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Age-ranked hydrological budgets and a travel time description of catchment hydrology

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Abstract. The theory of travel time and residence time distributions is reworked from the point of view of the hydrological storages and fluxes involved. The forward and backward travel time distribution functions are defined in terms of conditional probabilities. We explain Niemi's formula and show how it can be interpreted as an expression of the Bayes theorem. Some connections between this theory and population theory are identified by introducing an expression which connects life expectancy with travel times. The theory can be applied to conservative solutes, including a method of estimating the storage selection functions. An example, based on the Nash hydrograph, illustrates some key aspects of the theory.

1 Introduction

Hydrological travel times have been studied extensively for many years. Various investigators have published different aspects of the time of travel (Rodriguez-Iturbe and Valdes (1979), Rinaldo and Rodriguez-Iturbe (1996), Rodriguez-Iturbe et al. (1999), Rigon et al. (2015)), but the recent work of Rinaldo and others (Rinaldo et al. (2011), Botter et al. (2011)) started a new branch of the theoretical framework, which is the focus of the present work. In particular, Botter et al. (2010) and Botter et al. (2011) introduced a newly formulated storage selection function (called SAS by them, but denoted as SSF here) related to the backward probability density function (pdf) of the water age or travel-time distribution. Although the concept of the SSF was introduced previously, aspects of the relationship between backward and forward pdfs remain unclear in the literature. Furthermore, older applications of the SSF mostly assumed the simplest case of complete mixing within a watershed or control volume of study. Others (van der Velde et al. (2012),Benettin et al. (2013) Benettin (2015), Harman (2015b)) introduced a new form of the SSF and the age-ranked distribution of water and

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associated compounds. First, van der Velde et al. (2012) made the SSF a function of the residence time PDFs using actual time, rather than using the "injection time". Subsequently, Harman (2015b) reformulated the SSF to be a function of the watershed storage and actual time.

These were valuable advances to the theory, but the literature remains obscured by different terminologies and notations, as well as model assumptions that are not fully explained. Thus there remains a need for theoretical developments that are clearly explained and developed using a consistent set of notations. Questions also remain about how to apply the theory of age-ranked distributions in terms of the model form and parameter estimation. Harman (2015b) noted the importance of selecting an appropriate SSF, but until very recently ((Harman, 2015a)) there was no proposed method for selecting the form of an SSF and estimating it from available data. Selection of a SSF for a given watershed remains a topic of importance, because it should not be imposed arbitrarily.

Here, we explore some complex cases of the SSF that are consistent with the theoretical advances and can be estimated from available data in some watersheds. In the following sections, the theory to date is reviewed and synthesized into a framework with consistent notation. This alone will advance the reader's understanding of how to solve the travel-time distribution problem. The SSF is also defined within the theoretical framework, and the concepts of forward and backward PDFs are fully explored. These conceptual developments are followed by improved methods for selecting the appropriate form of a SSF and estimating its parameters. Guidance for hierarchical approaches to parameter estimation is given based on available data. Finally, the proposed framework and methods are illustrated using data from experimental watersheds.

2 Definitions of age-ranked quantities

Residence time, travel time and life expectancy of water and associated constituents flowing through watersheds are three related quantities whose meaning is well defined by the following equation:

$$T = \underbrace{(t-\tau)}_{T_r} + \underbrace{(\iota - t)}_{L_e} \tag{1}$$

where T [T] ([T] means time units) is the travel time, t [T] is the actual time measured by a clock, τ [T] is the injection time (*i.e.*, the time in which a certain amount of water enters the control volume) and ι [T] is the exit time (*i.e.*, the time in which a certain amount of water exits the control volume). Based upon these definitions, $T_r := t - \tau$ [T] is the so called residence time, or the age of water entered at time τ, and $L_e := \iota - t$ [T] is the life expectancy of the same water molecules which are inside of the control volume.

Consider, for example, a control volume as the one shown in figure 1. Its (bulk) water budget is written as:

$$\frac{dS(t)}{dt} = J(t) - Q(t) - AE_T(t) \tag{2}$$

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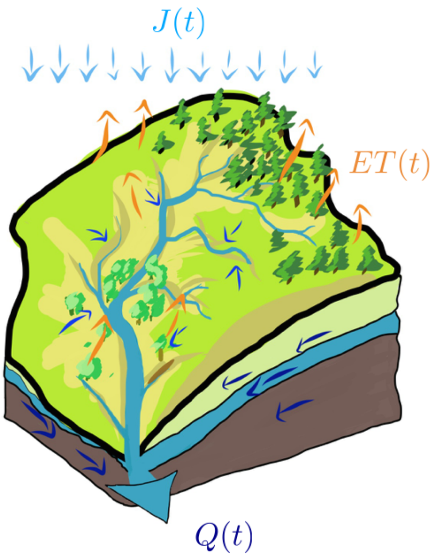

Figure 1. A single control volume is considered in which the fluxes are the total precipitation, evapotranspiration and discharge.

where $S(t)$ [L^3] is the time evolution of the water storage, ([L] denotes length units), but instead of volume, we can measure the storage either as mass, or a depth of water [L] (volume per unit area), $J(t)$ is the precipitation, usually a given (measured) quantity, while the discharge and the actual evapotranspiration, $Q(t)$ and $AE_T(t)$, are modeled. Common simple estimates for the two latter quantities are:

$$Q(t) = \frac{1}{\lambda} S^b(t) \tag{3}$$

and

$$AE_T(t) = \frac{S(t)}{S_{max}} E(t) \tag{4}$$

where λ $[T]$ and b are the parameters of the non-linear reservoir model, S_{max} is the maximum water storage and $E(t)$ is the potential ET, temporal function of the radiation inputs and atmospheric conditions. Assuming that radiation and various parameters used to model Q and AE_T are given, eq.(2) can be solved and $S(t)$ obtained. If $b = 1$ the budget is a linear ordinary differential equation, and its solution is analytical as in Coddington and Levinson (1955); otherwise, the solution can be obtained through an appropriate numerical solver (e.g. Butcher (1987)).

Being interested in knowing the age of water we need to consider a more general set of equations.

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Assume that the water storage $S(t)$ can be decomposed in its sub-volumes $s(t,\tau)$ [L^3 T^{-1}] which refer to water injected into the system at time τ. Thus:

$$S(t) = \int_0^t s(t,\tau)d\tau \tag{5}$$

where the initial time $t = 0$ comes before any input into the control volume. Analogously, $Q(t)$ [L^3 T^{-1}] is the discharge out of the control volume, and $q(t,\tau)$ [L^3 T^{-2}] is the part of the discharge exiting the control volume at time t composed of water molecules that entered at time τ:

$$Q(t) = \int_0^t q(t,\tau)d\tau \tag{6}$$

Actual evapotranspiration, $AE_T(t)$ [L^3 T^{-1}], is the sum of its parts $ae_T(t,\tau)$ [L^3 T^{-2}] as:

$$AE_T(t) = \int_0^t ae_T(t,\tau)d\tau \tag{7}$$

Finally, let $J(t)$ [L^3 T^{-1}] denote the input to the control volume. This input can have an "age", and therefore, it can be defined

$$J(t) = \int_0^t j(t,\tau)d\tau \tag{8}$$

All these bivariate functions of t and τ, $s(t,\tau)$, $q(t,\tau)$, and $ae_t(t,\tau)$ are null for $t < \tau$ and can present a derivative discontinuity at the origin $(t = \tau)$. Given the above definitions, we can rewrite the water budget as a set of age-ranked budget equations:

$$\frac{ds(t,\tau)}{dt} = j(t,\tau) - q(t,\tau) - ae_T(t,\tau), \tag{9}$$

These equations were introduced first by van der Velde et al. (2012) and named by Harman (2015b).

3 Backward and forward approaches

"Backward" and "forward" are well known concepts in the study of travel time distributions. They were firstly introduced by Niemi (1977), Cornaton and Perrochet (2006), to cite few, and recently refined by Benettin (2015). Benettin (2015), in particular, related the concept of backward to the travel times analysis and forward to the life expectancy analysis. However, according to us, these previous works didn't fully disclose the inner meaning of the two concepts. In fact, in our theory, the probabilities are defined as backward when they "look" in time to the history of water molecules and forward when they "look" in time till their exit from the control volume. According to the previous statements, we can define a backward travel time probability, which is conditioned to t and "looks" backward to τ, and a forward travel time probability, which is conditioned to τ and "looks" forward to t. In the same way, we can define a backward life expectancy probability, which is conditioned to ι and "looks" backward to t, and a forward life expectancy probability, which is conditioned to t and "looks" forward to ι. All these concepts will be better clarified in the following sections.

4 Backward Probabilities

Based on the previous definitions, it is easy to define the pdfs of the residence time, travel time and evapotranspiration time. In particular, the pdf of residence time conditional on the actual time t, $p(T_r|t)$, can be defined as:

$$p(T_r|t) \equiv p(t-\tau|t) := \frac{s(t,\tau)}{S(t)} \quad [\mathrm{T}^{-1}] \tag{10}$$

where "≡" means equivalence, and ":=" a definition. Benettin (2015) denoted $p(T_r|\tau)$ as $\overleftarrow{p}(T_r,t)$ but since this probability density is conditional to the actual time, standard probability notation is clear and unambiguous.

It is evident that this probability is time variant, since the integral in equation (1) that gives $S(t)$ stops at the actual time t.

The pdf of travel time for water exiting the control volume as discharge, $p_Q(t-\tau|t)$, can be defined as:

$$p_Q(t-\tau|t) = \frac{q(t,\tau)}{Q(t)} \quad [\mathrm{T}^{-1}], \tag{11}$$

Eventually, the pdf of travel time for water exiting the control volume as water vapor, $p_{E_T}(t-\tau|t)$, can be defined as:

$$p_{E_T}(t-\tau|t) = \frac{ae_T(t,\tau)}{AE_T(t)} \quad [\mathrm{T}^{-1}], \tag{12}$$

It is also possible to define the mean age of water for any of the two outlets, which is given by:

$$\langle T_r(t)\rangle_i = \int_0^t (t-\tau)p_i(t-\tau|t)d\tau \tag{13}$$

for $i \in \{Q, E_T\}$, which is a function of the sampling time.

After the above definitions, the age-ranked equation (9), can be rewritten as:

$$\frac{d}{dt}S(t)p(T_r|t) = J(t)\delta(t-\tau) - Q(t)p_Q(t-\tau|t) - AE_t(t)p_{E_T}(t-\tau|t) \tag{14}$$

when a single "new water" injection of mass is considered, and the bulk quantities $S(t)$, $Q(t)$, $AE_T(t)$ are known as soon as the bulk water budget, equation (2), is solved. The travel time probabilities on the right side of (14) are not known. Consequently Botter et al. (2011) introduced a storage selection function, $\omega(t,\tau)$ [-], for each of the outputs, so that:

$$p_Q(t-\tau|t) := \omega_Q(t,\tau)p(T_r|t) \tag{15}$$

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and:

$$p_{E_T}(t-\tau|t) := \omega_{E_T}(t,\tau)p(T_r|t) \tag{16}$$

Therefore equation (14), after the proper substitutions, becomes:

$$\frac{d}{dt}S(t)p(T_r|t) = J(t)\delta(t-\tau|t) - Q(t)\omega_Q(t,\tau)p(T_r|t) - AE_t(t)\omega_{E_T}(t,\tau)p(T_r|t) \tag{17}$$

Once assigned the $\omega(t,\tau)$ values on the basis of some heuristic, as in Botter et al. (2011), equation (17) represents a linear ordinary differential equation and can be solved exactly as:

$$p(T_r|t) = e^{-\int_\tau^t g(x,\tau)dx}\left[p(0|t) + \int_\tau^t \frac{J(y)\delta(y-\tau)}{S(y)}e^{\int_\tau^t g(x,\tau)dx}dy\right] \tag{18}$$

where :

$$g(x,\tau) = \frac{1}{S(x)}\left[\frac{dS(x)}{dt} + Q(x)\omega_Q(x,\tau) + AE_t(x)\omega_{E_T}(x,\tau)\right] \tag{19}$$

and $p(0|t)$ is the initial condition. Figures 2 and 3 show, respectively, a representation of $P(T_r|t)$, as function of t (so it does not integrate to one), and of $p(T_r|t)$, obtained by considering three different injection times, named generically τ_1, τ_2 and τ_3, and assuming $\omega_Q(t,\tau) = \omega_{E_T}(t,\tau) = 1$. In particular, what is evident from figure 2 is that for those time intervals in which $J(t) = 0$, $P(T_r|t) = const$. In fact, if we consider $\omega_Q(t,\tau) = \omega_{E_T}(t,\tau) = 1$, equation (17) is simplified in:

$$\frac{d}{dt}S(t)p(T_r|t) = -Q(t)p(T_r|t) - AE_t(t)p(T_r|t) \tag{20}$$

and, therefore,

$$\frac{dp(T_r|t)}{dt} = -\frac{p(T_r|t)}{S(t)}\left[\frac{dS(t)}{dt} - Q(t) - AE_t(t)\right] = 0 \tag{21}$$

Figure 4 shows the evolution of $p(T_r|t)$ with the actual time t, obtained for the same three injection times. The integral of the area under the curves, in this case, is not equal to 1 and the three functions shown in the figure are not pdfs.

5 Forward Probabilities

Consider again the budget age-ranked equation (9) in its integral form:

$$s(t,\tau) = J(\tau) - \int_0^t q(t,\tau)dt - \int_0^t ae_T(t,\tau)dt \tag{22}$$

It can be rewritten as a probability conditional to τ:

$$P[t-\tau|\tau] := 1 - \frac{s(t,\tau)}{J(\tau)} = \frac{V_Q(t,\tau)}{J(\tau)} + \frac{V_{E_T}(t,\tau)}{J(\tau)} \tag{23}$$

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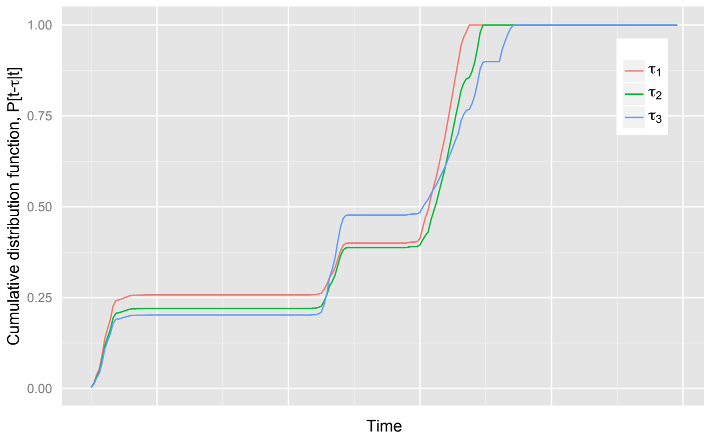

Figure 2. Representation of the backward cumulative distribution function for three injection times (τ_i, where i = 1,3), as varying with the actual time t

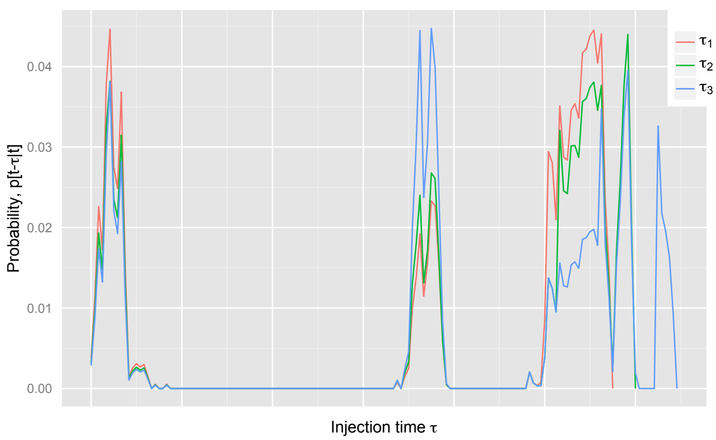

Figure 3. Representation of the evolution of the backward pdf as varying with the injection time τ.

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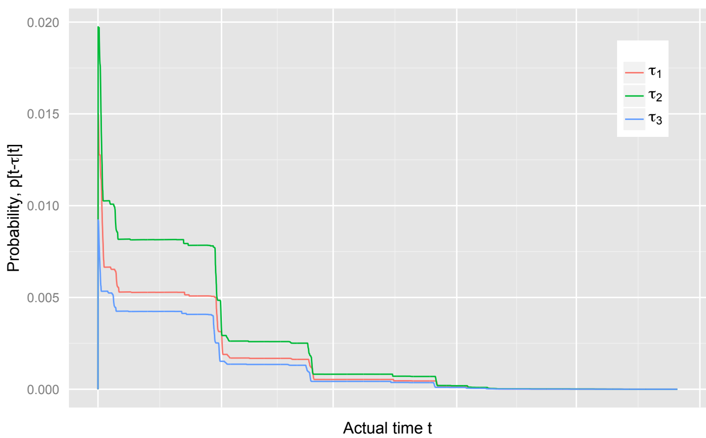

Figure 4. Representation of the evolution of the backward pdf versus the actual time t. In this case, the area below the curves is not equal to 1.

having defined:

$$V_Q(t,\tau) := \int_0^t q(t,\tau)dt \tag{24}$$

and

$$V_{AE_T}(t,\tau) = \int_0^t ae_T(t,\tau)dt \tag{25}$$

$P[t-\tau|\tau]$, as shown in figure 5, varies (with t), as expected, between 0 and 1 and has density:

$$p(t-\tau|\tau) = -\frac{1}{J(\tau)}\frac{ds(t,\tau)}{dt} = \frac{q(t,\tau)}{J(\tau)} + \frac{ae_T(t,\tau)}{J(\tau)} \tag{26}$$

It can be observed instead that:

$$\mathcal{F}(t-\tau|\tau) := \frac{V_Q(t,\tau)}{J(\tau)} \tag{27}$$

and

$$\mathcal{G}(t-\tau|\tau) := \frac{V_{E_T}(t,\tau)}{J(\tau)} \tag{28}$$

are not probability functions, because, their asymptotic value is not 1. Because the forward probabilities are derived, in the case we are describing, on empirical bases from the budgets terms, and

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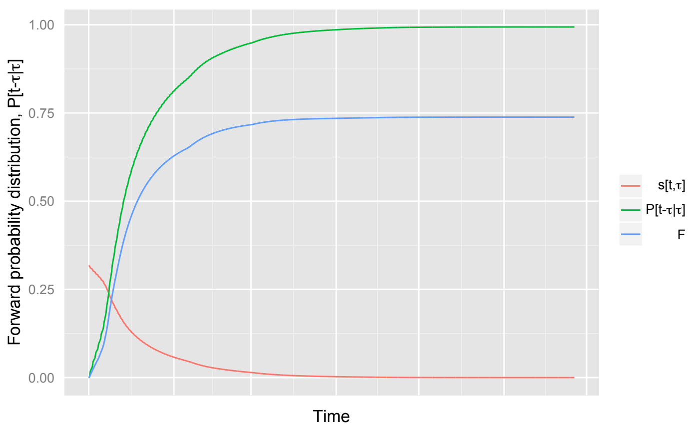

Figure 5. Forward probability distribution: in red the relative storage, in green the foraward distribution and in blu the relative discharge function.

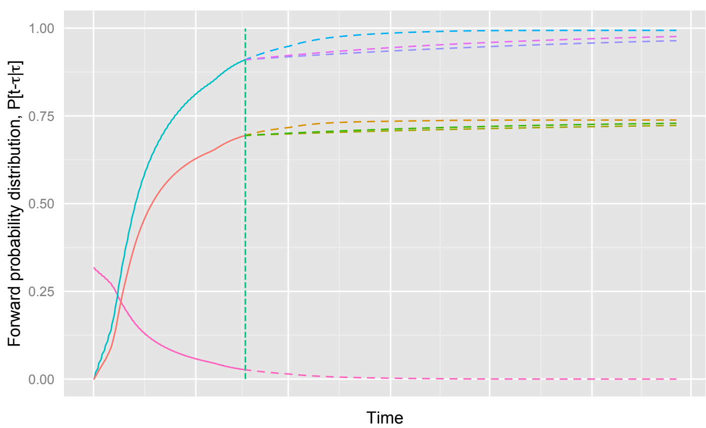

Figure 6. Representation of the forward probability of the outputs: in pink the relative storage, $s(t,\tau)$, in light blue the output probability, $P[t-\tau|\tau]$ and in red the relative discharge function $\mathcal{F}$, defined in the text. The difference between $P[t-\tau|\tau]$ and $\mathcal{F}$ is the function $\mathcal{G}$, defined in the text. The green dashed line represents the generic instant t, after which $P[t-\tau|\tau]$ and $\mathcal{F}$ are unknown.

not assumed apriori, their complete shape is known only at $t \to \infty$. For any finite time the actual knowledge we have, is better represented in Figure 6, which shows that the progress of the three
165 curves P, $\mathcal{F}$ and $\mathcal{G}$ is unknown for future times.

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What is necessary to normalize $\mathcal{F}$ and $\mathcal{G}$ and define therefore probabilities function is the asymptotic value of the partition coefficient among the two fluxes:

$$\Theta(\tau) := \lim_{t\to\infty}\Theta(t,\tau) := \lim_{t\to\infty}\frac{V_Q(t,\tau)}{V_Q(t,\tau)+V_{E_T}(t,\tau)} \tag{29}$$

Then, it is easy to show that:

$$p_Q(t-\tau|\tau) := \frac{q(t,\tau)}{\Theta(\tau)J(\tau)} \tag{30}$$

and

$$p_{E_T}(t-\tau|\tau) := \frac{ae_T(t,\tau)}{(1-\Theta(\tau))J(\tau)} \tag{31}$$

are the forward probabilities density function of discharges and evapotranspiration, which properly normalize to 1 when integrated over t. The missing knowledge of Θ at any finite time, obviously does not prevent to know the actual state of the system, which is obtained by solving the budget equation. More information and details on this partition coefficient are provided in Appendix A.

6 Niemi's relation

As a results of definitions made in sections (4) and (5) there exist two relations involving $q(t,\tau)$, i.e. equations (11) and (30), and $ae_T(t,\tau)$, i.e. equations 12 and 31. Equating the correspondent two expression, it results:

$$Q(t)p_Q(t-\tau|t) = \Theta(\tau)p_Q(t-\tau|\tau)J(\tau) \tag{32}$$

and:

$$AE_T(t)p_{E_T}(t-\tau|t) = [1-\Theta(\tau)]p_{E_T}(t-\tau|\tau)J(\tau) \tag{33}$$

The above relations are known in literature as Niemi's relations or formulas, after Niemi (1977) and also reworked by Botter et al. (2010).

Dividing, for instance (32), for the total volume of water:

$$S = \int_0^\infty J(\tau)d\tau = \int_0^\infty Q(t)+AE_T(t)dt \tag{34}$$

and observing that:

$$p(\tau) := \frac{J(\tau)}{S} \tag{35}$$

can be considered the marginal pdf of the injection times, and:

$$p_Q(t) := \frac{Q(t)}{\Theta(\tau)S} \tag{36}$$

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the marginal pdf of the outflow as discharge, Niemi relation becomes:

$$p_Q(t-\tau|t)p_Q(t) = p_Q(t-\tau|\tau)p(\tau) \tag{37}$$

which has the form of the well known Bayes theorem. More than being of some practical utility, this shows that the interpretation of the backward and forward probabilities as conditional ones is fully consistent. On the other hands, this reveals that the joint probability of T_r and t is:

$$p(T_r, t) = p_Q(t-\tau|t)p(t) = p_Q(t-\tau|\tau)p(\tau) \tag{38}$$

Following what written in section 5 there should be a working Niemi's relation for any finite time t, which does not require the knowledge of the asymptotic value $\Theta(\tau)$. This can be easily derived after having defined:

$$g(t-\tau|\tau) := \frac{ae_t(t,\tau)}{J(\tau)} \equiv \frac{d\mathcal{G}}{dt} \tag{39}$$

and

$$f(t-\tau|\tau) := \frac{q(t,\tau)}{J(\tau)} \equiv \frac{d\mathcal{F}}{dt} \tag{40}$$

From these definitions, it is trivially:

$$q(t,\tau) = f(t-\tau|\tau)J(\tau) \tag{41}$$

and

$$ae_t(t,\tau) = g(t-\tau|\tau)J(\tau) \tag{42}$$

and, therefore,

$$Q(t)p_Q(t-\tau|t) = f(t-\tau|\tau)J(\tau) \tag{43}$$

for discharges and

$$AE_T(t)p_{AE_T}(t-\tau|t) = g(t-\tau|\tau)J(\tau) \tag{44}$$

for evapotranspiration.

These relations become useful when the backward probabilities are the known quantities (up to time t) and can be used to obtain the forward functions, f and g. As a by product, the SSF and the forward functions are also shown to be related, because, for instance, for the discharges is, for any time t:

$$f(t-\tau|\tau) = \frac{Q(t)\omega_q(t,\tau)p(t-\tau|t)}{J(\tau)} \tag{45}$$

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7 Residence times, travel times and life expectancy

The forward probabilities can be put in relation with the life expectancy, i.e. the expected time the water molecules remain in the storage, and their probability.

In the control volume, we can conceptually denote the subsets of the storage which contains the water molecules expected to exit at time ι as:

$$s_\iota(t, \iota) \tag{46}$$

Analogous to what was done before, we can observe that the quantity

$$p_\iota(\iota - t|t) := \frac{s_\iota(t,\iota)}{S(t)} \tag{47}$$

has the structure of a probability density function once integrated over all ι-s, and it is reasonable to call it the probability density of storage-life expectancy for particles in the control volume at time t.

Based on equation (1) for any t:

$$p(T|t) = p_\iota(\iota - t|t) \star p(t - \tau|t) \tag{48}$$

where $\star$ indicates convolution among the probability density functions.

However, $p_\iota(\iota - t|t)$ can also be related to the forward probabilities discussed in the previous section. In fact, it can be observed that the probability of storage-life expectancy satisfies the following relation with the age-ranked forward quantities:

$$s_\iota(t,\iota) = \int\limits_0^t \left[q(\iota,\tau) + ae_t(\iota,\tau)\right] d\tau \ = \int\limits_0^t \left[\Theta(\tau) p_Q(\iota - \tau|\tau) + (1 - \Theta(\tau)) p_{AE_t}(\iota|\tau)\right] J(\tau) d\tau \tag{49}$$

The integral spans the time interval up to t because we are considering the storage at this time. In (49) the first equality says that the life-storage at time time is equal to the water injected at time τ which is expected to exit as discharge or evapotranspiration at time ι, integrated over all τs. This integral is not effectively known, at time t, because, what is happening between time t and ι is unknown, and so the pdfs (as in Figure 6), unless they are specified from some educated guess, as made in the last section of this paper. Then, it follows:

$$p(\iota - t|t) = \frac{\int_0^t \left[\Theta(\tau) p_Q(\iota - \tau|\tau) + (1 - \Theta(\tau)) p_{AE_t}(\iota|\tau)\right] J(\tau) d\tau}{S(t)} \tag{50}$$

Thus, either as a convolution (i.e. as in equation (48)) or as related to forward probabilities, (i.e. as in equation (50)), the relation between the storage-life expectancy and the previously introduced backward and forward probabilities, is mediated by an integral.

8 Passive and reactive solutes

The formalism developed in section 2 to 6 is applicable, in principle to any substance, say indicated by a superscript i. Therefore we have a bulk budget equation for substance i, and age-ranked budget

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for the same substance:

$$\frac{dS^i(t)}{dt} = J^i(t) - Q^i(t) \tag{51}$$

and

$$\frac{ds^i(t)}{dt} = j^i(t,\tau) - q^i(t,\tau) \tag{52}$$

which represent trivial extensions of equations (2) and (9), where for making the illustration simpler, we have neglected evapotranspiration, which will be re-introduced eventually. However, if the substance is diluted in water, it is usually treated as concentration in water (either in term of mass, moles or volume). Because we have various terms in the equations, concentrations are possibly as many as the terms that appear. In this case, three:

$$C_S^i(t) := \frac{S^i(t)}{S(t)} \tag{53}$$

for the concentration in storage;

$$C_J^i(t) := \frac{J^i(t)}{J(t)} \tag{54}$$

for concentration in input;

$$C^i(t) := \frac{Q^i(t)}{Q(t)} \tag{55}$$

for discharges. The latter is actually the one which is usually covered by literature, since it is the one measured at the outlet of a control volume/catchment. For the solute discharge, in fact, it is usually assumed the validity of an integral expression like:

$$Q^i(t) = \int_0^t \Theta(t) p(t-\tau|\tau) J^i(\tau) d\tau \tag{56}$$

with the usual interpretation of the symbols, and where the i has been dropped from the probability distribution function, assuming that a passive solute moves like water does. Dividing (56) by the water discharge, it is obtained:

$$C^i(t) = \int_0^t \frac{p(t-\tau|\tau)}{Q(t)} J^i(\tau) d\tau \tag{57}$$

and, finally, applying the Niemi's formula:

$$C^i(t) = \int_0^t p(t-\tau|t) \frac{J^i(\tau)}{J(\tau)} d\tau = \int_0^t p(t-\tau|t) C_J^i(\tau) d\tau \tag{58}$$

Therefore the concentration of the passive solute in discharge is known once the concentration of the solute in input is known together with the backward probability [Rinaldo et al. (2011)]. The

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concentration estimated in this way groups substance injected at any time, in agreement with the measure practice. When a sample is taken, the action implies perfect mixing of all the age-ranked water and their load of substance. The bulk substance budget can instead be written as:

$$\frac{dS^i(t)}{dt} = J^i(t) - Q^i(t) = J^i(t) - C^i(t)Q(t) \tag{59}$$

and the missing concentration $C^i_S(t)$ can be easily estimated with the help of (53) since $S(t)$ is also known.

However, the age-ranked formalism can be used to understand a little more about the processes in action. Starting from the quantities that appear in equation (52), the backward probability can be defined as:

$$p^i(t-\tau|t) := \frac{s^i(t,\tau)}{S^i(t)} \tag{60}$$

and analogous definitions (e.g. equation 11) can be given for the discharge and the inputs, such as to obtain, after the appropriate substitutions:

$$\frac{d}{dt}S^i(t)p(t-\tau|t) = J^i(t)p^i_J(t-\tau|t) - Q^i(t)\omega_Q(t,\tau)p(t-\tau|t) \tag{61}$$

which is the master equation (equation 17) for the substance i. Many of the superscripts i where dropped, accordingly to the fact that the i-substance is a passive tracer (i.e., it behaves like water). Surprisingly, in (61) all the quantities are known, either because solution of the solute budget (51) or the water master equation (equation 17), or a known input ($J(t)$). The only quantity that is unknown (and usually guessed) is the SSF $\omega_Q(t,\tau)$. However, (61) and (17) can be seen as two coupled equations, in $p(t-\tau|t)$ and $\omega_Q(t,\tau)$ and we can conclude that the SSF cannot be arbitrarily imposed, but viceversa, derived.

From a practical point of view there could be some obstacles in the correct determination of the SSF, because, the distribution of the input of the substance can be unknown. In this case (61) can be used to back-trace the the passive solute injection, after educated guesses on the SSF.

For sake of simplicity we neglected evapotranspiration. However, now that the concepts are hopefully fixed, we can observe that AE_T re-introduction back brings in the formalism a second SSF, which remain undetermined. Various closures can be chosen to overcome this fact. For instance, it can be assumed $\omega_Q(t,\tau) = \omega_{E_T}(t,\tau)$. Nevertheless the main experimental way to determine would be to find a second passive tracer transported trough vegetation. In this case, if a third equation, similar to (61), but containing evapotranspiration, would hold, it would permit the determination of the missing SSF coefficient.

Finally, reactions that transform the substance i into another or fix it to the matrix, can be seen as a further output. If, for instance, we assume that the rate of decreasing of a substance due to chemical reactions follows a first order kinetic, independent from τ, then this output (to be subtracted from, for instance, equation 61), could be:

$$r^i(t,\tau) := k_1(s^i(t,\tau) - k_2 s^i_{eq}) \tag{62}$$

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where k_1 and k_2 are suitable reaction's constants and s^i_{eq} represents an equilibrium storage. Whilst more complex type of reactions can be envisioned, this type of reaction (or sink term), being linear, do no alter the essential traits of the theory described above.

9 An example of the other way around

With the scope to further clarify the formalism, we assume in this section that the forward pdfs introduced in the previous sections are assigned. To this scope we use the concept of linear reservoir, which has a long history in surface hydrology, Dooge (2003).

Let's consider first just only one outflow.

The bulk equation for the water budget of a single linear reservoir is:

$$\frac{dS(t)}{dt} = \sum_{\tau=1}^{n} R_\tau - \frac{1}{\lambda} S(t) \tag{63}$$

where it has been assumed, for simplicity, that $J(t) = \sum_{\tau=1}^{n} R_\tau$, i.e. that the precipitation is accounted as a sequence of instantaneous impulses at different times τs. It is also, by definition of the linear reservoir:

$$Q(t) = \frac{1}{\lambda} S(t) \tag{64}$$

where λ [T] is the mean travel time in the reservoir. If this is the case, the age-ranked water budgets can be written as:

$$\frac{ds(t,\tau)}{dt} = R_\tau \delta(t-\tau) - \frac{1}{\lambda} s(t,\tau) \tag{65}$$

where it is

$$q(t,\tau) = \frac{1}{\lambda} s(t,\tau) \tag{66}$$

Equation (65), after integration over τ reduces to equation (63). By definition, it is $s(t,\tau) = 0$ for $t < \tau$ and the solution, for $t > \tau$ is well known as:

$$s(t,\tau) = R_\tau e^{\frac{\tau - t}{\lambda}} \tag{67}$$

The equivalent solution, for $S(t)$ gives:

$$S(t) = \int_{\tau}^{t} R_\tau e^{-(t-\tau)/\lambda} d\tau \tag{68}$$

and the backward probability can be written, then as:

$$p(t-\tau|t) = \frac{R_\tau e^{\frac{t-\tau}{\lambda}}}{\int_\tau^t R_\tau e^{-(t-\tau)/\lambda} d\tau} \tag{69}$$

If, and only if, $R_\tau = const$ the probability simplifies, and it is time invariant, i.e. dependent only on the residence time $T_r = t - \tau$. Please, notice that, in this case we did not appeal to equation (17) to estimate the backward probability but we could use directly definitions in equation (69).

Because discharge is just linearly proportional to the storage, it is easy to show that $p_q(t-\tau|t) = p(t-\tau|t)$ and, therefore, in this case, $\omega(t,\tau) = 1$. This shows that the linear reservoir case, where for all injection times the mean residence time is equal (to λ), the SSF function is necessarily unitary. However, a more general case, can be set if the mean residence time is a function of τ, meaning that equation (65) can be modified into:

$$\frac{ds(t,\tau)}{dt} = R_\tau \delta(t-\tau) - \frac{1}{\lambda_\tau} s(t,\tau) \tag{70}$$

and its solution for $t > \tau$ is the same as (67), but with λ muted into λ_τ. However, due to the dependence of λ_τ on the injection time, the SSF is not anymore a constant, being equal to:

$$\omega_Q(t,\tau) := \frac{p_q(t-\tau|t)}{p(t-\tau|t)} = \lambda_\tau^{-1} \frac{\int_\tau^t R_\tau e^{-(t-\tau)/\lambda_\tau} d\tau}{\int_\tau^t \lambda_\tau^{-1} R_\tau e^{-(t-\tau)/\lambda_\tau} d\tau} = \lambda_\tau^{-1} \frac{\int_\tau^t R_\tau e^{+\tau/\lambda_\tau} d\tau}{\int_\tau^t \lambda_\tau^{-1} R_\tau e^{\tau/\lambda_\tau} d\tau} \tag{71}$$

This seems to suggest that imposing the characteristics of the pdf could completely determine the $\omega_Q(t,\tau)$. Viceversa as already known, assigning $\omega_Q(t,\tau)$ from some heuristic, obviously, would determine a mean residence time dependence on the injection time.

Non trivial $\omega(t,\tau)$ can also derive from assuming as a model for discharge a sequence of linear reservoir, as in the so called Nash model, Dooge (2003). Without entering in details, a sequence of linear reservoirs implies that just le last reservoir maintain a linear relation between storage and outflow. Instead a nonlinear relationship exists between the whole storage and the same outflow, implying also a nonlinear SSF.

Using non-linear reservoirs does not allow to obtain semi-analytical results, but the fact suitably tuning the parameters of each age-ranked equation that control the mean residence time affects the form of the SSF cannot change, as is also suggested by arguments below.

Other aspects come into play when the outputs are multiple. Expanding the previous linear case to include evapotranspiration, the bulk equation, under liner hypothesis becomes:

$$\frac{dS(t)}{dt} = \sum_{\tau=1}^{n} R_\tau - \left(\frac{1}{\lambda} - aet(t)\right) S(t) \tag{72}$$

where, the further assumption made is that the actual evapotranspiration is equal to:

$$AE_T(t) = S(t) aet(t) \tag{73}$$

with a linear dependence on the soil water content, as for instance in Rodriguez-Iturbe et al. (1999). The equations of water budget for the generations becomes then:

$$\frac{ds(t,\tau)}{dt} = R_\tau \delta(t-\tau) - \left(\frac{1}{\lambda_\tau} + ae(t,\tau)\right) s(t,\tau) \tag{74}$$

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where the bivariate dependence of $ae(t,\tau)$ on the actual time and the injection time can be justified by arguing that, being the water of different ages not perfectly mixed in the control volume, plants roots sample water of different ages in different modes, according to spatial arrangements. Since the above equation (74) remains a linear ordinary differential equation, it is exactly solvable, and:

$$s(t,\tau) = R_\tau e^{-\Lambda(t,\tau)} \tag{75}$$

where:

$$\Lambda(t,\tau) := \int\limits_\tau^t \left(\frac{1}{\lambda_\tau} + ae(t',\tau)\right) dt' \tag{76}$$

and:

$$S(t) = \int\limits_0^t R_\tau e^{-\Lambda(t,\tau)} d\tau \tag{77}$$

Notably, soon as the outflows terms are expressible as a function of the storage multiplying the age-ranked storage:

$$q(t,\tau) + aet(t,\tau) = \mu(t,\tau)\, s(t,\tau) \tag{78}$$

the problem remains linear and analytically solvable. The quantity $\mu(t,\tau)$ is usually called age and mass-specific output rate, Calabrese and Porporato (2015). Solving equation (74) it is not even necessary to show that:

$$\omega_{E_T}(t,\tau) \neq 1 \tag{79}$$

The latter condition is regained if and only if $aet(t,\tau) = aet(t)$, i.e. it depends only on the current time (which is a condition which requires the perfect mixing of aged waters). In fact, in case a dependence on τ remains, then, trivial algebra says that:

$$p_{E_T}(t-\tau|t) = \frac{ae(t,\tau)s(t,\tau)}{\int_\tau^t ae(t,\tau)s(t,\tau)d\tau} \tag{80}$$

which implies:

$$\omega_{E_T}(t,\tau) := \frac{p_{E_T}(t-\tau|t)}{p(t-\tau|t)} = \frac{ae(t,\tau)\int_\tau^t R_\tau e^{-\Lambda(t,\tau)}}{\int_\tau^t ae(t,\tau)S(t,\tau)d\tau} \tag{81}$$

Obviously these results, obtained by imposing a travel time probability, can be inconsistent with tracers results, because both approaches pretend to establish what ωs are. However, this proves that the theory is falsiable.

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10 Conclusions

This paper reworked the concepts of the travel time and residence time distributions theory, trying, first of all, to clarify the notation and unify concepts between previous related works. This was necessary to the obtain understanding of the theoretical framework, which was in some aspects still unclear. The theory in terms of age-ranked storages and fluxes was reworked to obtain a form of the master equation, which allows an easy computation of the backward pdfs.

The relationship between the backward and forward formulation was clarified better defining and discussing the role of the partition coefficient between the two outputs, discharge and evapotranspiration. The importance of a correct estimate of the partitioning coefficient is a key point in the description of the watershed processes, as explained in the appendix.

Niemi's relationship was rederived usign our new definitions, obtaining the Bayes theorem. The consistency of the interpretation of the backward and forward pdfs as conditional ones was demonstrated.

To complete the theory, the life expectancy pdf was also defined in two different ways, through the convolution among the residence time and travel time pdfs and in relation with the forward pdfs.

Some aspects connected with the predictability of life expectancy were singled out and discussed.

The extension of the theory to any passive substance diluted in water, showed how the SSF function can be determined by appropriate use of tracers. In fact, a new form of the master equation, in case of the passive solutes, was obtained to be coupled with the master equation of water, showing that the SSF functions cannot be imposed arbitrarily. This latter achievement clearly opens the way to new developments of the theory and applications of tracers.

Finally the abstract theory of age-ranked reservoirs was analyzed through the use of linear reservoirs, which hopefully clarifies the meaning and utility of SSFs for travel time analysis.

Appendix A: Symbols, Acronyms, and Notation

A1 The partition coefficient Θ

$\Theta(\tau)$ has been introduced to complete the algebra of probabilities, in presence of more that one outflow. However studying it is important by itself, because it summarizes the relevant element of hydrologic fluxes partition.

The first plot in figure 7 shows a time-series of $\Theta(\tau)$ values obtained from a single injection time, using data from the Posina River generated from the simulation of the hydrological budget reported in Abera et al. (a) and Abera et al. (b). At the beginning $\Theta(t, \tau)$ (figure 7, top) shows large oscillations due to hourly and daily oscillations, especially in evapotranspiration. Because $\Theta(t, \tau)$ is defined through integrals, these oscillation are progressively dumped and become irrelevant after

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Symbol	Name	Units
t	actual time	T
τ	injection time	T
ι	exit time	T
T_r	travel time	T
L_e	life expectancy	T
$S(t)$	volume of water stored in a control volume	L ^{3}
$J(t)$	rainfall rates	L ^{3} T $^{-1}$
$Q(t)$	discharge	L ^{3} T $^{-1}$
AE_T	actual evapotranspiration	L ^{3} T $^{-1}$
λ	coefficient of the non-linear reservoir model	T
b	exponent of the non-linear reservoir model	–
S_{max}	maximum value of the storage	L ^{3}
$s(t,\tau)$	age-ranked water storage	L ^{3} T $^{-1}$
$j(t,\tau)$	age-ranked rainfall rate	L ^{3} T $^{-2}$
$q(t,\tau)$	age-ranked discharge	L ^{3} T $^{-2}$
$ae_T(t,\tau)$	age-ranked evapotranspiration	L ^{3} T $^{-2}$
$p(T_r,t)$	residence time backward pdf	–
$p_Q(t-\tau,t)$	travel time backward pdf	–
$p_{E_T}(t-\tau,t)$	evapotranspiration time backward pdf	–
$\omega_Q(t,\tau)$	SSF for discharge	–
$\omega_{E_T}(t,\tau)$	SSF for evapotranspiration	–
$\Theta(t)$	partitioning coefficient	–
$P(t-\tau,\tau)$	residence time forward probability function	–
$p(t-\tau,\tau)$	residence time forward pdf	–
$p_Q(t-\tau,\tau)$	travel time forward pdf	–
$p_{E_T}(t-\tau,\tau)$	evapotranspiration time forward pdf	–
$V_Q(t,\tau)$	time integral of the age-ranked discharge	L ^{3} T $^{-1}$
$V_{AE_T}(t,\tau)$	time integral of the age-ranked evapotranspiration	L ^{3} T $^{-1}$
$\mathcal{F}(t-\tau\|\tau)$	relative discharge function	–
$\mathcal{G}(t-\tau\|\tau)$	relative evapotranspiration function	–
$p_\iota(\iota-t,t)$	life expectancy forward pdf	–
R_τ	instantaneous rainfall impulses	L ^{3} T $^{-2}$
$C_S^i(t)$	concentration in storage	–
$C_J^i(t)$	concentration in input	–
$C_Q^i(t)$	concentration in discharge	–

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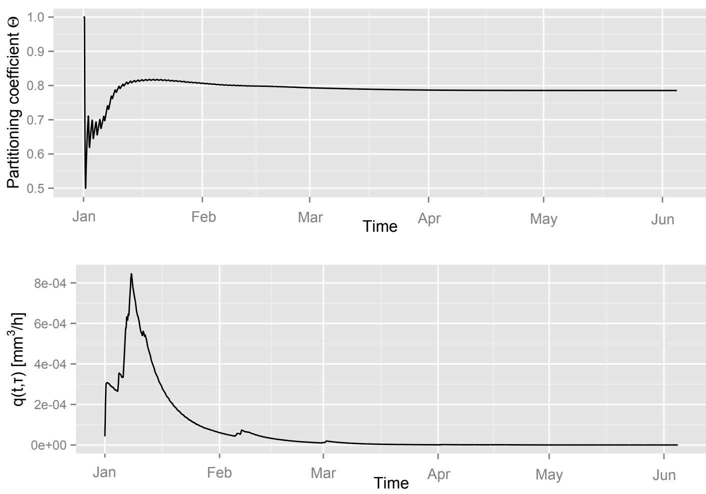

Figure 7. Variation of the partitioning coefficient in time, for a single injection time: after a time scale of 5 months its oscillation became irrelevant and its value tends to its final value of 0.78

a couple of weeks (when discharge is still higher than baseflow, as appears from the age-ranked disharge in figure 7, bottom).

Figure 8 shows twelve different time-series of the partition coefficient: each curve represents the time evolution of $\theta(t,\tau)$ obtained considering twelve precipitation events, one for each month of one year of rainfall data. The highest values of the coefficient ($\theta(t,\tau) = 0.75$, in this case, are achieved during the coldest months of the year, in which the evapotranspiration flux is lower. On the contrary, smaller $\theta(t,\tau)$ values were obtained in the summer months, with a minimum in June around 0.25.

A2 Reproducible research

In order interested researchers can replicate or extend our results, our codes are made available at https://github.com/geoframecomponents. Instructions for using the code can be found at: http://geoframe.blogspot.com. All the material, with further information, is also linked at http://abouthydrology.blogspot.com/search/label/Residence%20time.

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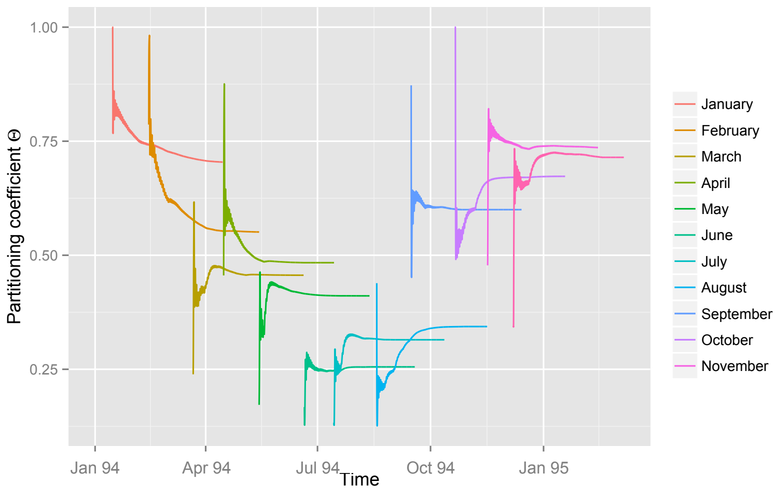

Figure 8. Evolution of the partitioning coefficient in one year of hourly simulation: the highest value are achieved in January while the lowest in June.

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