration of replicability of the observed time series of each probe tracer under periodic steady state. (left) The part of information observed on the time-transit time space from four probe tracer injections is illustrated by colored diagonal components. The hatched areas indicate where the information is not obtainable from the tracer injections, and (right) replicability of the observed time series under periodic steady state is shown by repeatedly colored irrigation and its corresponding diagonal components on the time-transit time space.

components are repeated identically for every cycle (see the right plot of Figure 3). Thus the amount of water 6 h old in the discharge sample taken, say, 30 h after the first injection is assumed to be identical to the amount of water 6 h old in the sample taken 6 h after the first injection (since $30 - 24 = 6$). Indeed, this is assumed to be true for all discharge samples at hour $24n + 6$ after the injection, where n is an integer. In total the regular outflow sampling provided information about more than 17 intervals of backward transit times up to the last sample at $T_{max} = 5$ days.

3.4. Estimation of rSAS Theory Components

The estimated bTTDs can be served as a basis to estimate the age-ranked storage which is needed to estimate the rSAS function.

Age-ranked storage $S_T(T, t)$ can be estimated by integrating the age-ranked density $s_T(T, t) = \frac{\partial S_T(T, t)}{\partial T}$ over transit time. The age-ranked density can be estimated by:

$$s_T(t - \bar{t}_i, t) = \bar{J}(\bar{t}_i) - \int_{\bar{t}_i}^t Q(\tau) \bar{p}_Q(\tau - \bar{t}_i, \tau) d\tau \quad (19)$$

Integrating this function up to each value of $\bar{t}_i = t - T$ yields the age-ranked storage $S_T(T, t)$.

The rank SAS (rSAS) function can be estimated using the age-ranked storage and the bTTDs using the fact that:

$$\Omega_Q(S_T(t - \bar{t}_i, t), t) = \bar{P}_Q(t - \bar{t}_i, t) \quad (20)$$

In other words, by constructing a parametric plot of x, y points $x, y = \{f_x(\xi), f_y(\xi)\}$ with $\xi = t - \bar{t}_i$, and $f_x = S_T$, $f_y = \bar{P}_Q$, one obtains a plot of the rSAS function $\Omega_Q(S_T, t)$ at each time t .

4. Results

4.1. Water Mass Balance and Periodic Steady State

The lysimeter water balance over the 28 days experiment included 4526 mm of influx, 4243 mm of outflux, 74 mm of evaporation from the soil surface, 4 mm increase in storage, and 62 mm of water loss from a leak.

The two irrigation rates were calibrated prior to the experiment; however, we noted imperfect flow rates delivered by the diaphragm pump over prolonged operation times, which affected the spray patterns generated by the sprinkler heads and compromised the calibration values. Alternatively, we calculated irrigation time series as the sum of 3 min moving averages of outflux and storage change, assuming that evaporation was negligible during irrigation periods. A small leak from a venting apparatus on one of the bulkhead fittings was noted early in the experiment, and the 24 h accumulation of water was measured throughout the remainder of the experiment. We calculated the average leak rate and summed that rate over the 28 day experimental period, assuming the leak was active prior to us detecting it. A normalized depth of 143 mm of water was unaccounted for constituting the mass balance error, and it is less than 4% of the total amount of irrigated water.

Moreover, the generation of a periodic steady state (PSS) is the essential condition for applying the PERTH method. The time series of supplied flow rate (measured by the magnetic flow meter which located ahead of sprinklers; see Figure 1), storage, and discharge time series were decomposed into three components, a trend (T), periodic (P), and random (R) component. (Note that the supplied flow rate is used here instead of the calculated irrigation rate, because the irrigation time series is estimated from the mass balance, rather than measured directly.) The trend component is a 24 h moving average of the time series. The periodic component is an average of detrended time series over each time of day. The random component is the remaining signal. A measure related to the signal-noise ratio, $(\text{Var}(T) + \text{Var}(R)) / (\text{Var}(T) + \text{Var}(R) + \text{Var}(P))$ was used to evaluate the contributions of the aperiodic components relative to the total signal, and was found to be 0.06%, 4.6%, and 1.4% for the supplied flow rate, storage, and discharge time series, respectively; these values suggest that the noise (trend and random part) are negligible compared to the signal (periodic part).

4.2. Breakthrough Curves and Forward Transit Time Distributions

The probe tracer BTCs are presented in the left plot of Figure 4. The BTC differ between the four injection pulses, but appear to be strongly controlled by the subsequent sequence of irrigation. The respective

Figure 4. Observed breakthrough curves and forward transit time distributions. (left) Each probe tracers' BTC shifted to its injection start time $C_i(t - \bar{t}_i)$, and (right) Forward transit time distributions $\bar{p}_Q(t - \bar{t}_i, \bar{t}_i)$ for each timing of injections of probe tracers. (top) Time series of all probe tracers to emphasize its relative difference. Other plots show each signal with light-gray shaded periods which indicate the time periods of irrigation events. In the plots, thick-colored lines show the signals obtained by CI^- analysis, and thin gray lines show the signals obtained by the EC probe. The green-colored horizontal bars in the left columns indicate the three characteristic periods—mobilization, transition, and dilution. (Here the transition periods were defined first where breakthrough dynamics are not well correlated with flow dynamics in general. The periods are indicated as black dotted lines in the left plots.)

effects of antecedent condition and irrigation intensity are difficult to distinguish amongst the large fluctuations induced by each irrigation event.

While the shape of each BTC are different from each other, they all display three characteristic periods—mobilization, transition, and dilution. During the initial mobilization period, which was estimated to last 24–26 h in all cases, concentration increased with increasing discharge, both during the injection irrigation and during subsequent unlabeled irrigations in general. Concentration mostly decreased during the intervening discharge recessions. Conversely during the late-time dilution period these dynamics reversed; concentration generally decreased during irrigation periods, and increased during recession periods. The transition period, which lasted 12–13 h for probe 0 and 2, and 21–24 h for probe 1 and 3, showed indeterminate behavior—in general, concentration increases regardless of the flow dynamics in this experiment. The periods and their (visually approximated) durations are illustrated in Figure 4. The fTTDs are illustrated in the right plot of Figure 4. The form of the fTTDs reflects the dynamics of the associated BTC, with some subtle differences resulting from the discharge normalization.

4.3. Backward Transit Time Distributions, Age-Ranked Storage, and Rank StorAge Selection Functions

Based on the SAS theory, we can use the fTTD to reconstruct the volume of water from each injection period that remains in storage at each moment in time, and the rate of discharge originating from each of the irrigation events. The top plots of Figure 5 illustrates the time-evolution of this “tagged” water in the storage and discharge by its associated irrigation pulses. We have taken advantage here of the periodicity of the system to illustrate how the dynamics of storage and discharge would be revealed if four distinct tracers could be added every day.

One thing can be noted from this is that the amount of water in storage originating from a particular injection reduces gradually in time after its injection, though the discharge varies significantly in time. These time variabilities are more thoroughly examined by looking at age-ranked storage density and bTTDs at four different times (two wetter and two drier conditions) indicated by the dotted lines in the figure.

The age-ranked storage densities at four different times are illustrated in the lower part of Figure 5. The age-ranked storage only has nonzero values for ages corresponding to periods in the past when there was an irrigation event. Also, as we can expect from above, the structure of those are stable over time, differing only slightly between wet and dry conditions. The estimated bTTDs at four different times are also shown in Figure 5. As we can expect from above, these vary in time significantly. Specifically, the contribution to discharge of young water is higher under wetter conditions than dry. In fact the median transit time was negatively correlated with discharge ($r = -0.94$, $p < 0.0001$) and with the lysimeter storage ($r = -0.93$, $p < 0.0001$). This time variability suggests that the rSAS function will also vary in time significantly.

The estimated rank StorAge Selection (rSAS) function is illustrated in the bottom plots of Figure 5 at the same four times. Unlike other distributions shown here, the rSAS function does not show the recapitulation of the irrigation time series. The use of the age-ranked storage to express age compositions smoothes out the fluctuations in the observed bTTDs caused by the temporal variability of the inputs. The cumulative rSAS function (obtained by integrating the density form) has a sigmoidal form that seems to vary with storage (see Figure 7e). The form of rSAS function shows that discharge from the system was more uniformly representative of the age-ranked storage at high flows, and was skewed away from the young water at low flows. Also, the value of function is negligible at all times when age-ranked storage is less than about 50 mm, implying that the youngest part of the water does not contribute to discharge. This could be associated with the vertical movement of water through the vadose zone in the lysimeter. The rSAS function is only shown up to around 85% of the total storage because even after 5 days about 15% of water in the storage was older than 5 days.

5. Discussion

The observed rSAS functions and bTTD demonstrated the importance of the variability in the irrigation input, but also revealed a consistent additional pattern that enhanced the temporal variability of the tracer breakthrough—discharge was relatively younger under wetter conditions, and relatively older under drier.

Figure 5. “Tagged” water in storage and discharge, and observed bTTDs, age-ranked storage, and rSAS function at four different times (each different color represents a distinct injection period). In the storage and discharge figures, total storage and discharge are represented by black bold lines, and the area between the lines and the tagged (colored) water represents old waters which were injected prior to 5 days ($= T_{max}$). In the rSAS function plots, the upper bounds of the support (at total storage $S(t)$) are shown in the plots as vertical-dotted lines (black for Wet A and Dry A, and red for Wet B and Dry B conditions, respectively).

In other words, the highly dynamic transit time distributions seem to have been determined by both the “external” effects of variable input and output fluxes, as well as “internal” effects causing variable mobilization of old and new water. However, it is not immediately clear how the internal and external variability each play a role in the age variability, how they are related to the physical system, or how they are expressed in the SAS functions.

5.1. Toward Definitions of Internal and External Transport Variability

We can begin to understand the dynamics observed in these transit time distributions by defining internal and external variability more clearly. We will arrive at a definition by way of a thought experiment. Consider advective transport through a hydrodynamic system in which the flow velocity field is separable into independent time and space components, so that $\mathbf{v}(\bar{x}, t) = \mathbf{v}^*(\bar{x})\phi(t)$. In such a system, an increase in inflows is associated in a proportional increase in flow velocity everywhere, and a corresponding increase in outflows. Total storage, therefore, does not change. A proportional increase in velocity in response to changing inflows is a feature of saturated systems where storage does not change, such as (idealized) groundwater flow through a confined aquifer. This is a fundamental difference between such systems and unsaturated systems, where storage always changes with changing inflows.

Such a system could be regarded as one in which “internal” variability is absent. Flow paths (that is, the trajectories of transport through space) are fixed, and only the velocity of flow along the flow path varies in time. Several useful properties can be derived for such a system, as demonstrated in Appendix A:

1. The transformation of the system into flow-weighted time results in a velocity field that is “frozen” in (transformed) time. The flow-weighted transit time along any one streamline is therefore invariant, as is the total storage in the streamtube surrounding that streamline. This has been referred to as a time-invariant flow pattern or flow pathways [Niemi, 1977; Rodhe et al., 1996; Ali et al., 2014].
2. The transit time distribution of the system as a whole is invariant when expressed in terms of flow-weighted age.
3. The rSAS function of the system is invariant in time, regardless of whether time is expressed in terms of clock or flow-weighted time.
4. The invariance of this function arises in this case from two facts: the invariance of the flow-weighted transit time along each streamline, and the time-invariant proportion each streamline contributes to the total discharge $Q(t)$.

Based on the conceptual definitions of internal and external variability presented in the introduction, it would therefore be reasonable to equate the absence of internal variability with invariance in the rSAS function, and invariance in the transit time distribution in flow-weighted time. Variability that is fully accounted for by a transformation to flow-weighted time is exclusively of the external type. Conversely, the temporal variabilities of the rSAS function can be usefully regarded as quantifying the internal variability of the system. Thus the decomposition of age-ranked flux $Q_T(T, t)$ into the product:

$$Q_T(T, t) = Q(t)\Omega(S_T, t) \quad (21)$$

represents the decomposition of the total variability in transit time into its external and internal components. A corollary of this definition is that variability in the rSAS function (or equivalently in the flow-weighted TTD) implies time-variability in flow pathways through the system, and/or in the proportions of flow traveling along each flow pathway. Examples of a system of which has different variabilities are illustrated in Figure 6. It shows the conditions under which transit time and flow-weighted time along a specific streamline k varies (or not), as well as variability of rSAS function from the reference case.

There are several potential objections to this definition that must be addressed. First, the transit time distribution, and therefore the rSAS function, may be invariant even if the velocity field is not invariant, or separable in the manner assumed above. That is, flow paths can vary with no effect on the rSAS function. For example, flow paths vary continuously in a well-stirred tank, but the rSAS function remains a uniform distribution. We must therefore specify that the term “internal variability” is limited to that variability that has an effect on the transit times, and excludes the situation where internal flow pathways are altered with no effect on the transit time distributions. That type of TTD variability (which might be referred to as “symmetric” since it is a transformation that preserves a measure) might nevertheless alter biologic or chemical processes, and so have important implications for the fate and transport of particular solutes, but is not considered here.

Second, the derivation above assumes a fixed total storage S . Under such conditions the rSAS function Ω_Q and the fSAS function Ω_Q^f defined by van der Velde et al. [2012] are equivalent: $\Omega_Q(S_T, t) = \Omega_Q^f(P_S, t)$ with cumulative residence time distributions $P_S(T, t) = S_T(T, t)/S(t)$. Why should the rSAS function be used to define internal variability, rather than the fSAS function? Temporal variability in the rSAS and fSAS functions

Figure 6. Examples of a system which have different variabilities. Noted transit time (TT) and flow-weighted transit time (FWTT) on the figure are those of streamline k . (a) The reference case of a system. (b) A case which has only external variability compare to the reference case—flow pathways are the same as the reference case while fluxes are different. In this case, flow-weighted transit time and rSAS function are the same as the reference case. (c) A case which has only internal variability compared to the reference case. While fluxes are the same as the reference, flow pathway is changed compared to the reference due to such as a macro-pore in the permeable layer. In this case, transit time, flow-weighted transit time, and rSAS function are different from the reference case. (d) A case which has both external and internal variabilities—every noted quantities are different from the reference case. (Note that in unsaturated or variably saturated systems, the case (b) is unlikely to occur (since the flow paths are strongly affected by flow rate) and the case (c) will only occur in circumstances where phenomena like animal burrowing and internal erosion accompany very steady infiltration.)

are not equivalent. Since the domain of the fSAS function is normalized by the total storage of a system while the rSAS function is not, they will respond differently to changes in total storage. Consider a well-mixed tank with variable total storage $S(t)$. The fSAS function for this system is invariant—it is a uniform distribution on $P_S \in [0, 1]$. The rSAS function is not invariant—it is also a uniform distribution, but one with a variable domain: $S_T \in [0, S(t)]$. We argue that variability in total storage should be considered as “internal variability” in this canonical case. Total storage determines the degree to which inflows are diluted by resident water—a basic property of the transport dynamics. Therefore invariance in the fSAS function cannot be regarded as indicating the absence of internal variability, and so the rSAS function should instead be used to define it.

5.2. Relative Controls of External and Internal Temporal Variability in the Experimental Lysimeter

These definitions provide a basis for deciding whether (or not) in any particular system a time-variable rSAS function is required to estimate the bTTDs. If most of time variability on the bTTDs is caused by external variability, it would be enough to use the flow-weighted time approach. The flow-weighted time approach has the advantage that it is relatively better understood by other scientists, and the time-invariant TTDs that have been theoretically derived under the steady state can directly be applied in flow-weighted time.

We can examine the relative controls of internal and external variability in the experiment described here by converting the observed bTTD to flow-weighted time. If one transforms bTTDs into the flow-weighted time space, the effect of external variability on the bTTDs would be eliminated, and in the absence of internal variability the time-variable bTTD should collapse into a single curve. Thus time variability of the bTTDs

Figure 7. Illustrations of the bTTDs, the rSAS functions, and the modeled BTCs. (a) and (b) The observed bTTDs (blue colored with varying color saturations indicating the storage state) and the steady state TTD (red colored) on the transit time space. (c) The observed bTTDs (blue colored) and the time-invariant TTD (red colored) on the flow-weighted transit time space. The time-variability of the TTD on the transit time space is illustrated in (d) with varying color saturations indicating the storage state. (e) The observed rSAS functions (blue colored) and the time-invariant rSAS function (red colored), and the time-variable TTDs determined by the invariant rSAS function are shown in (f). (g)–(i) The modeled BTCs with the bTTDs shown in the left plots.

in flow-weighted time would indicate the effect of internal variability. The transformation can be done using equation (10). The resulting transformed time-variable bTTDs are the time-varying kernel of equation (7).

Blue-colored lines in Figures 7a and 7c illustrate the observed bTTDs in clock time and transformed into the flow-weighted time space, respectively. Much of the fluctuations in each bTTD present in clock time are smoothed out in flow-weighted time, but the bTTDs are still significantly time-varying. Thus internal variability plays a major role in the time-varying nature of the observed bTTDs.

Moreover, the role of internal variability on bTTDs appears to be closely tied to the physical state of the system. The bTTDs are colored by the contemporaneous storage of the soil-lysimeter, revealing how the bTTDs vary as total storage varies.

We can further examine the importance of internal and external variability by constructing a time-invariant TTD, and using it two different ways. In the first case, we can simply convolve it with the observed tracer inputs, thus generating transport predictions that ignore the effect of both internal and external variability (the “steady state” case). Second we can treat it as invariant in flow-weighted age, but variable in clock time (the “external only” case). Time-variable bTTDs can be determined for this constructed flow-weighted TTD with equation (10). This can be used to determine what the reference tracer breakthrough curve would look like if internal variability is neglected.

There is no standard way to determine the “correct” time-invariant TTD approximating the observed time-variable TTDs. The method used here is to average the bTTDs at each age in flow-weighted time. This is mathematically identical to the flow-weighted transit time described by *Peters et al.* [2014], and the marginal transit time distribution described by *Benettin et al.* [2015b] when outflow time series is used as a weighting factor (see Appendix B).

The time-invariant TTD is illustrated in Figures 7a and 7b as the red-colored line. The bTTDs generated using this, which only account for external variability, are also displayed in Figure 7d. Compared to the full variability in TTD shown in Figure 7a (blue-colored lines), the variability in Figure 7d is considerably reduced. The modeled BTCs are shown in Figures 7g and 7h. For the time-invariant TTD case, it was assumed that the tracer was injected during the entire first day. The modeled BTC using the time-invariant TTD is only able to reproduce the broadest structure of the reference tracer BTC. The flow-weighted time approach performs little better. In contrast, the BTC modeled using the bTTDs extracted from the probe tracer BTC almost exactly matches the observed reference tracer BTC—differences are mainly due to the tracer mass recovery issue mentioned in the results. These results suggest that in this case capturing the internal variability is necessary for capturing the high-frequency dynamics of hydrologic transport. Nevertheless, it may should be noticed here that, in applications to field sites, the “flow-weighted time” approach might perform better than how it did in this experiment, where large fluctuations in the flow pathways were generated (as seen in Figure 2).

We can further visualize the effect of internal transport variability by examining the temporal variability of the rSAS function since, as discussed above, the rSAS function is invariant in the absence of internal variability. The cumulative form of the observed rSAS function is illustrated in Figure 7e where the function at each time step is colored by the storage state of the lysimeter at that time.

To examine the importance of the time-variability of rSAS function in modeling BTC, we can generate an approximately-equivalent (nearly) time-invariant rSAS function by averaging the value of the cumulative rSAS function at each value of S_T . For this exercise, the parts of the rSAS function corresponding to large S_T for which data did not exist were assumed to be uniformly sampled, including the part of the rSAS function that fluctuates with fluctuating storage (hence this rSAS function is not completely time-invariant). This can then be used to generate time-variable bTTDs, and predict the shape of the reference tracer breakthrough. The time-averaged rSAS function and resulting BTC are shown in Figures 7e and 7i, respectively, as red lines.

Figure 7i shows that the modeled BTC again fails to reproduce the fluctuating behaviors of the breakthrough curve, just as the steady state or flow-weighted time TTD did above. The modeled BTC here is slightly different from the flow-weighted time approach. This is because the bTTDs estimated by the flow-weighted time approach does not reflect the changes in storage, which is accounted for in the bTTDs estimated by the time-invariant rSAS function. The failure again emphasizes that a time-varying SAS function is essential to model transport of this system properly.

5.3. Internal Variability and the Inverse Storage Effect

A full analysis of the structure and origins of the temporal variability of the rSAS function is reserved for future work, but some basic features are noted here. The observed time-variability in the rSAS functions exhibits the “inverse storage effect” discussed by *Harman* [2015]. This is a particular mode of rSAS variability in which the distribution shifts to increase the contribution of younger water (smaller S_T) under wet conditions, and older water under drier conditions [*Harman*, 2015]. That is, the mean of the distribution $\bar{S}_T$ decreases, while the total storage $S = \max(S_T)$ increases. This is inverse to the behavior of a well-mixed system, where these two quantities would both increase. This type of behavior has been observed in several

studies at catchment scale [van der velde *et al.*, 2014; Harman, 2015; Benettin *et al.*, 2015b; Birkel *et al.*, 2015]. In fact, the median of rSAS function was negatively correlated with the lysimeter storage ($r = -0.84$, $p < 0.0001$). (Median is used here rather than mean since the complete rSAS distribution is unknown.)

Moreover, the inverse storage effect helps to explain features of the all probe tracer BTCs and the reference tracer BTC. As discussed above in section 3.2 the tracer BTCs exhibit three periods, referred to as mobilization, transition, and dilution periods. During the mobilization period, BTC concentration increases with increasing storage during irrigation (olive-colored box in the left plot of Figure 4 for example), while during the dilution period it reduces with increasing storage. This is due to the fact that during the early part of the breakthrough the tracer is located in the younger part of the storage. As storage rises during irrigation the contribution of younger water increases, and so the concentration of tracer increases, leading to the dynamics of the “mobilization” phase. During the late period, the young water is free of tracer, and the tracer is now associated with the older water in the system. Under increasing storage and increasing contributions of young water, the tracer becomes increasingly diluted.

Based on the available evidence, we can develop hypotheses regarding the physical mechanisms that control the main characteristics of the breakthrough dynamics. After introducing a tracer in the lysimeter, the position of the water table (see Figure 2) suggests that tracer would be retained mainly in the unsaturated zone. Following the subsequent irrigation, the tracers were transported further downward. Vertical hydraulic gradients likely dominate in the unsaturated zone. However, at the same time, or even faster than the downward movement, the water table rises in response to the pressure wave (whose importance has been demonstrated with this type of soil and boundary conditions [Gevaert *et al.*, 2014]). The first arrival of the tracer at the outlet coincides with the rising water table (see Figure 2 and/or 4), suggesting some portion of the leading edge of the tracer plume is transported by the saturated zone, where lateral flow dominates. The lateral dynamics can discharge the tracer out of the seepage face; thus, the concentration at the outlet can be expected to, in general, increase during the rising limb of the hydrograph. During the subsequent recession periods, the falling water table does not completely drain the pore space—the data suggests that only about 25% of the pore space above the water table is typically drained at most. At the upper part of the saturated zone, only some portion of water with tracer (equivalent to the concept of effective drainable porosity) would be mobilized in the saturated zone, while another portion would remain behind in the (again) unsaturated zone. The reducing contribution of tracer-labeled water in this scenario (as more of it is left behind in the unsaturated zone by the falling water table) accounts for the decreasing concentration during the recession period. This mechanism explains the “mobilization” period, and also explains the “dilution” period. Under the PSS irrigation, the tracer plume is progressively transported further from the soil surface over time, eventually reaching a zone where the soil is always saturated. During this period, the concentration decreases during the rising limb of the hydrograph as the rising water table mobilizes more recently irrigated tracer-free water in the upper part of the system. The concentration increases during the falling limb as the tracer-free water is left behind in the saturated zone, allowing the relative contribution of the tracer-dosed water to increase. During the “transition” period, the tracer-dosed water is frequently switching between saturated and unsaturated conditions; thus, the BTCs showed indeterminate behavior.

This hypothesized mechanism emphasizes the role of the water table fluctuations rapidly transmitting pressure waves through the system, and reorganizing flow vectors—these dynamics occur much faster than the movement of individual parcels of fluid. It is therefore an example of the important difference between wave celerity and particle velocity in controlling macroscale hydrologic responses—celerity is faster than velocity [e.g., McDonnell and Beven, 2014]. Of course, irrigation intensity, antecedent condition, and intrinsic and incipient heterogeneity of soil (such as pore-size distribution) likely also play a certain role in the transport dynamics along with the above hypothesis. Time-variable flow and transport dynamics through heterogeneous (at microscale) soil has been extensively examined, and multidomain models developed to account for their effects on transport dynamics [e.g., Steenhuis *et al.*, 1990; Durner and Flühler, 1996; Vogel and Roth, 2003]. Close examination of this hypothesis and alternative interpretations are reserved for future work.

5.4. Implications for Modeling Transport With Internal Variability

This study has isolated and provided a clear definition of internal variability, but its effects have been accounted for in previous models in a variety of ways. For example, several studies have developed models where several time-invariant TTDs are assumed to apply to individual storage components in a system [Roa-García and Weiler, 2010; Segura *et al.*, 2012]. While the individual TTDs are time-invariant, the overall TTD is

time-varying because their relative contribution to the total discharge varies over time. Thus the models account for the internal variability caused by shifts in the contributions of different flow pathways in the system. Several other types of models have been developed [Heidbüchel *et al.*, 2012; Hrachowitz *et al.*, 2013] using time-varying rules for combining water moving through lumped storages. The rules are coupled to internal state variables of a system, such as relative wetness, which are taken as proxy measures of the hydrologic states controlling the internal variability, such as the hydrologic connectivity [Hrachowitz *et al.*, 2013].

These methods were variously effective in the circumstances in which they were employed but are, in a sense, ad hoc and lack the generality of the rSAS approach. The rSAS function encapsulates the emergent effect of internal variability in a physically meaningful and measurable function (see Figure 5), operating as a closure of a governing conservation equation. They are convenient to work with since they can be parameterized by probability distributions defined continuously over a support defined by the storage in the system (again, see Figure 5). Furthermore, rSAS functions are explicitly separated from external variability; thus, time-variability of the function only reflects internal variability, while application of the governing equations imparts external variability to the estimated time-variable backward transit time distributions. Thus it is possible to model hydrologic transport through a system by parameterizing the functions using internal state variables of a system such as storage. For example, at a catchment scale, the rSAS and fSAS function frameworks have been successfully used to model hydrologic transport by applying storage dependent time-variable SAS functions [van der velde *et al.*, 2014; Harman, 2015]. Operating as an inverse model, the internal variability of a hydrologic system can be measured by observing the rSAS function, or can be inferred by fitting rSAS function on field measurements of mass influxes and mass outfluxes. This is due to the fact that rSAS function entails all internal variabilities without “contamination” by external variability (unlike the aSAS function suggested by Botter *et al.* [2011], or the loss function described by Porporato and Calabrese [2015]).

6. Conclusions

In this study, time-variable transit time distributions were observed in a 1 m³ variably-saturated sloping soil lysimeter filled with loamy sand using the PERiodic Tracer Hierarchy (PERTH) method.

The empirical results showed that the observed backward transit time distributions (bTTDs) are varying significantly in time. We have proposed that the observed time variability of the TTD can be decomposed into “internal” variability (i.e., changes in the arrangement of flow pathways and/or in partitioning among flow pathways) and “external” variability (i.e., changes in flow rates in and/or out).

The observed time variability of TTDs in this experiment is determined in large part by internal variability. Thus the “flow-weighted time” approach for modeling outflow concentration was not able to reproduce important features of the observed tracer breakthrough curves (BTCs)—in particular, fluctuations in BTCs triggered by the irrigation pulses—because the approach neglects the internally generated TTD variability.

StorAge Selection (rSAS) function approaches provide a way to determine TTDs and to model BTCs accounting for both internal and external variability. In this paper, we have demonstrated that the rank SAS (rSAS) function—the closure relation for the governing equation of the rSAS approach—encapsulates the internal variabilities, while external variability is accounted for when the conservation law is used to convert the rSAS function to a time-varying TTD. Thus observing the rSAS function (or fitting a function using influx and outflux concentration) is key to understanding the internal variability of a system, as well as to forward modeling of hydrologic transport. The use of the rSAS function as a measure of a system’s internal variability could help us understand and model time variability of complex flow pathways at hillslope and/or catchment scale [McGlynn *et al.*, 2002; Weiler *et al.*, 2003], Tothian flow [Tóth, 2009; Gomez and Wilson, 2013], “two water worlds” [Brooks *et al.*, 2010; McDonnell, 2014; Evaristo *et al.*, 2015], and hyporheic exchange [Harvey *et al.*, 1996; Cardenas *et al.*, 2008]. For this purpose, future studies are needed to understand the dynamics of rSAS functions of different hydrologic fluxes such as evaporation, transpiration, and discharge, and the effect of a system’s heterogeneity on the rSAS function.

The observed rSAS function revealed significant time variability that depended on the internal state of the lysimeter. More specifically, the observed behavior can be characterized by the “inverse storage effect”—younger water is discharged in greater proportion under wetter conditions than drier conditions. The “inverse storage effect” helps to explain the temporally varying breakthrough dynamics (mobilization,

transition, and dilution periods) as arising from the movement of the tracer pulse through different parts of the age-ranked storage. This direct observation is in accordance with other catchment scale studies in which SAS function was inferred by fitting the function using measured in and out fluxes rates and concentrations [van der velde *et al.*, 2014; Harman, 2015; Benettin *et al.*, 2015b]. Moreover, the direct observation and observed data set in this study open up an opportunity for further investigation to understand the physical controls on the time variability of rSAS function and the inverse storage effect.

Appendix A: Time-Invariance of Rank StorAge (rSAS) Function in a Special Case of Unsteady Flow

In this section, we show that the rSAS function is invariant for the special case in which the velocity field within the system $\mathbf{v}(\bar{x}, t)$ is separable in time and space so that $\mathbf{v}(\bar{x}, t) = \mathbf{v}^*(\bar{x})\phi(t)$. This is consistent with a system in which the trajectories of each streamline in a system are fixed in time, while water particle velocity at a point along a streamline fluctuates. In this case, assuming fluid density is invariant ($\rho(\bar{x}, t) = \rho = \text{const.}$) it can be shown that the inflows and outflows must be equal to each other $J(t) = Q(t)$, though they may vary together in time, and $\phi(t)$ is a scalar multiple of these fluxes, determined as follows:

$$J(t) = Q(t) = \oint_{B_Q} \rho \mathbf{v} \cdot d\boldsymbol{\sigma} = \phi(t) \oint_{B_Q} \rho \mathbf{v}^* \cdot d\boldsymbol{\sigma} \quad (\text{A1})$$

where B_Q is an area of the outflux boundary. Thus $\gamma\phi(t) = Q(t)$ where the scalar constant $\gamma = \oint_{B_Q} \rho \mathbf{v}^* \cdot d\boldsymbol{\sigma}$.

Transit time along a streamline k (arbitrarily chosen among all streamlines that connect the injection point $\bar{x}_i$ and the exit point $\bar{x}_e$) of length L_k can be estimated based on the equation of motion of a particle, neglecting the effects of molecular diffusion,

$$\frac{ds}{dt} = v_k(s, t) = \phi(t)v_k^*(s) \quad (\text{A2})$$

where s is the distance a particle has travelled from the injection point along the streamline k , v_k is a velocity at s along the streamline k , and $v_k^*(s) = |\mathbf{v}^*(\xi(s))|$, where ξ is a function which associates s with its Cartesian coordinate $\bar{x}$. The transit time is varying over time depending on $\phi(t)$. From the separability of the velocity field, we can define a time-invariant quantity associated with the particular flow path k , which has a dimension of time, by rearranging and integrating the equation (A2):

$$T_k = \int_0^{L_k} \frac{1}{v_k^*(s)} ds = \int_{t_i}^t \phi(\tau) d\tau \quad (\text{A3})$$

However, the integral of $\phi(t)$ is by definition given by:

$$\int_{t_i}^t \phi(\tau) d\tau = \frac{1}{\gamma} \int_0^t Q(\tau) d\tau - \frac{1}{\gamma} \int_0^{t_i} Q(\tau) d\tau = t_Q(t) - t_Q(t_i) = T_Q(t - t_i, t) \quad (\text{A4})$$

from the definition of the flow-weighted exit time (5), with the arbitrary scaling factor β chosen to be γ . Thus the time-invariant quantity T_k is in fact the transit time along flow path k in flow-weighted time T_Q :

$$T_k = t_Q(t) - t_Q(t_i) = T_Q(t - t_i, t) \quad (\text{A5})$$

The time invariance of $T_Q = T_k$ is due to the fact that the time-variable velocity field $\mathbf{v}_Q$ is in fact invariant in flow-weighted time $(d\bar{x}/dt)(dt/dt_Q) = \mathbf{v}(\bar{x}, t) dt/dt_Q = \mathbf{v}^*(\bar{x})$.

We would now like to place this result in the context of SAS theory. To do this, we will develop rSAS functions for a single stream line, then sum these for the whole control volume. Let us assume that the streamline k is associated with a perpendicular area element $A_k(s)$ that varies with the streamwise coordinate s such that the volume flux in flow-weighted time $Q_k^* = A_k(s)v_k^*(s)$ is constant along the streamline. Then the age-ranked storage in flow-weighted time $S_{T,k}(T, t) = S_{T,k}^*(T_Q, t_Q)$ is given by (Note that T_Q here is an age of water at s in the flow-weighted time space):

$$S_{T,k}^*(T_Q, t_Q) = \int_0^s A_k(s') ds' = \int_0^s \frac{Q_k^*}{v_k^*(s')} ds' \quad (\text{A6})$$

where s is the streamwise coordinate chosen such that:

$$T_Q(s) = \int_0^s \frac{1}{v_k^*(s')} ds' \quad (A7)$$

Thus, since Q_k^* is a constant, we have simply $S_{T,k}^*(T_Q) = T_Q Q_k^*$ for $T_Q < T_k$. The total storage in the area around the streamline is $S_k = T_k Q_k^*$, which is a constant. This shows that the age-ranked storage for the streamline, when expressed in flow-weighted time, is a linear function of T_Q only, and is independent of time.

Since we assume purely advective flow (plug-flow) along the streamline, the cumulative transit time distribution for the streamline, P_k^* is a Heaviside step function that changes from 0 to 1 when $T_Q = T_k$:

$$P_k^*(T_Q) = H(T_Q - T_k) \quad (A8)$$

Recall that from the definition of the rSAS function:

$$P_k^*(T_Q) = P_k(T, t) = \Omega_k(S_{T,k}(T, t), t) \quad (A9)$$

where $\Omega_k(S_{T,k}, t)$ is the rSAS function for the streamline. From the above results, we can deduce that since P_k^* is a function only of T_Q and not of t_Q , and since $S_{T,k}(T, t) = S_{T,k}^*(T_Q)$ depends only on T_Q , and not on t_Q , $\Omega_k(S_{T,k}, t)$ cannot vary independently with t , and must, in fact be invariant in time:

$$\Omega_k(S_{T,k}^*(T_Q)) = \Omega_k(S_T(T, t)) = H(S_{T,k}^*(T_Q) - S_k) = H(S_{T,k}(T, t) - S_k) \quad (A10)$$

for $T_Q = T_Q(T, t)$. That is, the rSAS function is a step function at $S_{T,k} = S_k$.

To extend this result to the whole volume, we can simply add up the total storage and discharge with an age (in flow-weighted time) less than T_Q :

$$S_T^*(T_Q) = \sum_{k \in V} S_{T,k}^*(T_Q) \quad (A11)$$

$$Q_T^*(T_Q) = Q^* P_Q^*(T_Q) = \sum_{k \in V} Q_k^* P_k^*(T_Q) \quad (A12)$$

where $Q_T^*(T_Q) = Q^* P_T^*(T_Q)$. We can move from consideration of discrete flow paths to a continuous formulation by introducing a partition function $\psi_T(T_k)$, which is a density determining the proportion of total flow that travels along streamlines for which equation (A3) evaluates to T_k . The density $\psi_T(T_k)$ is determined by the particular nature of the time-invariant flow field $\mathbf{v}^*(\vec{x})$, and is therefore itself invariant in time. Then, drawing on the results above, we can write:

$$Q_T^*(T_Q) = \int_0^{T_Q} Q^* \psi_T(T_k) H(T_Q - T_k) dT_k \quad (A13)$$

which is a convolution between $\psi_T(T_k)$ and a Heaviside step function. From the properties of the convolution and the step function, this simply implies that:

$$P_Q^*(T_Q) = \int_0^{T_Q} \psi_T(T_k) dT_k \quad (A14)$$

In other words, $\psi_T(T_k) = p_Q^*(T_Q)$, and so the partition function is nothing more than the transit time distribution in flow-weighted time. Following a similar procedure for the rSAS function, we can define a partition function $\psi_S(S_k)$, which is a density determining the proportion of total flow that travels along streamlines for which the total storage is $S_k = T_k Q_k^*$. The partition functions are related to each other as $\psi_S(S_k) dS_k = \psi_T(T_k) dT_k$. With this we can see that:

$$Q^* \Omega_Q(S_T) = \int_0^{S_T} Q^* \psi_S(S_k) H(S_T - S_k) dS_k \quad (A15)$$

where again, implying that:

$$\Omega_Q(S_T) = \int_0^{S_T} \psi_S(S_k) dS_k \quad (A16)$$

demonstrating that the invariance of the rSAS function for the individual flow paths translates into time invariance of the flow paths of the whole system.

Appendix B: Average Flow-Weighted Transit Time

The flow-weighted mean transit time [Peters *et al.*, 2014] and the marginal transit time distribution [Benettin *et al.*, 2015b] has been suggested to get a representative time-invariant TTD from the time-varying transit time distribution. Both were suggested to account more discharged water at higher discharge.

Mathematically, the marginal TTD, when it uses flow time series as a weighting factor is indeed a TTD averaged over flow-weighted time:

$$\bar{P}_Q(T) = \frac{1}{d(\Gamma)} \int_{\Gamma_Q} \bar{P}_Q(T, t_Q) dt_Q \quad (B1)$$

$$= \frac{1}{d(\Gamma)Q} \int_{\Gamma} \bar{P}_Q(T, t) Q(t) dt \quad (B2)$$

Where Γ is a period of interest, Γ_Q is the period in the flow-weighted time space, and d is a function which measure of duration of the period.

Notation

t, t_i, T	exit time, injection time, and transit time in calendar time space.
t_Q, τ_Q, T_Q	flow-weighted exit time, injection time, and transit time in flow-weighted time space.
J, Q	volume flux of water.
M, M_Q	mass flux of a solute.
C, C_Q	solute concentration.
C_j^*, C_Q^*	solute concentration in flow-weighted time space.
$p_Q, \bar{p}_Q^*$	time-invariant transit time distribution in calendar and flow-weighted time space.
$\bar{p}_Q, \bar{p}_Q^*, \bar{p}_Q^*$	forward and backward transit time distributions in calendar time space, and backward transit time distributions in flow-weighted time space.
$\bar{P}_Q, \bar{P}_Q^*$	cumulative backward transit time distributions in calendar and flow-weighted time space.
s_T, S_T	Age-ranked storage density, and age-ranked storage.
Q_T	age-ranked flux.
ω_Q, Ω_Q	rSAS functions in pdf., and in cdf.

Acknowledgments

This work is supported by the National Science Foundation under grants EAR-1344552 and EAR-1417175, and a CUAHSI Pathfinder fellowship awarded to Minseok Kim. Pierre Quéloz, and two anonymous reviewers provided valuable comments. The data presented in this paper are available from the corresponding author on request.

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