Catchment travel time distributions and water flow in soils

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[1] Many details about the flow of water in soils in a hillslope are unknowable given current technologies. One way of learning about the bulk effects of water velocity distributions on hillslopes is through the use of tracers. However, this paper will demonstrate that the interpretation of tracer information needs to become more sophisticated. The paper reviews, and complements with mathematical arguments and specific examples, theory and practice of the distribution(s) of the times water particles injected through rainfall spend traveling through a catchment up to a control section (i.e., "catchment" travel times). The relevance of the work is perceived to lie in the importance of the characterization of travel time distributions as fundamental descriptors of catchment water storage, flow pathway heterogeneity, sources of water in a catchment, and the chemistry of water flows through the control section. The paper aims to correct some common misconceptions used in analyses of travel time distributions. In particular, it stresses the conceptual and practical differences between the travel time distribution conditional on a given injection time (needed for rainfall-runoff transformations) and that conditional on a given sampling time at the outlet (as provided by isotopic dating techniques or tracer measurements), jointly with the differences of both with the residence time distributions of water particles in storage within the catchment at any time. These differences are defined precisely here, either through the results of different models or theoretically by using an extension of a classic theorem of dynamic controls. Specifically, we address different model results to highlight the features of travel times seen from different assumptions, in this case, exact solutions to a lumped model and numerical solutions of the 3-D flow and transport equations in variably saturated, physically heterogeneous catchment domains. Our results stress the individual characters of the relevant distributions and their general nonstationarity yielding their legitimate interchange only in very particular conditions rarely achieved in the field. We also briefly discuss the impact of oversimple assumptions commonly used in analyses of tracer data.

1. Introduction

[2] It has long been the case that hydrologists have been content with the analysis and prediction of hydrographs. This is (still) a challenging problem given the limited information content of hydrological measurements. However, the hydrograph does not provide a full picture of the hydrological response of catchments. A full hydrological theory of catchment response needs to be able to treat the analysis and prediction of travel time distributions and residence time distributions in both unsaturated and saturated zones (and surface runoff) in understanding variations in water quality from point and diffuse sources [e.g., McDonnell et al., 2010; Beven, 2010]. This raises, however, an interesting issue. Travel and residence times on hillslopes will be strongly controlled by water flow processes in the soil and regolith. The details of those processes, including the heterogeneities of soil properties, preferential flow pathways and bypassing, details of root extraction etc., are essentially unknowable using current measurement techniques, including modern geophysics. Such details, however, my be important in the response of the hillslopes [see, e.g., Beven, 2006, 2010]. One way of learning about the bulk effects of such complexity at the hillslope and catchment scales is the interpretation of tracer observations to provide information about Lagrangian velocity distributions. This information differs from that given by the hydrograph response because of the differences between the mechanisms controlling wave celerities and water velocities. This paper will demonstrate that the interpretation of tracer information needs to become

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more sophisticated and, in particular, to consider more explicitly the variation in time of travel and residence time distributions, precisely defined in what follows.

[3] There are dynamic models that deal with both flow and transport that have been developed primarily within the groundwater field. Such models can be purchased with complete graphical interfaces and, as well as flow and transport calculations, and be linked to chemical reaction codes. The theory on which such models are based is, however, restrictive. It (mostly) assumes that flow is Darcian and dispersion is Fickian and requires spatial distributions of flow and transport parameters to be specified. Experiments and theory suggest that those parameters are both place and scale dependent [e.g., *Dagan*, 1989]. The patterns of effective parameter values are not easy to either specify a priori or infer by calibration. In addition, the problem of groundwater transport has often been simplified, for convenience in obtaining analytical solutions, to transport and dispersion in steady flows in appropriately defined stream tubes [e.g., *Destouni and Cvetkovic*, 1991; *Cvetkovic and Dagan*, 1994; *Destouni and Graham*, 1995; *Gupta and Cvetkovic*, 2000, 2002; *Lindgren et al.*, 2004, 2007; *Botter et al.*, 2005; *Darracq et al.*, 2010]. While applicable to regional groundwater systems, this approach is not well suited to the type of catchment hillslopes with relatively shallow flow pathways that is of interest here where the flow system may include transient saturation, macropores and other types of small-scale preferential flows [*Beven and Germann*, 1982; *Hooper et al.*, 1990; *Peters and Ratcliffe*, 1998; *Burns et al.*, 1998, 2001; *Freer et al.*, 2002; *Seibert et al.*, 2003].

[4] An alternative strategy, that does not require specifying spatial distributions of parameters has been to work directly at the catchment scale, taking advantage of tracer information to try and identify travel time distributions directly from observed concentration series of inputs and outputs. Such tracer information has had a revolutionary effect on the understanding of hydrological processes, especially since the papers of *Crouzet et al.* [1970] and *Dinçer et al.* [1970]. Later, *Sklash and Farvolden* [1979] showed how the interpretation of tracer concentrations implied a large contribution of preevent or "old" water to the hydrograph and, in some storms, even to surface runoff. Both artificial tracers (generally at small scales) and environmental tracers have been used. The problem then has been to identify a suitable set of assumptions about travel time distributions that were consistent with the observational data [e.g., *Dinçer and Davis*, 1984; *Lindstrom and Rodhe*, 1986; *Rodhe et al.*, 1996; *McGuire and McDonnell*, 2006; *McGuire et al.*, 2007; *Botter et al.*, 2008, 2009; *Soulsby et al.*, 2009, 2010; *Tetzlaff et al.*, 2008, 2009; *van der Velde et al.*, 2010].

[5] A primary assumption, commonly made, concerns the time invariance of the travel time distribution implying that the fraction of water particles entering the catchment at time t_i as rainfall and exiting through the control surface (CS) as discharge at time t strictly depends on the delay $\tau = t - t_i$. The ensuing simple identification of the travel time distribution as a linear transfer function between inputs and outputs has problems. In particular, the assumption of time-invariant transfer functions will not be valid when catchment storage is changing (see, e.g., the rigorous demonstration by *Niemi* [1977]) and/or when advection fields are in unsteady

conditions and thus expected fluxes and travel times will change significantly and nonlinearly with wetting and drying. This limitation has been recognized by a number of authors in the past [e.g., *Zuber*, 1986; *Lindstrom and Rodhe*, 1986], but the method is still being applied widely without a proper recognition of the effects that it can have on the inferred travel time distributions [e.g., *Kirchner et al.*, 2010]. Moreover, when transport of reactive tracers is studied to infer travel time distributions, mass exchanges between fixed and mobile phases [e.g., *Rinaldo and Marani*, 1987; *Rinaldo et al.*, 1989] or the effects of tracer "half-life" [see, e.g., *Stewart et al.*, 2010; *McDonnell et al.*, 2010] are unavoidable sources of time-variant behavior. Thus analysis of travel time distributions at the catchment scale has many attractions, but there has been little work reported in the literature that has attempted to assess the practical effects of the time invariance assumption (but see *Botter et al.* [2010] and *van der Velde et al.* [2010]).

[6] In this paper we will review and complement the recent progress that has been made toward a unifying theory of flow and transport in shallow pathways at the catchment scale. This involves: issues of the time variance of flow and transport in inferring travel time and residence time distributions; the differences between celerities and velocities in controlling the hydrograph and tracer responses; and the contributions of old water to the hydrograph. We will show how certain traditional assumptions are not tenable except under special restrictive conditions. We will also briefly consider what observational data are required to be able to differentiate between models of flow and tracer response at the catchment scale. Specifically, section 2 provides precise definitions of travel and residence time distributions, and conditions for their equivalence, with a view to the transport features implied. It also derives rigorous linkages among the various quantities, including the relation between residence and travel time distributions and basic hydrological quantities that can be computed or measured. Section 3 highlights key differences, emerging from the dependence of the output fluxes from the sequence of states experienced by the system, obtained from the exact solution to a minimalist model. Section 4 examines the outcomes of very detailed numerical modeling that limit the number of assumptions to a minimum and integrate flow and transport in heterogeneous catchments from first principles. From comparing these results with exact solutions to oversimplified schemes, we illustrate the validity and limitations of the results proposed. Section 5 discusses the identification of variant catchment travel time distributions. A set of conclusions then closes the paper.

2. Catchment Residence and Travel Time Distributions

[7] Water flow in soils (and within other natural formations) is seen as a transport process where water particles injected through rainfall are stored and move within the catchment control volume toward different exit surfaces, in particular (Figure 1), (1) a compliance (or control) surface (CS), acting as an absorbing barrier where runoff Q is released to a receiving water body (or collecting channel), and (2) the surface area A of the catchment, where evapotranspiration, ET, usually abstracts significant amounts of water that is not then available for runoff production. We
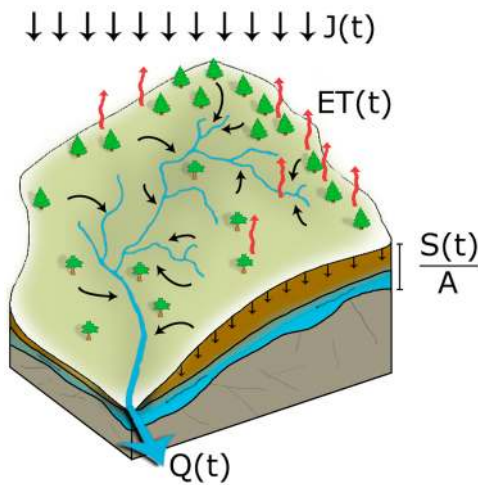
Figure 1. Sketch of the catchment control volume V.

neglect for simplicity losses to deeper horizons, pumping or water pathways that bypass the catchment closure CS, but note that they could be treated in the same framework.

[8] Water particles are advected by a hydrologic flow field $\mathbf{V}(\mathbf{x}, t)$ of water flow through the soil (with $\mathbf{x}$ a coordinate vector of Cartesian components x_1, x_2, x_3; t is time), generally assumed to be unsteady at catchment scales. Indeed, hillslope saturated zone dynamics, especially those involved in age partitioning (but also groundwater ridging, saturation overland flow and various throughflow processes), prove markedly unsteady [e.g., *Beven*, 2001; *Fiori and Russo*, 2008]. A Lagrangian representation of flow is based on the trajectories $\mathbf{x} = \mathbf{X}(t, \mathbf{a})(\mathbf{a} \in \mathbf{A}$ being the injection point with $\mathbf{X} = \mathbf{a}$ for $t = 0$) of marked fluid particles. They satisfy the kinematic equations: $d\mathbf{X}/d\mathbf{t} = \mathbf{V}(\mathbf{X}, t)$. The functions $t_{EX}(\mathbf{x_E}, \mathbf{a})$ defining the exit time of a tagged fluid particle (i.e., injected at $\mathbf{x} = \mathbf{a}$ at $t = 0$) to any exit boundary of the control volume (that is, at an exit point of coordinate $\mathbf{x_E}$ belonging to any exit surface) are solutions of the equation $\mathbf{x_E} - \mathbf{X}(t_{EX}, \mathbf{a}) = \mathbf{0}$ [*Cvetkovic and Dagan*, 1994]. Note that if an arbitrary injection time $t = t_i$ were chosen the proper notation for exit times would become $t_{EX}(\mathbf{x_E}, \mathbf{a}, t_i)$.

[9] Non–point source areas are defined by a collection of spatially distributed tagging sites $\mathbf{a}$ and by a sequence of input fluxes $J(\mathbf{a}, \mathbf{t_i})$. The latter is usually simply assumed to be a function of time alone, $J(t_i)$. This assumption is realistic if the correlation scale of precipitation fluctuations in space is larger than the catchment size (e.g., the square root of the area). Note that spatially constant rainfall J does not imply spatially constant evapotranspiration ET for its variability may stem from uneven vegetation cover and water table depths. Because typically in hydrologic contexts $\mathbf{X}$ is a random field [e.g., *Dagan*, 1989], exit times are viewed as random variables characterized by probability distributions.

[10] Here, we differentiate exit times with respect to the type of exit surface. In particular, we define the travel time $t_T = t_{EX}(\mathbf{x_{CS}}, \mathbf{a}, \mathbf{t_i})$ as the travel time to any point $\mathbf{x_{CS}}$ of the control surface CS where runoff Q leaves the catchment control volume (i.e., t_T is defined as time elapsed between the injection of the particle and its passage through the control section as Q). Analogously, t_{ET} is the time elapsed

between injection and release in the atmosphere as $ET(t)$. The exit time t_{EX} of each particle thus equals either t_T or t_{ET}.

[11] In what follows we employ the following definitions and notation:

[12] 1. We define $p_T(t_T, t_i)$ to be the probability density function of the travel times t_T conditional on a given injection time t_i, i.e., the normalized count of the travel times to CS of the relative fraction of particles injected at t_i anywhere at the injection surface A.

[13] 2. We define as $p'_T(t_T, t)$ the travel time distribution conditional on the exit time t [*Niemi*, 1977]. This function is defined by tracking each travel time for all particles that exit at a given time t, properly normalized, and is related to the so-called inverse travel time distribution [*van der Velde et al.*, 2010]. Note that generally p_T and p'_T are different unless for very special circumstances which we shall consider below.

[14] 3. We further define as $p_{RT}(t_R, t)$ the probability distribution of residence times t_R of the water particles stored within the control volume V at time t (the time spent in the transport volume by each particle injected at t_i when gauged within V at t is $t_R = t - t_i$). Thus the relative fraction of particles injected at t_i that have not exited V has residence time $t_R = t - t_i$, and one computes all such fractions for any relevant injection time from $-\infty$ to t (obviously particles injected at $t = t_i$ hold null residence time, or $t_{RT} = 0$).

[15] Normalized rainfall fluxes define the probability distribution of injection times t_i. Likewise, exit times through evapotranspiration t_{ET} (and their pdf p_{ET}) are defined by analogy with the cases described above.

[16] A large body of literature suggests that travel and residence time distributions integrate complexities and uncertainties associated with hillslope and catchment transport, and are naturally suited to comparison with observational data that record outgoing fluxes from/to the various compartmental control surfaces and should thus be seen as robust descriptors of complex hydrologic transport phenomena [e.g., *Dagan*, 1989; *Destouni and Cvetkovic*, 1991; *Rodriguez-Iturbe and Rinaldo*, 1997; *McDonnell*, 1990; *Beven*, 2001; *McGuire and McDonnell*, 2006; *Tetzlaff et al.*, 2008; *Beven*, 2010; *Soulsby et al.*, 2010]. The key point here, however, is that in the general case the probability functions p_T and p'_T do not coincide. Significantly, *Niemi*'s [1977] theorem (suitably extended) allows to recover one given the other. In fact, if $\theta(t_i)$ is the fraction of the rainfall flux $J(t_i)$ that ends up as runoff Q (Appendix A), by continuity the following general relation holds:

$$p'_T(t - t_i, t)Q(t) = J(t_i)\theta(t_i)p_T(t - t_i, t_i) \tag{1}$$

whose physical meaning consists of equating the fraction of particles that enters V at t_i and exits at t as Q (left-hand side) to the relative fraction of rainfall entered at t_i that exits as Q at time t (right-hand side). One may show that only in quite restrictive cases will these be the same. These imply (1) steady state advective velocity fields determining travel times τ, i.e., $\mathbf{V}(\mathbf{x}, \mathbf{t}) \sim \mathbf{V}(\mathbf{x})$, and (2) the linearity in the partition between rainfall and runoff/evapotranspiration. Only then will the two distributions collapse into a single curve becoming invariant $p_T(t - t_i, t_i) \approx p_T(t - t_i) = p'_T(t - t_i)$. It then follows from *Taylor*'s [1921] theorem, if no water particle is lost ($ET = 0$, $\theta = 1$), that the stored volume at t is proportional to the probability of travel time being larger
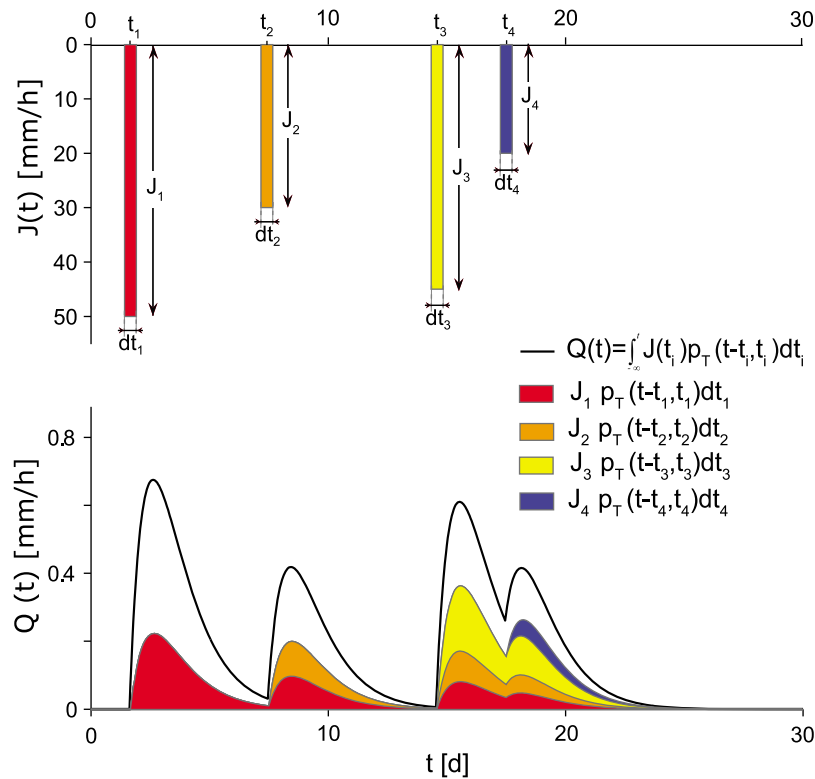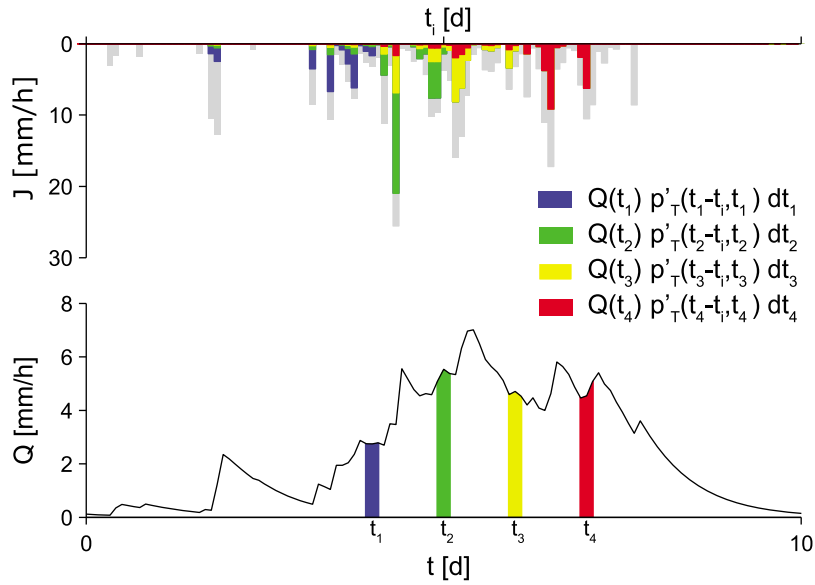
Figure 2. An illustration of the physical meaning of $p_T(t - t_i, t_i)$. (top) An arbitrary sequence of rainfall fluxes $J(t_i)$ is shown. (bottom) The discharge time series $Q(t)$ may be expressed as a convolution between the rainfall input and a set of time-variant exit time pdfs, $p_T(t - t_i, t_i)$, once remobilization of old water is allowed. The temporal evolution of the contributions to Q due to water belonging to each of the four input pulses reported in the top plot are represented by the shaded areas (which are coded by the same color of the corresponding input). Note that the white area in the bottom plot represents water volumes whose exit time is larger than $t - t_1$.

than t and that the normalized flux Q at the outlet (CS) in response to a pulse (the IUH) is the probability density function of travel times to the CS [see, e.g., *Rinaldo and Rodriguez-Iturbe*, 1996; *Rinaldo et al.*, 2006a, 2006b]. This has been the basis for the classic engineering hydrology concept employing the isochrones of travel times for effective rainfall to define the catchment response [e.g., *Beven*, 2001; *Brutsaert*, 2005], and also for the geomorphological theory of the hydrologic response that sees the overall catchment travel time distributions as nested convolutions of statistically independent travel time distributions along sequentially connected, and objectively identified, geomorphic states whether channeled or unchanneled [*Rodriguez-Iturbe and Valdes*, 1979]. This allows one to find exactly the moments of catchment travel time distributions under arbitrary geomorphic complexity [*Rinaldo et al.*, 1991], but only under this special case of invariant conditions. Note also that in the nonstationary case the IUH for the hydrograph response will not be equal to $p'_T(t - t_i, t)$ because of the difference between celerities that control the hydrograph response and velocities that control the transport process. In general, celerities will be faster than pore water velocities in soils [e.g., *Beven*, 2001, p. 141] and streamflow velocities in open channels [*Rinaldo et al.*, 1991].

[17] Figures 2 and 3 illustrate the physical meaning of $p_T(t_T, t_i)$, the pdf of the travel times conditional on a given injection time t_i, and its counterpart, $p'_T(t_T, t)$, with the pdf of travel times conditional on the exit (or sampling) times t, respectively. The former distribution of $p_T(t_T, t_i)$ (Figure 2) is described by tracking the travel times to the control surface of the relative fraction of particles injected at t_i anywhere at the injection surface. The latter ($p'_T(t_T, t)$) is determined by tracking the travel times for all particles that exit the catchment at a given time t. This paper aims, in particular, to provide quantitative evidence of the significant differences that should be expected between p_T and p'_T except in very special cases. This differences are important, both theoretically and practically, as the former is needed for rainfall-runoff transformations whereas the latter is what is actually measured by sampling concentrations at the catchment outlet. Note that in the particular case of a well-mixed reservoir, the distributions $p'_T(t_T, t)$ and $p_{RT}(t_R, t)$ coincide (Appendix A), as the particles exiting the control volume at time t are randomly sampled among all particles within V. We assume this case for our examples.

[18] In most cases relevant to field conditions, travel time, exit time and residence time distributions will depend on the temporal patterns of storage and partitioning between discharge and evapotranspiration losses which in turn control the remobilization of old water induced by each rainfall event [e.g., *Botter et al.*, 2010]. This suggests that the analyses of environmental tracer data determining catch-

Figure 3. An illustration of the physical meaning of $p'_T(t - t_i, t)$. The graph shows how the discharge time series $Q(t)$ sampled at t is made up of water particles injected at different times t_i whose various travel times are $t_T = t - t_i$. As stressed in the text, this distribution is the one measured by any age-dating techniques and may differ notably from the travel time distribution p_T conditional on injection time. The fractions of the total flux $J(t_i)$ (color coded in grey) exiting the catchment as Q at time t are color coded as the corresponding output.

ment travel time distributions by assuming stationarity of the transfer function between input and output time series need be reexamined [e.g., *Kirchner et al.*, 2010]. With the above positions, we can generally characterize catchment transport phenomena. For simplicity, we shall examine here the case of the transport of passive scalars advected by the velocity field and undergoing no reactions between fixed and mobile phases (for treatment of more complex cases involving chemical, physical or biological reactions the reader is referred, e.g., to *Ozyurt and Bayari* [2005], *Botter et al.* [2010], and *van der Velde et al.* [2010]). Passive scalars are injected onto the catchment through rainfall with concentration $C_{in}(t)$, and are measured as flux concentrations at the control surface (as $C_{out}(t)$). In the above framework the input-output concentration relation is

$$C_{out}(t) = \int_{-\infty}^{t} C_{in}(\tau) p'_T(t - \tau, t) d\tau \qquad (2)$$

where p'_T is the proper transfer function. Note that invariant versions of equation (2) have been questionably used to interpret tracer field data [e.g., *Kirchner et al.*, 2010]. If a pulse of mass M in $t = 0$ (lasting a conventionally short time Δt) endowed with concentration C_0 is uniformly applied through a spatially uniform rainfall $J(0)$, one has the interesting result:

$$C_{out}(t) = C_0 \, \Delta t \, p'_T(t, t) = \frac{M}{J(0)} p'_T(t, t) \qquad (3)$$

leading to the observation that the exit concentration samples the subset of values $p'_T(t, t)$ at increasing times. This subset had been termed the weight function [*Maloszewski and Zuber*, 1982].

[19] From equations (1) and (3) one obtains that the outflowing solute mass flux $Q_M(t)$ [M/T] is given by

$$Q_M(t) = C_{out}(t)Q(t) = M\theta(0)p_T(t, 0) \qquad (4)$$

with usual symbols' notation. Note that for an arbitrary injection of M at time $t = t_i$ one would have had $Q_M(t) = M \, \theta(t_i) \, p_T(t - t_i, t_i)$.

[20] Finally, one must define the resident concentration, say $\overline{C}_R(t)$, as the average of the individual concentrations of the water particles in storage within the catchment at time t as a function of the residence times (or age) distribution [see, e.g., *Maloszewski and Zuber*, 1982]. For passive solutes, the mean resident concentration $\overline{C}_R(t)$ of the stored particles at time t is given by

$$\overline{C}_R(t) = \int_{-\infty}^{t} C_{in}(t_i) p_{RT}(t - t_i, t) dt_i \qquad (5)$$

which derives from the accounting of the relative fractions of particles entered at $t = t_i$ that at time t have age $t - t_i$ in the control volume [see, e.g., *Rinaldo et al.*, 1989; *McDonnell*, 1990; *McDonnell et al.*, 1991; *Maloszewski et al.*, 1992; *Evans and Davies*, 1998; *Weiler et al.*, 2003; *McDonnell et al.*, 2010]. Recently, the watershed equivalent of the Lagrangian description used by *Cvetkovic and Dagan* [1994] (inspected for large-scale properties by *Botter et al.* [2005]) has been discussed by *Duffy* [2010] (see also *Duffy and Cusumano* [1998]), leading to dynamic modeling of concentration-age-discharge through deterministic conservation equations.

[21] For reactive solutes, resident concentrations are harder to pin down. Individual concentrations of water particles may be defined as $C_R(t, t_i)$ and controlled by transport
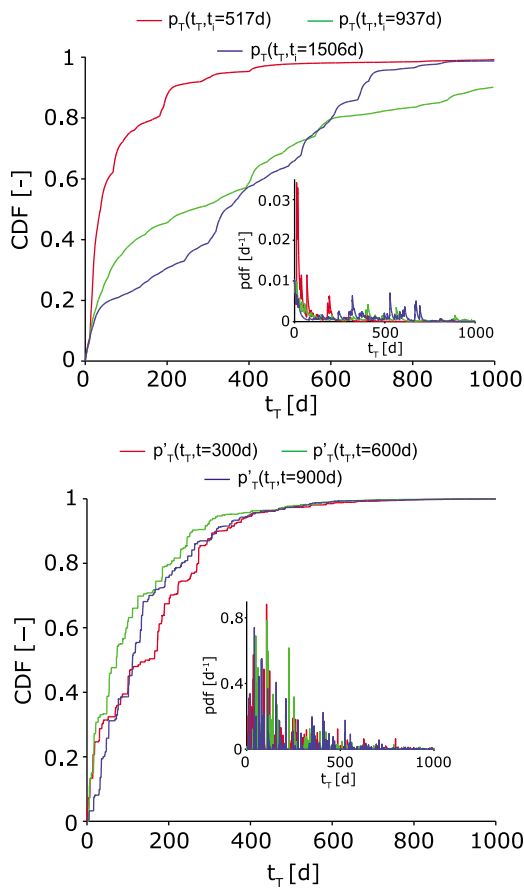
Figure 4. A comparison of (top) $p_T(t_T, t_i)$ for different injection times t_i and (bottom) $p'_T(t_T, t)$ for different sampling times t for a dry climate. Cumulated density functions and probability distributions (insets) are shown. Here total precipitation is fixed at 180 mm/yr with 10% of rainy days (average interarrival rate $\lambda = 0.1$ d^{-1}, average rainfall pulse $\alpha = 5$ mm) (see auxiliary material for computational details).

phenomena driven by the contact time $\tau = t - t_i$ (as an example, a reaction kinetics of the type $\partial C_R(t, t_i)/\partial \tau = \mathcal{F}[C_R(t, t_i) - B(t)]$ where B is a relevant concentration in 'fixed' (as opposed to mobile) phases, $\mathcal{F}[\cdot]$ being a suitable mass exchange scheme [e.g., *Rinaldo et al.*, 1989]). To avoid issues of spatial variability, one may assume the system to obey the mass response function postulate [*Rinaldo and Marani*, 1987; *Rinaldo et al.*, 1989; *Botter et al.*, 2005]; that is, whenever the characteristic size of the injection area is large with respect to the correlation scale of heterogeneous properties of the catchment control volume (say, land use and cover, heterogeneity of the soils), resident concentrations are solely driven by the contact time between fixed and mobile phases, which is the residence time of the water particle within the transport volume V. Spatial effects may thus be conceptualized in the non–point source framework. This is the case for the assumption of a reservoir for mass exchanges uniformly distributed over the catchment allowing C_R not to depend on **x** because averaging over a large number of stream tubes yields a significant mean field property of the transport volume [*Botter et al.*, 2005]. In such a case one may write the analog of

equation (6) as [*Rinaldo and Marani*, 1987; *Botter et al.*, 2005, 2010]:

$$\overline{C}_R(t) = \int_{-\infty}^{t} C_R(t, t_i) p_{RT}(t - t_i, t) dt_i \qquad (6)$$

which is a mass response function approach for reactive solute transport at catchment scales.

[22] The above equations define a general framework for the nonlinear, time-variant description of travel time distributions for water flow through soils at the catchment scale. The predictions of the theory are dependent on mixing assumptions (Appendix A), which must reflect the distributions of flow velocities, the distributed nature of the inputs, and the difference between advective velocities of water particles and the celerities that control the hydrograph response over the length scales of the hillslopes in the catchments. The mixing assumptions approximate the details of the distributed responses but, as will be shown below, can do so effectively in particular when compared to the results of a detailed simulation that tackle the relevant physical processes operating at the catchment scale.

3. Catchment Travel Times From an Exact Minimalist Model

[23] To illustrate the differences between the travel time distributions $p_T(t_T, t_i)$ and $p_T(t_T, t)$, this section describes a series of examples showing a summary of the behavior of the relevant quantities obtained using an exact solution of a lumped model of dynamic catchment behavior [*Botter et al.*, 2010], described in Appendix A (see also auxiliary material for a complete description of the computational details, including the synthetic generation of diverse rainfall inputs J, the calculation of evapotranspiration fluxes ET and the parameters' values adopted).[1] Note that in the specific case considered here, the particles exiting the control volume at time t are assumed to be randomly sampled among all particles within V, leading to the equivalence between the distributions p_T and p_{RT} (Appendix A).

[24] Figures 4 and 5 show the travel time distributions conditional on three different injection times chosen at random within Poissonian sequences of forcing rainfall (Figures 4 (top) and 5 (top)), and the travel time distributions conditional on three different exit times (Figures 4 (bottom) and 5 (bottom)) for a dry and a wet climate, respectively. Figures 4 and 5 show both the probability density functions of travel times (insets) and their integral (i.e., the cumulated probabilities), to better appreciate the overall differences smoothed by integration. It clearly appears that, in general, the distributions p_T and p_T do not coincide whatever the injection/exit time chosen. The radical departures between the two types of travel time distributions is evidenced in both cases (Figures 4 and 5). Moreover, one readily notes the substantial differences arising in the travel times conditional on different injection times t_i for the dry catchment (Figure 4, top), which suggest the marked time variance of the system. Such differences are attenuated, but far from negligible, in the wet case (Figure 5, top).
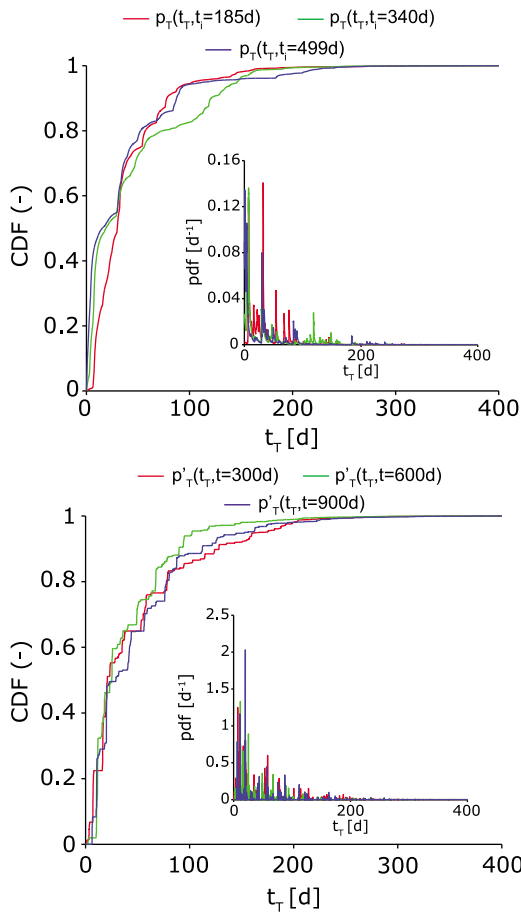
Figure 5. As in Figure 4 but for a wet climate (total precipitation is 2000 mm/yr with 30% of rainy days, average rainfall interarrival rate $\lambda = 0.3$ d^{-1}, and average rainfall pulse $\alpha = 20$ mm).

[25] An important synthesis of the above results is shown in Figure 6, where the distributions of the average travel times (computed from p_T over all injection times t_i) and the average residence times (computed from p'_T over all sampling times t, being in this case (Appendix A) $p_{RT} \equiv p'_T$) are shown for the dry and wet cases, respectively. Interestingly, one notes that the wetter the catchment, the closer the mean residence and travel time distributions become. This was somewhat expected, because time-invariant conditions tend to be approximated only for consistently wet conditions and for the bulk of the distribution rather than in its tails, whereas in dry cases such differences can never be overlooked for they are substantial as highlighted by the vast difference in their means. Suffice here to note that the implications of the differences in travel and residence time distributions are often overlooked in catchment hydrology with various consequences. In particular, isotope hydrology is based on measuring the mix of travel times of exiting particles conditional on the sampling at time t (a proxy of p'_T) whereas it is often used to infer travel time distributions conditional on injection times (which requires the definition of p_T). Note that only in particular cases, notably for wet conditions, a reasonable degree of invariance is observed as indicated by the collapse of different cumulated distributions. Thus we suggest that differences between p_T and p'_T emerge in many cases of practical interest owing to their

differing dependence on the sequence of hydrologic forcings and thus of the state variables that control catchment behavior.

[26] Of course, it remains to be seen whether the above remarks are tied to the specifics of the examples chosen. One notices, however, that similar results have been obtained by *Botter et al.* [2010] for a two-layer model where the first embeds soil moisture dynamics, and by *van der Velde et al.* [2010] for a study using p'_T to describe nitrate and chloride circulation at catchment scales. In section 4 we shall show by comparison with sophisticated numerical solutions that such effects are not the byproduct of the specific assumptions built into the particular model chosen for proof of concept, much less a numerical artifact, but rather reflect a general tendency of catchment transport.

4. Catchment Travel Times From Complete Numerical Simulation of Flow and Transport in a Spatially Heterogeneous Hillslope

[27] To stress the general nature of our results, we have computed the same kinematic quantities through a completely different approach, specifically one that operates under a minimum of assumptions on the behavior of the system. In the next example, in fact, we simulate the transport of a tracer in a variably saturated, spatially heterogeneous hillslope connected to a surface water stream. The tracer is used in order to mark the water in the system,
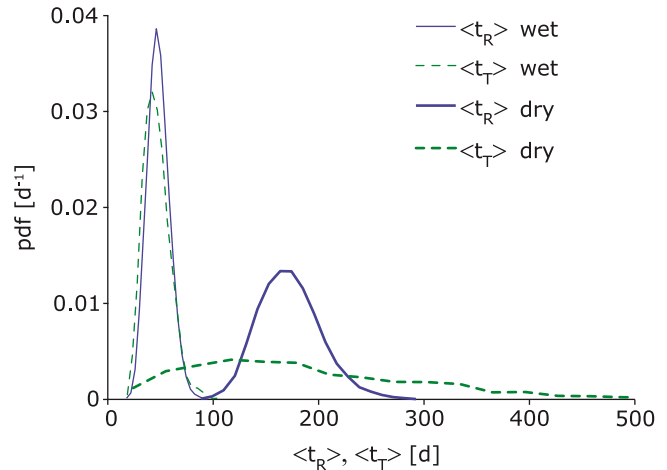
Figure 6. Distribution of the mean travel times $\langle t_T \rangle$ generated from all injection times t_i ($\langle t_T \rangle = \langle t_T \rangle_{ti} = \int_0^\infty p_T(t_T, t_i)t_T dt_T$) in the wet and dry cases dealt with in Figures 6 and 7 compared with the distribution of the mean residence times $\langle t_R \rangle$ generated for a large batch of sampling times t for the cases in Figures 6 and 7 ($\langle t_R \rangle = \langle t_R \rangle_t = \int_0^\infty p'_T(t_T, t)t_T dt_T$). Note that here the residence time is generated via the distribution p'_T owing to the well-mixed assumption (Appendix A) that allows for $p_{RT} \equiv p'_T$. Note also the vast differences in the mean values emerging in dry cases, which are progressively reduced as wet conditions are attained (in this case tuned by a proper choice of rainfall interarrival rates). Single realizations (i.e., single travel time distributions conditional on different initial times) may nonetheless be very different even in very wet cases, depending on initial conditions and on the actual sequence of rainfall events triggering runoff and speeding up the discharge formation process.
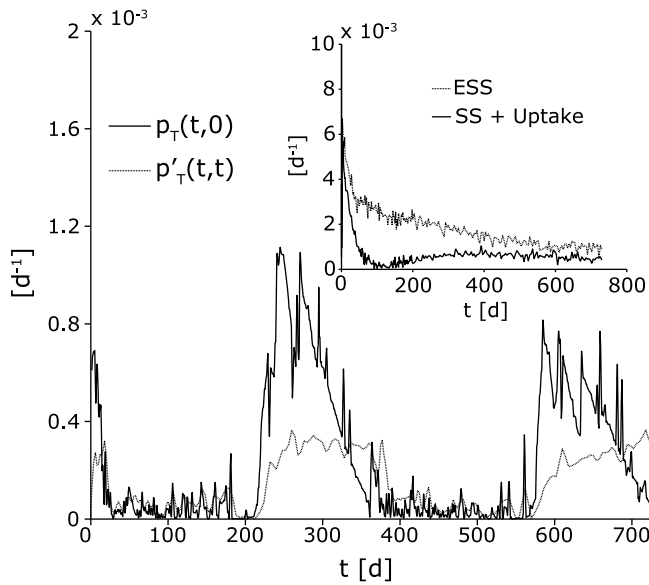
Figure 7. The probability distribution $p_T(t, 0)$ and the function $p'_T(t, t)$ for the APR case computed by the complete numerical integration of the flow and transport equations in the heterogeneous saturated or unsaturated 3-D hillslope modeled by *Fiori and Russo* [2008]. Here water flow and tracer transport are simulated for a year starting on 1 April (APR; pulse release during "dry" season). Note that the curves display significant periodicity driven by the seasonal variability of precipitation and evapotranspiration. The inset shows steady state travel time distributions (where, by definition, verified computationally to precision, $p_T(t, 0) = p'_T(t, t)$) in two relevant cases: (1) steady state flow with prescribed mean annual net recharge (ESS) and (2) steady flow with prescribed mean annual precipitation and a root zone with given, constant mean annual uptake (SS + UP). The steady state travel time distributions are significantly different from their time-variant counterparts, do not show any periodicity, and show a more persistent tail. Differences between the two curves stem from the different spatial distribution of solute uptake by roots, which is spatially uniform for ESS and nonuniform for SS + UP.

including uptake by plant roots. This case study is analogous to the one considered by *Fiori and Russo* [2007, 2008]. The formation consists of a relatively shallow layer of a high-conductive soil overlying a relatively thick layer of low-conductive subsoil (bedrock). Details of the flow domain, the relevant equations, the computational scheme, and the boundary conditions embedding climatic conditions are reported elsewhere (see auxiliary material; suffice here to recall that the flow parameters are heterogeneous and spatially distributed, the statistics of their relevant soil parameters being given by *Fiori and Russo* [2008, Tables 1 and 2]. Complete details on the numerical schemes involved in the solutions of the governing equations are given by *Russo et al.* [2001, 2006], *Russo and Fiori* [2008], *Fiori and Russo* [2007, 2008], and *Russo* [2011]).

[28] Critical to the scheme, and to a comparison with other schemes, is the evaluation of exit fluxes. Considering water uptake by plant roots, water flow and solute transport in the three-dimensional, heterogeneous flow system were simulated by employing numerical solutions of the "mixed" form of Richards equation and the classical, single-component, convection dispersion equation (CDE), respectively. Water flow and tracer transport were simulated for a sequence of two identical successive years, starting on 1 April (APR; pulse release during "dry" season) or 1 September (SEP; pulse release during "wet" season). A flow domain initially tracer free was considered (see auxiliary material).

[29] The numerical scheme (and any tracer experiment) does not allow to compute $p'_T(t_T, t)$ for different sequences of injections at times t_i unless individual particle tracking schemes are enforced onto the transport model. Thus, in the following $p'_T(t_T, t)$ is represented as a function of exit time t ($p'_T(t, t)$ of equation (3)), which corresponds to the weight function [*Maloszewski and Zuber*, 1982] that one would obtain from application of the convolution model to flux averaged concentration data as consequence of an instantaneous release of tracer at the surface. The travel time distribution $p_T(t_T, t_i) = p_T(t, 0)$ (where $t_i = 0$ and $t_T = t$ are the time of injection and the travel time, respectively) is given (equation (4)) by $p_T(t, 0) = F(t)/(M\theta(0))$; in the latter F is the solute flux $[M/T]$ at the control section and $M\theta(0)$ is the total mass flowing to the river, the difference between the tracer injected and that uptaken by the roots. The function $p'_T(t_T, t) = p'_T(t, t)$ (equation (3)) is obtained by $p'_T(t, t) = \overline{Q_i}F(t)/(M\theta(0)Q(t))$, with $\overline{Q_i}$ and Q the mean net rainfall during injection (i.e., rainfall minus ET) and discharge through the control section (here the river), respectively.

[30] The distribution $p_T(t, 0)$ and the function $p'_T(t, t)$ as a function of t_T are represented in Figure 7 for the APR case, as an example. The curves display a significant periodicity driven by the seasonal variability of precipitation and evapotranspiration. The role of ET on transport is subtle, as it removes solutes in both the initial (i.e., the injection) and the final (the discharge) stage of the transport process. In fact, when the plume approaches the river, the water table in the riparian area is near the surface and roots are very effective in draining water and the tracer; this feature thus derives from the combined effect of ET and of the system geometry. It is worth mentioning that a significant portion of the injected mass is still present in the system after 2 years, around 40% for both cases APR and SEP. Thus, the distributions depicted in Figure 7 miss the late-time tail, which would require additional years of simulation to be adequately captured. The mass fraction which left the system by transpiration strongly depends on the injection period, and after 2 years it was around 45% (APR) and 25% (SEP). Hence, a correct evaluation of the actual ET fluxes appears as a fundamental prerequisite for assessing travel times in different periods of the year.

[31] Figure 7 clearly shows that the distribution $p_T(t, 0)$ and the function $p'_T(t, t)$ are quite different even though in the steady state they must coincide. Their time integrals differ as the integral of $p_T(t, 0)$ is unit, while that of $p'_T(t, t)$ depends on the entire discharge history and is not unit unless ins steady sate conditions. It is seen that $p_T(t, 0)$ is typically more noisy than $p'_T(t, t)$, which is somewhat smoothed out as it represents the more regular flux averaged concentration [e.g., *Kreft and Zuber*, 1978]. The APR case (Figure 7) exhibits a relatively small peak at the injection time followed by larger peaks after periods of 1 year lag. This happens because the injection occurs in a relatively dry period, and the tracer initially does not move much from its
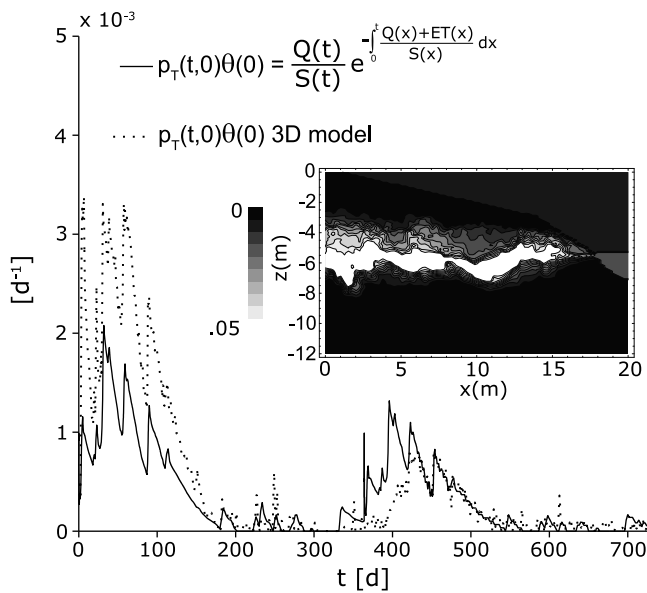
Figure 8. Comparative analysis of the computations of $p_T(t, 0)\theta(0)$ from the numerical 3-D model (SEP case) and the exact solution to the lumped model described in Appendix A. The wet case (SEP) is represented here for comparative purposes. Note that the complete formulation of the exact solution is given in equations (A4) and (A5), properly normalized. The inset shows a snapshot of an instantaneous concentration field of the passive solute [*Fiori and Russo*, 2008; *Russo and Fiori*, 2009], color coded in a grey tone scale (white is the maximum concentration, and black is null concentration). Note the lack of complete mixing exhibited by the field and, nevertheless, the surprisingly effective match of the exact solution postulating it. Indeed, when continuity of the total mass within the control volume V is considered (by integration in space of instantaneous concentrations over V), differences smooth out and the exit fluxes sum well the entire process. Such result highlights the robustness of the travel time formulation of transport owing to its integrative nature and the potential for determining variant travel time distributions upon direct measurement of the relevant macroscopic fluxes (J, Q, and ET) at the catchment scale.

initial location; also, a significant fraction of the mass leaves the system by transpiration. The later peaks of the distribution correspond to the beginning of the "wet" period in which the increased precipitation (and reduced ET) contribute to the flushing of the tracer out of the hillslope. Interestingly enough, the largest mode of the distribution is not the first one, as one would expect along the usual, time-invariant representation of the travel time pdf. The SEP case (Figure 8) displays a different behavior, with a larger peak near the injection time, which is reasonable as the injection is performed at the beginning of the wet period. Although both distributions display significant periodic features, the overall shape and sequence of modes are quite different from the APR case, indicating a strong dependence of the distributions on the time of the injection.

[32] For comparison, we also show the travel time distributions for steady state flow, leading to the classic time-invariant formulation of travel time (Figure 7, inset). In

such a case one derives exactly, and finds numerically, that $p_T(t, 0) = p'_T(t, t)$. We analyzed two different steady state configurations: (1) steady state flow with prescribed mean annual net recharge (i.e., total precipitation minus total actual ET), denoted as ESS, and (2) steady flow with prescribed mean annual precipitation and a root zone with given, constant mean annual uptake (SS + UP). The travel time distributions for the two configurations are depicted in Figure 7 and significantly different from their time-variant counterparts. Steady state results do not show any periodicity, and the tail of $p_T(t, 0) = p'_T(t, t)$ is always more persistent than those depicted in Figures 7 and 8. The difference between the two curves in the inset of Figure 7 derives from the different spatial distribution of solute uptake by roots, which is spatially uniform for case ESS [*Russo and Fiori*, 2008] and nonuniform for SS + UP [*Russo*, 2011]. In particular, the role played by solute uptake in the riparian area is quite significant and responsible for the observed nonmonotonous behavior of p_T with travel time. Altogether, the case study emphasizes a significant difference between the time-invariant and time-variant formulations of the travel time distributions. In the time-variant case the distributions p and p' are markedly different and strongly depend on the time of injection and generally on the history of meteorological forcings (precipitation and ET) as well as the system configuration. Thus an accurate representation of the ET fluxes proves fundamental for a correct representation of solute fluxes, which may strongly differ with the tracer/flow initial conditions.

[33] A snapshot of the concentration fields in space at a particular time is shown in the inset of Figure 8. It emphasizes the marked effects on the transport features of physical heterogeneities and the strong instantaneous spatial gradients of concentration underlying a far from complete mixing (where concentration would be spatially uniform) exhibited by the passive tracer. Nonetheless, Figure 8 shows the results of a comparative exercise with a minimalist scheme (Appendix A) implying complete mixing. In the exercise, the boundary fluxes $P(t)$, $ET(t)$ and $Q(t)$ (deriving by continuity the instantaneous storage $S(t)$) are computed by the numerical code by *Russo and Fiori* [2009]. For comparative purposes, we have computed the equivalent travel time distribution obtained exactly by *Botter et al.* [2010] from the minimalist model described in Appendix A. The comparative analysis of the travel time distributions shown in Figure 8 shows differences, of course, and yet reveals a surprising overall match of the results, critically including the nonstationary characteristics induced by the periodicity of rainfall forcings. The minimalist lumped catchment model seems to capture the bulk of the transport processes once fluxes are properly assigned. We suggest that this might prove an important result. In fact, the lumped nature of the exact approach to the conceptual scheme, and in particular the unrealistic complete mixing assumption, endows the system with an integral nature that smooths out much detail. This robustness is indeed a peculiar and attractive property of the formulation of transport by travel time distributions. This also suggests that field measurements of the relevant fluxes, as an alternative to computation, may provide direct information on the variant nature of travel times. Thus the key ingredient missing from past catchments models (the time-variant travel time distributions) may find a direct, analytical and reliable inclusion.

[34] While our results above should not be over-emphasized owing to the particular nature of the example, they are instructive and suggestive of possibly broad implications. Certainly, the integral nature of the exact solution obscures the process mechanisms that lead to differences between celerities (controlled by storage deficits) and velocities of particles in storage in the timing of hydrograph and travel time responses. These differences will be length-scale dependent and, depending on changes in storage and storage deficits, time variable. They underly the expected hysteresis in the control volume response [see *Beven*, 2006]. This additional complication is left for future work.

5. Identification of Time-Variant Travel Time Distributions

[35] The analysis above has revealed that residence and travel time distributions can vary significantly, particularly under dry antecedent conditions. Thus inferences about catchment travel times based on assumptions of linearity and stationarity will be gross (and misleading in the case of solute transport) approximations, even when simulated data are used in the analysis. In real catchments, the approximation will be greater since most published analyses are based on relatively poor information about the time and space variability of environmental tracers due to sampling limitations. Under the stationarity assumption they have also generally ignored variations in discharges, relying only on relating input to output concentrations even though there is evidence that tracer concentrations can vary significantly with discharges and in sequences of events [e.g., *Iorgulescu et al.*, 2005, 2007; *Rinaldo et al.*, 2006a, 2006b], that there may be mass imbalances between inputs and outputs [e.g., *Page et al.*, 2007], and that tracers such as the environmental isotopes of water might be affected by fractionation and vegetation uptake [e.g., *Brooks et al.*, 2010].

[36] To allow more realistic inferences about residence times better data sets will be required in which the time variability of input and output concentrations and flow rates are better characterized, particularly during hydrographs (even if it is accepted that the spatial variability might remain much more difficult to characterize). For environmental isotopes this is now becoming possible with the availability of a new generation of laser mass spectrometers, while some catchment experiments have committed to measuring water chemistry to much finer time resolution (e.g., *Kirchner and Neal* [2010] at Plynlimon, although the 7 h sampling time step used there is still relatively long compared with the response time of the catchment).

[37] It is still likely, however, that for the foreseeable future, analysis of residence and travel time distributions will still be based on bulk input and output concentrations and fluxes at the catchment scale. Direct measurements of concentrations within catchment storage will be prohibitive when the expectation is that there will be marked spatial variability of sample concentrations for different types of storage in different parts of the hillslope. This means therefore that any representation of the evolution of residence times in a catchment area will be dependent on fitting the multiple parameters associated with potential sets of assumptions to the observed bulk concentrations and fluxes. *Iorgulescu et al.* [2005, 2007] did this for a three component

end-member mixing model that allowed for dynamic mixing between the components. Even a simplified representation of the three components (rainfall, soil water and groundwater) resulted in 17 parameters. They sampled 2 billion parameter sets and accepted 216 as behavioral within specified limits of acceptability based on information about sampling variability and measurement accuracy. This allowed some testing of different hypotheses about the nature of the responses. The results showed quite clearly that the mixing of different sources and effective residence times (i.e., ages) were changing during the wetting up sequence of storms covered by the observations. This is an indication that more sophisticated analyses, allowing for the nonconservative nature of selected tracers, will be required as the observational data get better. This might also involve rethinking hypotheses about the mixing of different water sources in a catchment (see, e.g., the model of *Davies et al.* [2011]). It remains to be seen, however, what types of assumptions and method of fitting will be appropriate, since there will continue to be significant epistemic errors about the nature of the catchment characteristics and the details of its hydrological response (see also the discussion of *Beven* [2010]).

6. Conclusions

[38] In this paper we have discussed the issues that arise in considering the different types of travel time distributions within a catchment area. We have shown that the travel time distribution for water particles in an increment of discharge, will be different from the travel time distribution for a water particles in the inputs for a particular time step. These will also be different from the residence time distribution of water in storage on the hillslope/catchment transport volume. All of these distributions can be incorporated into a consistent formal theoretical framework, that implies that these distributions must be nonstationary and nonlinear, and formal relationships among them can be established. The implications of this more complete theory are in conflict with the normal assumptions made in the analysis of environmental tracer data at the catchment scale in which both linearity and stationarity are assumed. This means that the inferences made in such analyses might be incorrect (as also indicated by the dependence of inferred mean residence times from different tracers [e.g., *Stewart et al.*, 2010]).

[39] Moreover, we have shown that flow-weighted rescaling techniques [e.g., *Niemi*, 1977] used to obtain a surrogate stationary travel time distributions rely on assumptions (e.g., constant storage) rarely achieved in any real hydrologic setting, yielding misleading or wrong inferences, e.g., on the tails on travel/residence time distributions [e.g., *Kirchner et al.*, 2010]. The radical departures of travel time distributions from the age (or residence time) distributions appear clearly in all the cases presented, and is now justified theoretically. It is thus evident that such distributions should be expected to be different, in general, on kinematic grounds irrespective of the details of the transport model employed. This fact is often overlooked in hydrology, with various consequences. In particular, isotope or tracer hydrology is based on measuring the mix of ages of exiting particles conditional on the sampling at time *t* (a proxy of travel time distributions conditional on exit time) whereas it is often used to infer input-output transfer functions which require

the definition of travel time distributions conditional on injection times. This, we suggest, needs to be corrected: in the past, the limitations of the available observations have not justified the use of more sophisticated analyses than types of steady state analyses commonly used, but the time seems ripe, owing to our improved measuring capabilities and to the general theoretical framework now available, for a true paradigm shift in theory and practice.

[40] The interpretation of travel and residence time distributions would be greatly facilitated if it was possible to know more details of the complexity of water flows on hillslopes. Unfortunately, this still seems a long way off, except at very local scales, and the most important source of field evidence about the water flow velocities in the soil system is likely to be natural and artificial tracers. But as we have shown here, the interpretation of tracer information requires that the time variability of the water flow in soils be considered.

[41] Some aspects still need to be addressed. In particular, we have noted that the travel time distributions controlling hydrograph shape, related to the distribution of wave celerities in the system will be different from the travel time distributions for water particles controlled by the water velocities. Both are also dependent on the length scales of the flow pathways in the system. These differences will affect the mixing assumptions required in the kinematic theory at catchment scale presented here to provide good simulations of the actual concentration responses in a catchment given estimates of the exit fluxes. This will be explored further in future work.

Appendix A: Derivation of an Exact Solution for Nonstationary Travel Time Distributions

[42] We shall derive exact nonstationary solutions for a particular lumper kinematic wave model. Reference is made to the control volume V in Figure 1, bounded by the catchment/hillslope surface through which water particles enter as precipitation, a no-flux lateral surface defined by the catchment divides, and the outlet collecting the hydrologic response $Q(t)$. Deep losses and recharge terms supplying deep groundwater bypassing the catchment control section are neglected. The processes affecting the time evolution of water storage $S(t)$ in the control volume V (Figure 1) are macroscopic fluxes: precipitation $J(t)$, evapotranspiration $ET(t)$ and discharge $Q(t)$. Mass balance yields

$$\frac{dS(t)}{dt} = J(t) - Q(t) - ET(t) \qquad (A1)$$

[43] Transport features within V are described through exit times of the individual water particles into which the input can be ideally subdivided. Exit time of a given water particle (t_{EX}) is defined as the time elapsed between its injection within V through rainfall, and its exit through any boundary (as Q or as ET). t_{EX} is a random variable characterized by a pdf $p_{EX}(t - t_i, t_i)$, where $t - t_i$ is the time elapsed since injection, and the conditionality on t_i emphasizes the fact that exiting the catchment, say through ET, depends on the state of the system. Accordingly, $P_{EX}(t, t_i)$ is the exceedance cumulative probability of exit time for the water particles which have entered V at t_i (that is,

$P_{EX}(t, t_i) = 1 - \int_0^t p_{EX}(x, t_i)dx$). The instantaneous water storage $S(t)$ can be generally expressed as

$$S(t) = \int_{-\infty}^t J(t_i)P_{EX}(t - t_i, t_i)dt_i \qquad (A2)$$

[44] This is an exact result, derived from *Taylor*'s [1921] theorem [e.g., *Rinaldo and Rodriguez-Iturbe*, 1996] (see auxiliary material). Differentiating equation (A2) with respect to time, using the Leibniz rule, and comparing with equation (A1), yields

$$Q(t) + ET(t) = \int_{-\infty}^t J(t_i)p_{EX}(t - t_i, t_i)\, dt_i \qquad (A3)$$

which expresses the equivalence of a deterministic boundary value problem with a stochastic problem of arrivals at the boundaries of a tagged particle, and thus output fluxes (ET, Q) in terms of the input J and of the conditional exit time pdf. Let $\theta(t_i)$ be the hydrologic partition function, that is, $\theta(t_i)$ ($1 - \theta(t_i)$) is the fraction of water particles injected at t_i that exit V as $Q(ET)$. The exit time distribution is thus given by $p_{EX}(t - t_i, t_i) = \theta(t_i)p_T(t - t_i, t_i) + (1 - \theta(t_i))p_{ET}(t - t_i, t_i)$ with the usual notation. Note that if the evapotranspiration term is null (i.e., $\theta \equiv 1$), the exit time pdf p_{EX} coincides with the travel time pdf p_T. Otherwise, separating the contributions due to discharge and evapotranspiration we obtain the exit fluxes Q and ET as $Q(t) = \int_{-\infty}^t J(t_i)\theta(t_i)p_T(t - t_i, t_i)dt_i$ and $ET(t) = \int_{-\infty}^t J(t_i)(1 - \theta(t_i))p_{ET}(t - t_i, t_i)dt_i$, respectively.

[45] If the hillslope/catchment control volume may be described as a simple dynamical system, a lumped kinematic wave model can be setup by enforcing continuity and a storage-discharge equation [e.g., *Brutsaert and Nieber*, 1977; *Beven*, 1981, 2001; *Sloan and Moore*, 1984; *Brutsaert*, 2005; *Kirchner*, 2009]; that is, a constitutive relation $Q(S(t))$ between outflowing discharge Q and total catchment storage $S(t)$ is established. Mass balance is enforced through equation (A1) and momentum balance in this case is summarized by the functional relationship between Q and S, such as the commonly used $Q(t) = KS(t)^b$ where K, b are parameters possibly obtained from suitable hydrograph recessions [e.g., *Brutsaert and Nieber*, 1977]. A further assumption is needed, concerning the mixing of water particles' age sampled by the exit fluxes Q and ET. One may be concerned with the existence of macropores and preferential flow paths through which new (or old) water may be arriving early at the control section if those pathways are activated as often happens in structured soils [*Beven and Germann*, 1982], or old water- first assumptions may also be operating under conditions leading to piston flow activation. Moreover, in principle one may want to distinguish the mechanisms of sampling between ET and Q, as for instance, plants might detect newer water while mixing and dispersion in groundwaters might dominate age sampling of exiting fluxes [e.g., *Brook et al.*, 2010]. To obtain an exact solution, however, *Botter et al.* [2010] assumed that (1) sampling strategies for Q and ET are the same and (2) complete mixing occurs. Accordingly, water particles are randomly sampled among all the available particles (thus sampling is proportional to the volumes in storage of the different ages).

The resulting analytical expression for the travel time distribution is

$$p_T(t - t_i, t_i) = \frac{Q(t)}{S(t)} \frac{e^{-\int_{t_i}^{t} \frac{Q(x)+ET(x)}{S(x)}dx}}{\theta(t_i)} \qquad (A4)$$

where the hydrologic partition function θ is given by

$$\theta(t_i) = \int_{t_i}^{\infty} \frac{Q(\tau)}{S(\tau)} e^{\int_{t_i}^{\tau} \frac{Q(x)+ET(x)}{S(x)}dx} d\tau \qquad (A5)$$

[46] This is a particularly revealing expression. In fact, the linear, time-invariant reservoir scheme for travel times widely employed in engineering hydrology [see, e.g., *Beven*, 2001; *Brutsaert*, 2005] is easily recovered for $ET(t) = 0$ (hence $\theta \equiv 1$) and employing the linear reservoir model ($b = 1$). Indeed, setting $Q(t) = KS(t)$ (here K [T^{-1}] takes on the meaning of the inverse of the mean residence time) yields $p_T(t - t_i, t_i) \equiv p_T(t - t_i) = Ke^{-K(t - t_i)}$ from equation (A4). In the general case only the direct measurement of all relevant fluxes would thus allow a proper determination of the travel time pdf.

[47] Note, finally, that the only primary assumption underlying the derivation of a kinematic wave equation, whether for surface or subsurface flow, is a univalued (and possibly nonlinear) functional relationship between storage and discharge, imposed on a continuity equation [see *Beven*, 2001, p.178]. Thus the scheme described in this appendix qualifies as a kinematic wave model integrated over the entire control volume. This assumption allows for the simple analytical development presented but, as a lumped approach, neglects any length scale effects arising from the different mechanisms involved in wave celerity and particle velocities in controlling the hydrograph and travel time responses. Taking account of this scale effect is left for future work but does not negate the conclusions drawn from this analysis.

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