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Key Points:

- A synthesis of 15-years of transit time research shows progression in how lumped approaches are used at catchment scales
- That synthesis reveals open questions and emerging challenges in transit time research that are summarized here

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

P. Benettin,
paolo.benettin@epfl.ch

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Transit Time Estimation in Catchments: Recent Developments and Future Directions

Paolo Benettin[1], Nicolas B. Rodriguez[2], Matthias Sprenger[3], Minseok Kim[4], Julian Klaus[5], Ciaran J. Harman[6], Ype van der Velde[7], Markus Hrachowitz[8], Gianluca Botter[9], Kevin J. McGuire[10], James W. Kirchner[11,12,13], Andrea Rinaldo[1,9], and Jeffrey J. McDonnell[14,15]

[1]Laboratory of Ecohydrology ENAC/IIE/ECHO, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, [2]French National Institute for Agriculture, Food, and Environment (INRAE), Bordeaux, France, [3]Earth & Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, CA, USA, [4]Department of Civil Engineering, Pusan National University, Busan, South Korea, [5]Department of Geography, University of Bonn, Bonn, Germany, [6]Department of Environmental Health and Engineering and Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD, USA, [7]Faculty of Science, Earth and Climate, Vrije Universiteit, Amsterdam, Netherlands, [8]Department of Water Management, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, Netherlands, [9]Dipartimento ICEA, Università degli studi di Padova, Padua, Italy, [10]Department of Forest Resources and Environmental Conservation and Virginia Water Resources Research Center, Virginia Tech, Blacksburg, VA, USA, [11]Department of Environmental Systems Science, ETH Zürich, Zürich, Switzerland, [12]Swiss Federal Research Institute WSL, Birmensdorf, Switzerland, [13]Department of Earth and Planetary Science, University of California, Berkeley, CA, USA, [14]Global Institute for Water Security, School of Environment and Sustainability, University of Saskatchewan, Saskatoon, SK, Canada, [15]School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham, UK

Abstract Water transit time is now a standard measure in catchment hydrological and ecohydrological research. The last comprehensive review of transit time modeling approaches was published 15+ years ago. But since then the field has largely expanded with new data, theory and applications. Here, we review these new developments with focus on water-age-balance approaches and data-based approaches. We discuss and compare methods including StorAge-Selection functions, well/partially mixed compartments, water age tracking through spatially distributed models, direct transit time estimates from controlled experiments, young water fractions, and ensemble hydrograph separation. We unify some of the heterogeneity in the literature that has crept in with these many new approaches, in an attempt to clarify the key differences and similarities among them. Finally, we point to open questions in transit time research, including what we still need from theory, models, field work, and community practice.

1. Introduction

The transit time of water in catchments is a fundamental descriptor of catchment behavior. If we think of "age" as a label that is attached to any water particle resident within a hydrologic system (e.g., a catchment) and that tracks the time elapsed since arrival (e.g., as precipitation), the transit time is the particle's age when it leaves the system (e.g., as discharge or evapotranspiration). While slow to gain ground as a standard metric, transit times and their analyses now abound in the literature due in part to the increased availability of tracer data used to estimate water transit times. As a result, transit time is now a common means to improve process representation in models and a strong test of model output realism. Once, the review presented in McGuire and McDonnell (2006) was the starting point for newcomers interested in getting to grips with catchment transit time modeling. However, the explosion of the transit time literature since the mid-2000s—with new studies, terminology, theory, and mathematical approaches—means a newcomer to the field now is met with the challenge of absorbing these developments and harmonizing them with earlier approaches.

Over the last ∼15 yr, there have indeed been departures and advancements beyond what was summarized by McGuire and McDonnell (2006). That review provided the first "evaluation and review of the transit time literature in the context of catchments and water transit time estimation". It was motivated by "new and emerging interests in transit time estimation in catchment hydrology and the need to distinguish approaches and assumptions used in groundwater applications from catchment applications". At that time, hydrologists were mainly using time-invariant, lumped parameter transit time approaches largely focused on low temporal resolution sampling of tracers draining from catchments as baseflow. Since then, new approaches (e.g., Botter et al., 2011; Kirchner, 2019) and technological progress in water quality sensing and tracer measurement (Lis et al., 2007; Rode et al., 2016) have made fundamental steps forward.

There have been some targeted reviews on issues in transit time modeling and its application over the past 15 yr. McDonnell et al. (2010) presented a community-based list of open questions in transit time conceptualization, modeling, and analysis. Groundwater age concepts have been reviewed by Turnadge and Smerdon (2014) as have the physical and mathematical origins of steady state analytical solutions (Leray et al., 2016). There have been reviews of how transit times form a link between hydrology and water quality (Hrachowitz et al., 2016), on the use of tracer data to improve rainfall-runoff models (Birkel & Soulsby, 2015), and on multi-tracer inference and its implications for transit time estimation (Abbott et al., 2016). Many papers reviewed the mathematics and theory behind water age concepts (e.g., Benettin, Rinaldo, & Botter, 2015; Calabrese & Porporato, 2017; Rigon & Bancheri, 2021; Rigon et al., 2016), and computed time-variant transit time distributions (TTDs) from distributed hydrological models (Engdahl et al., 2016). Finally, the most recent review has been on the demographics of water age in the different compartments of the critical zone (Sprenger et al., 2019).

Despite these useful contributions, there has not been a systematic review of the catchment-scale transit time estimation literature that synthesizes the developments in this field and the challenges going forward. Here, we explore new challenges that have emerged and then address what lies ahead in terms of field studies and process investigations, as well as the theoretical and practical advancements that are needed to fully merge transit time research into the mainstream of hydrology. Lastly, we note that like any good review, critical focus is needed. Therefore, we concentrate our review on the following objectives, which highlight new advances and research directions, to:

1. Clarify and unify the different terminologies now used in the literature and show their historical roots;
2. Summarize the gradual but uneven progress in transit time research—specifically the time variance of TTDs and the co-evolution of storage and outflow age distributions—and how this has helped us learn about transport processes in catchments; and
3. Identify the open questions in TTD research, along with the emerging challenges for the next 15 yr.

2. The Basics

2.1. Hydrologic Response Versus Water Transit Times

The hydrologic response of a catchment is conventionally defined as the ensemble of processes that generate streamflow after a rainfall or snowmelt event. This response was originally thought to be tied to water transit times by interpreting the instantaneous unit hydrograph as a distribution of transit times (Gupta & Waymire, 1980; Rodriguez-Iturbe & Valdes, 1979). Instead, it depends on the *celerity* at which hydraulic potential gradients propagate in the subsurface, mobilizing water stored within the catchment. Celerities are controlled by the connectivity of saturated patches in the subsurface. A fully saturated confined aquifer can have celerities that are virtually infinite.

Transit times of precipitation (or snowmelt) through a catchment are determined by advection that is, the transport by *velocity* fields—the kinematics of water movement through the subsurface. Velocities are controlled by properties such as local hydraulic conductivity and the presence of preferential flow paths and macropores (see. Beven, 2020; Harman, 2019a; McDonnell & Beven, 2014, for in-depth discussions).

The difference between the flow velocities and the celerity of the hydrologic response has been known for decades. Even in some of the foundational literature on runoff processes, hydrologists envisioned “displacement” processes that rapidly release older water from storage as a primary component of runoff generation mechanisms (Hewlett & Hibbert, 1967). This work anticipated research into early process controls on the rapid response of stored older water. As the use of water isotopes as tracers developed in streamflow generation research, experimental evidence of the differences between water velocity and celerity began to emerge clearly. For example, early transit time work by Dinçer et al. (1970) and Martinec (1975) illustrated these rapid responses of older water hypothesized by Hewlett and Hibbert (1967). The discrepancy between the small velocities of subsurface flow and the rapid watershed response has then been called the “old water paradox”, a concept first discussed by Bishop (1991) and then popularized by Kirchner (2003) through the question: “how do these catchments

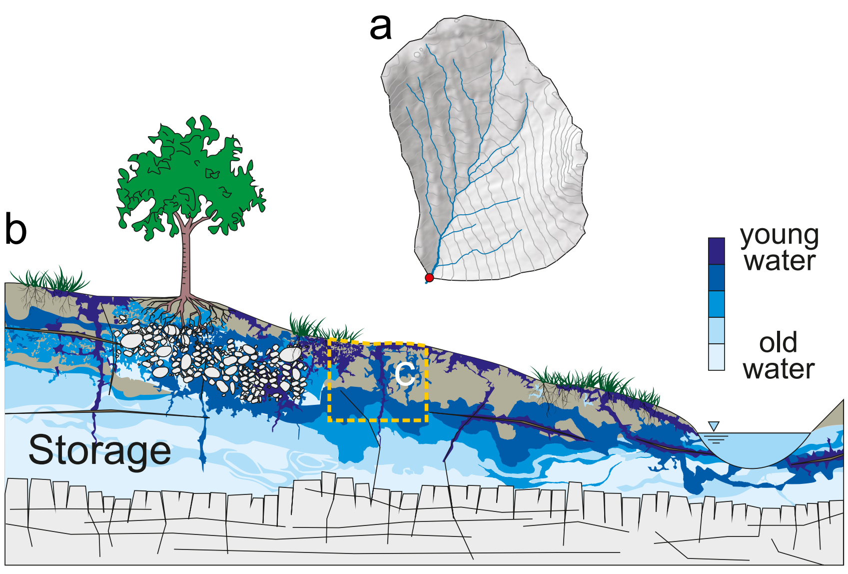

Figure 1. Conceptual example of water age mixing in the subsurface, here shown along a transect arbitrarily defined. The water storage comprises water parcels that entered at different times in the past and variously mixed along the way. Different water age distributions and mixing patterns are expected in different hydrologic systems such as a catchment (a), a hillslope (b) or a soil profile (c). Adapted from Rinaldo et al. (2015).

store water for weeks or months, but then release it in minutes or hours in response to rainfall inputs"? Transport processes (i.e., the movement of solutes, tracers, and other properties that are transported along with water) are not independent from flow processes (i.e., the generation of the streamflow hydrograph, without regard to the origins of the water released), but they are controlled by different mechanisms. Thus, models that want to tackle both flow and transport need to account for the different physical processes that control celerities and velocities in hydrological systems. For further discussion of the relationship between hydrologic response and transit times, see Harman (2019a).

2.2. Fundamental Definitions

Age-based approaches to modeling transport and interpreting tracer data use a confusing variety of terms. The meaning of and distinctions between these terms are not always clear. Here, we provide definitions for the terms that will be used consistently throughout this review.

These definitions are somewhat more complex than those presented in McGuire and McDonnell (2006). They have evolved from early theory (Bolin & Rodhe, 1973; Ginn et al., 2009; Niemi, 1977) and more recent work (Benettin, Rinaldo, et al., 2015; Botter et al., 2010; Harman, 2015; van der Velde et al., 2012). Our purpose here is not to review the diverse nomenclature that has been used in the past, but to provide a common foundation for the future. This foundation is adapted to the theoretical complications that arise from time-variability and from partitioning between multiple fluxes.

2.2.1. Control Volume and Hydrologic Balance

Here, we seek a means to describe transport dynamics at the scale of an entire landscape element, such as a plant root zone, hillslope, stream reach, or watershed. Any landscape element (Figure 1) can be seen mathematically as a control volume V with boundary δV. Water carrying material (solutes, tracers, etc.) across the boundary δV is treated as incompressible and quantified volumetrically. Within V, the volume of stored water $S(t)$ [L^3] increases with inflow at rate $J(t)$ [L^3T^{-1}] and decreases with outflows, such as discharge $Q(t)$ and evapotranspiration $ET(t)$ [L^3T^{-1}], so:

$$\frac{dS}{dt} = J(t) - Q(t) - ET(t) \tag{1}$$

The symbol J is used instead of the more traditional P (for precipitation) to avoid confusion with probabilities. To avoid mathematical complications that arise when tracking multiple inflows separately, we only focus here on a single inflow (precipitation plus snowmelt). We also only focus on two major hydrological outputs, Q and ET, but the same theory applies to a different number of outputs (e.g., to account for deep groundwater losses). Below, we will use subscripts Q to indicate a quantity is related to "discharge". However, unless otherwise noted equivalent quantities exist for evapotranspiration and any other exit pathway.

2.2.2. Age, Life Expectancy and Transit Time

The "age" of water is defined relative to the moment it crosses into V across the boundary δV. In catchments, water age is usually defined with respect to the time water lands on the catchment as rainfall. In the special case of snowfall, one may consider either the time of fall or the time of melt, depending on whether the snowpack is considered to be part of catchment processes or external forcing. For the purpose of this review, we will mainly focus on age with respect to rainfall. In general, we will use T to refer to ages, and t to clock times. At time t, water that entered V at some earlier time t_i has an *age*:

$$T_{age} = t - t_i \tag{2}$$

We can think of age as a clock labeling a water molecule that crosses into the control volume boundary δV coincident with a cohort "parcel" of water molecules, and transits through V. As age is defined with respect to a previous time, it can be useful to think of it as looking "backward" in time.

The "life expectancy" of a parcel of water is complementary to age, in that it describes the interval of time until a parcel passes out of δV. At time t, a parcel that exits at a later time t_e has a *life expectancy* of:

$$T_{exp} = t_e - t \tag{3}$$

Life expectancy can be seen as a "forward" concept because it is based on tracking a parcel forward in time, regardless of when it entered in the past (e.g., Cvetkovic et al., 2012).

The total time elapsed between a parcel's entry t_i and exit t_e is the *transit time* $T_{transit}$:

$$T_{transit} = t_e - t_i = T_{age} + T_{exp} \tag{4}$$

If we fix the entrance and exit times, the transit time can be interpreted both as the age at exit (because at $t = t_e$ the parcel has $T_{transit} = T_{age}$, and $T_{exp} = 0$) and as the parcel's life expectancy at entry (at $t = t_i$ $T_{transit} = T_{exp}$ and $T_{age} = 0$). Thus, $T_{transit}$ can be seen both as a forward and a backward concept. The distinction between age (or life expectancy) and transit time has often been a source of confusion, with the terms being used interchangeably by some. The term "residence time" is also often used ambiguously to indicate both age or transit time, as noted by Sierra et al. (2016) in the context of carbon age, and we refrain from using this terminology here. The term travel time is fully equivalent to transit time, but for consistency, we will use transit time throughout the manuscript.

It is important to clarify early in this review that the concept of water age is invaluable to understanding and interpreting transport processes in hydrological systems, but the water age itself is not a driver of transport processes. Water age should rather be conceived as a property that is transported along by the water velocity field (see Section 2.1), that is, water age is a consequence and not a driver of hydrologic transport.

2.3. Water Age Distributions

2.3.1. Age and Transit Time Distributions

The time spent by an ensemble of water particles in a system can be described through different types of distributions, both in the form of probability density functions (pdf, denoted by lowercase p) and cumulative distribution functions (denoted by uppercase P). Intuition suggests that water age distributions can vary over time due to changing hydrologic conditions (e.g., during a storm event when water tends to move quickly or during a dry summer when water tends to be retained within the soil matrix) and so they are in general a function of both age and time. We stress this dependency through the notation $p(T, t)$ (and $P(T, t)$). Time-variant age distributions can be equivalently termed unsteady, or transient, or time-varying. In the rest of this manuscript, we will only use the term "time-variant". It is useful to clarify that the notation $p(T, t)$ does not mean that the distributions are

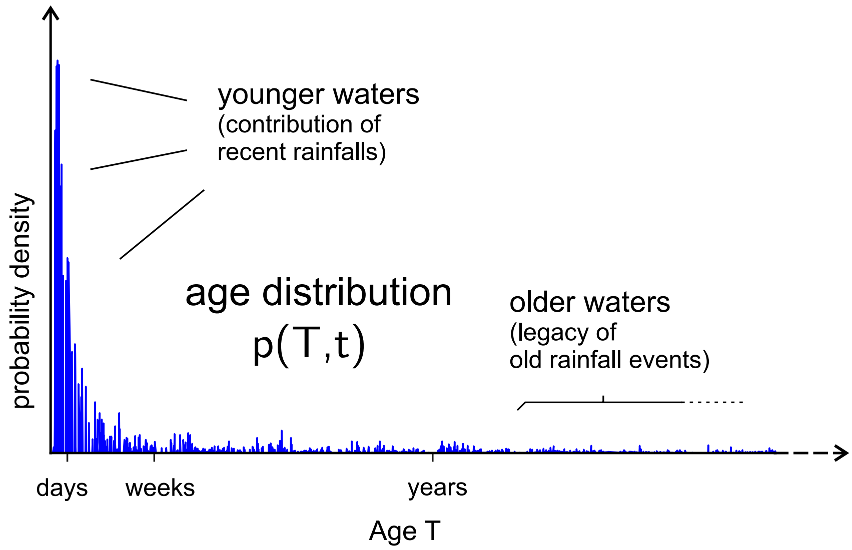

Figure 2. Conceptual example of a (backward) age distribution. A water sample collected at time t is composed of waters that entered through past precipitation events and thus have different ages T. For this reason, the "instantaneous" age distribution evaluated in t has an irregular shape and reflects the precipitation record that occurred before t. The temporal evolution of age distributions is described in Section 3.2.2.

bivariate and the use of conditional probabilities $p(T\,|\,t)$ (Botter et al., 2010; Rigon et al., 2016) would be formally more appropriate. However, for the sake of simplicity and to be consistent with the unified notation adopted since Rinaldo et al. (2015), we prefer to avoid the conditional probability formalism here.

We broadly classify distributions as "backward" or "forward" distributions (depending on whether they address age or life expectancy) and as "storage" or "flux" distributions (depending on whether they refer to water within the control volume or water flowing through the boundaries as input/output fluxes).

Both forward and backward distributions have played important roles in recent studies of time-variant transit time behavior, though the context of their use tends to differ. The forward distributions address water life expectancy and are closely related to the breakthrough curve of a discrete tracer injection. They have often been used to interpret data from tracer application studies (e.g., Benettin et al., 2021; Evaristo et al., 2019; Kim et al., 2016; Rodhe et al., 1996). The backward distributions are based on the concept of water age and are more often used for interpreting environmental tracer data at a catchment outlet. Water age can be seen as the identifier of a past precipitation event, and so the age distribution reflects the contribution of past rainfall and tracer inputs to a water sample collected at time t (Figure 2). The distinction between forward and backward formulations of the transit time is critical under time-variable flow conditions, but disappears if the system is at a steady state (see Niemi, 1977). The backward distributions are at the heart of the main approaches discussed in this review, and will be discussed in more detail below. Instead, forward distributions will not be addressed here and the reader is directed to work by Benettin, Rinaldo, et al. (2015), Calabrese and Porporato (2015), Cornaton and Perrochet (2006), Harman and Kim (2014), and Rigon et al. (2016).

The storage age distribution is termed $p_S(T, t)$, and its cumulative form $P_S(T, t)$ represents the fraction of storage with an age equal to or less than T at time t. The storage age distribution has been often referred to as the residence time distribution, but we avoid this nomenclature here. The flux age distribution describes the distribution of ages in an outflow like streamflow or evapotranspiration. It is termed $p_Q(T, t)$ (or $P_Q(T, t)$ in its cumulative form) for streamflow and $p_{ET}(T, t)$ (or $P_{ET}(T, t)$) for evapotranspiration. By definition, outflowing water leaves the control volume and so its age distribution can also be termed a TTD. The storage and flux age distributions are identical to each other in the special case that the outflow composition is perfectly representative of the storage composition. This situation is often referred to as "well-mixed", but is here given the name "uniform sampling" (see Section 3.2.3 for discussion of why). In this special case $p_Q(T, t) = p_S(T, t)$.

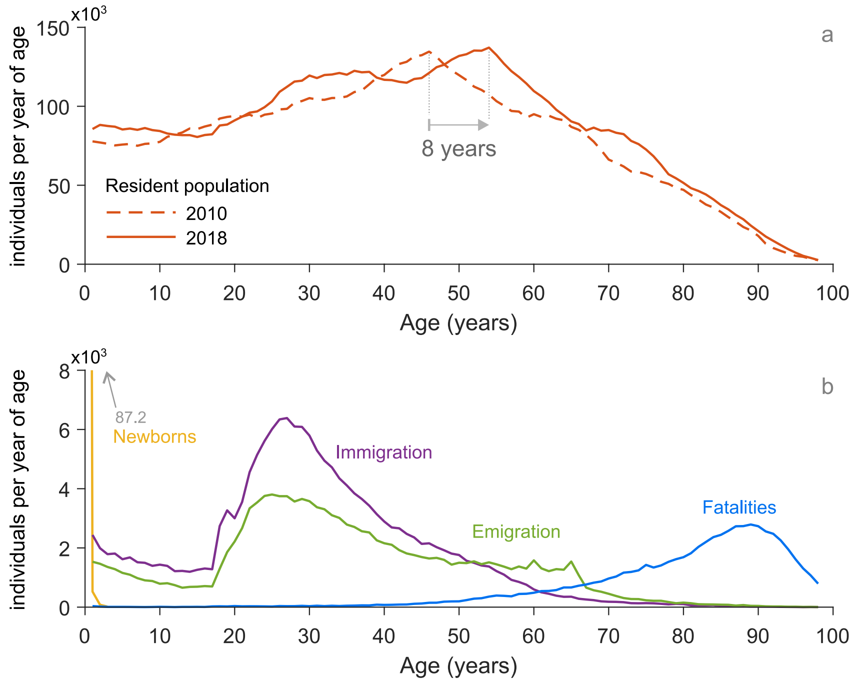

Figure 3. Age distribution of the Swiss resident population in 2010 and 2018 (a) and of the Swiss input/output population fluxes in 2018 (b). All these age distributions are different and change over time because they reflect different physical and social processes. Data from the Swiss Federal Statistical Office. Age distributions have a resolution of 1 yr.

2.3.2. Differences Among Age Distributions

Water age distributions can be easily understood through parallels with population demography, because intuitive concepts that apply to a population of individuals in a country can directly be translated to the "population" of water parcels within a catchment.

The storage age distribution of a human population describes how individuals that live in a certain area are distributed over age. The flux age distributions, instead, describe how the main input and output human fluxes (i.e., newborns, immigration, emigration, fatalities) are distributed over age. An example of these distributions is shown in Figure 3 for the Swiss population. The storage age distribution (Figure 3a), evaluated in two different years, shows a gradual increase in the population between 1 and 50 yr of age and then it declines until it hits the natural maximum age of about 100 yr. The input and output flux age distributions are shown in Figure 3b. Newborns are by definition concentrated at age 0, the emigration and immigration age distributions have multiple peaks (reflecting that people tend to migrate in their 20's–40's with their children), and the age distribution of fatalities is shifted toward elderly people (ages $\approx 80-100$). This simple example is used to show that the two output age distributions (emigration and fatalities) are very different from each other and from the storage age distributions. More generally, all these distributions are different and change over time because they reflect different physical (specifically, demographic) processes taking place within the population system. Similarly, we can expect that the age distribution of the *water* population within a given control volume will be shaped by the input and output water age fluxes and that these age distributions will evolve and differ among themselves. On the other hand, there are important differences between water and humans age distributions (see Section 3.2.2). In particular, age drives demographic processes while it does not drive hydrologic processes.

2.3.3. Steady State and Ensemble-Average Age Distributions

In many cases, for example, to define a characteristic catchment age signature, it is practical to deal with one single age distribution instead of dealing with a series of distributions. This can be done either assuming that the system is in some steady state or by taking an ensemble average (or long-term average) of the time-variant distributions. These time-invariant age distributions have been at the heart of transfer function approaches (Maloszewski & Zuber, 1996; McGuire & McDonnell, 2006) that are still very popular today due to their simplicity. Steady state

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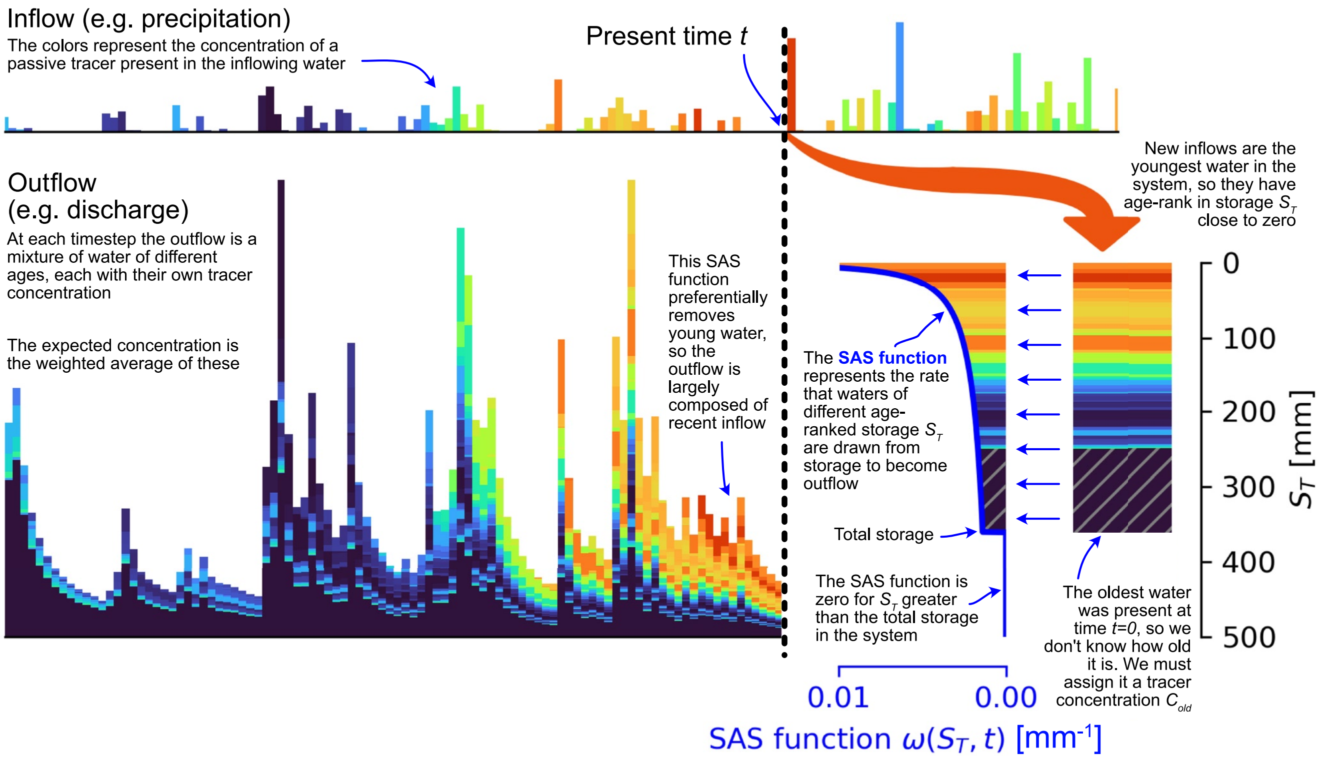

Figure 4. Illustration of the water age balance (Equation 16) using the transport column analogy. An educational video that further describes the water age balance is available in Harman (2022) and can be accessed online at https://www.youtube.com/watch?v=WBYy_iDPRv0 (October 2022).

characterizes an ideal situation in which the rates of change (time derivatives) of all water fluxes and volumes in the catchment are zero. For example, the steady state solution of the advection-dispersion equation leads to various types of time-invariant age distributions (see Kreft & Zuber, 1978), and a well-mixed (or uniformly sampled) system at steady state has an exponential age distribution with a characteristic time scale equal to the ratio between the storage and the flow rate. Leray et al. (2016) present many more examples. Time-averaged distributions are obtained from their time-variant versions by averaging over a given time interval:

$$< p(T) >= \frac{1}{t_b - t_a} \int_{t_a}^{t_b} p(T, t) dt \tag{5}$$

where p can be a flux or storage age distribution and t_a and t_b define a time interval. This time-averaged distribution has sometimes been called the master TTD (Heidbuechel et al., 2012) or the marginal distribution (Botter et al., 2010) because the averaging procedure is in fact equivalent to a marginalization in statistics. The averaging can also be done using weights such as flow (Kirchner, 2016b; Peters et al., 2014). The flow-weighted age distributions will differ from the non-weighted ones. For example, if a stream is dominated by young water during high flow and by old water during the rest of the time, then its flow-weighted age distribution will tend to have most of its mass over young water, even if high flow events have a shorter duration. In comparison, the non-weighted distribution will reflect the age distribution of an average day of flow rather than an average liter of flow. In the case of steady state, the flow-weighted and the non-weighted age distributions are equal, trivially, because flow is constant.

2.3.4. Age-Ranked Storage and the SAS Function

There are two functions that are somewhat more elaborate than the simple age distributions: the age-ranked storage S_T and the StorAge Selection (SAS) functions ω. They are defined here and they will be used later in the formulation of the water age balance (Section 3.2.2 and Figure 4).

The age-ranked storage $S_T(T, t)$ is defined (Harman, 2015) as the cumulative storage age distribution multiplied by the storage:

$$S_T(T,t) = S(t)P_S(T,t) \tag{6}$$

Thus, $S_T(T, t)$ can be seen as an un-normalized cumulative distribution whose maximum is $S(t)$ rather than 1. A number of similar reformulations and their potential uses are discussed in Harman (2019a), but only S_T will be further discussed here. The age-ranked storage quantifies the mass of water with age equal to or less than T at time t and it has units of volume. The terminology "ranked" stresses that the water storage volumes are classified according to their age. As it will be shown in Section 3.2, this ranking is a convenient way to tag stored water parcels.

Many recent advances in TTD approaches have come from better understanding the relationship between the distribution of ages in storage $p_S(T, t)$ and ages in an outflow $p_Q(T, t)$. SAS functions (see also Section 3.2.3) were originally defined by Botter et al. (2011) as:

$$\omega_Q(T,t) = p_Q(T,t)/p_S(T,t) \tag{7}$$

When this ratio is equal to 1 for all T, the outflow age distribution is the same as the age distribution in storage (i.e., the uniform sampling case). Values greater than (or less than) 1 for a given age T mean that water of that age is over-represented (or under-represented) in the outflow relative to its presence in storage. Starting from this initial definition, useful transformed versions of the SAS function have been developed (see Section 3.2.2 and Harman, 2015). The integral form of the SAS function is usually indicated as $\Omega_Q(T, t)$. The terminology "storage selection" should not induce a reader to think that outflows are expected to actively select water based on its age. The term selection was simply born in analogy to statistical sampling because it highlights the link between the pool of available waters (i.e., the water storage) and the subsample of that pool that is released to stream or evapotranspiration. Thus, while the processes generating outflows clearly do not operate through an age-based sampling mechanism, it turns out to be very convenient and practical to conceptualize the transport process *as if* stored waters were selected by the outflows based on age.

2.4. Tracers and TTDs

Here, we use the term "tracer" to refer to any substance that allows us to follow and infer water movements within a hydrologic system. Tracers can be either naturally present in the water cycle ("environmental" tracers) or deliberately introduced ("applied" tracers, such as artificial dyes). They can be (almost) passive and faithfully follow the water or they may react (e.g., due to degradation, mineral dissolution, evaporation) thus tracing a combination of transport and reaction. Tracer data are necessary to characterize velocities and distinguish water parcels in the subsurface. These data have been used to infer characteristic transport signatures (e.g., Kirchner & Neal, 2013) and to test or calibrate water age models (see below). Several publications (e.g., Kendall & McDonnell, 1998; Leibundgut et al., 2009; McGuire & McDonnell, 2015; Sprenger et al., 2019) specifically discussed advantages and disadvantages of different tracers and here we recall the main features that make tracers good for inferring water age in catchments. The ideal tracer is easy to sample in both input and output fluxes and easy to analyze; it is conservative or decays at a known rate; it is passive to evaporation and root water uptake; it does not actively interact with the soil matrix (sorption, ion exchange); it is naturally present in precipitation; it is sufficiently variable to distinguish precipitation that fell over different timescales (either due to input variability or because of decay/reactivity). While no tracer meets all these requirements, the tracers that satisfy most of them and thus are popular in catchment hydrology are the stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H), the radioactive isotope of hydrogen (tritium) (^{3}H) and, to some extent, chloride (Cl^-). In the last decade, ^{18}O and ^{2}H have become the most popular tracers because they are generally passive to root water uptake (not to evaporation, but the effects of evaporation can be usually compensated for; see Bowen et al., 2018), their measurement has become easier, and in many climates, they have enough variability at both seasonal- and event-scale that they may be used to investigate water age over those time scales. Tritium is a powerful tracer because the input signal in precipitation is now rather stable and its half-life of 12.32 yr enables the quantification of precipitation contributions over multiple years (M. K. Stewart & Morgenstern, 2016). However, its use is still limited by the costs and technical challenges of high-precision analyses and very few studies have used more than a dozen samples to characterize streamflow age (e.g., Visser et al., 2019). Tritium-based studies have traditionally focused on groundwater or baseflow age

(Cartwright & Morgenstern, 2015; Morgenstern & Daughney, 2012) but an application to stormflow conditions, including comparison with stable isotopes, exists (Rodriguez et al., 2021).

Tracer concentration can be simulated using TTDs (a so-called direct problem) or TTDs can be estimated starting from tracer data (a so-called inverse problem). The key step to do so is introducing an equation to link TTDs to tracer concentrations. To understand how tracer concentrations can be associated with the age distributions defined above, it can be helpful to consider that the parcels of water transiting the catchment storage each carry some tracer mass. An important—and reasonable—assumption here is that, upon mixing, mass is not exchanged among parcels, that is, the difference between the diffusion constant for the tracer and the self-diffusion constant of water is small compared to macrodispersion. The tracer concentration of a parcel is generally a function of both age and time (because it depends on the concentration in precipitation and on possible reactions, including decay, occurring with the catchment) and it is indicated as $c(T, t)$. Then, mass conservation guarantees that the tracer output concentration (e.g., C_Q or C_{ET}) is simply the average of the parcels' concentrations weighted by their contribution to the outflow. In mathematical terms, this leads to the integral:

$$C_Q(t) = \int_0^\infty c(T,t)p_Q(T,t)dT \tag{8}$$

In the case of an ideal tracer, the parcels' concentrations are equal to their concentrations when they entered the system: $c(T, t) = C_J(t - T)$ and Equation 8 simplifies into:

$$C_Q(t) = \int_0^\infty C_J(t-T)p_Q(T,t)dT \tag{9}$$

For a radioactive tracer, like tritium, the initial concentration decreases over time according to a decay constant α: $c(T, t) = C_J(t - T)\ exp(-\alpha\ T)$ (see Rodriguez et al., 2021). Equations 8 and 9 are the time-variant equivalents of the well-known lumped convolution integral (Maloszewski & Zuber, 1996; Zuber, 1986). However, strictly speaking, they are Volterra integrals rather than convolution integrals, because their kernels are time-variant. Early lumped approaches based on Equation 9 (see McGuire & McDonnell, 2006) assumed a time-invariant functional shape (e.g., a gamma distribution) for the TTD and then calibrated its parameters based on available tracer output measurements. The use of a time-invariant TTD ($p_Q(T)$, Section 2.3.3) comes with the assumption that the catchment behaves as if it were at hydrologic steady state or that the mean system state can be used to characterize the transport of tracers over time. Some of the new water age models (Section 3.2) still rely on Equation 8 but the TTD is generally time-variant and not assumed a priori.

3. New TTD Frameworks (2006–2022)

3.1. The Roots

The temporal variability of water age distributions in environmental systems has been known theoretically for a long time (Lewis & Nir, 1978) and already in the 1990s, several studies showed the usefulness of time-variant age distributions for accurately simulating tracer data (Barnes & Bonell, 1996; Capell, 2007; Lindström & Rodhe, 1992; Rodhe et al., 1996; Turner et al., 1987; Turner & Macpherson, 1990). Early approaches were borrowed from the theory of variable-flow processes in chemical engineering (Niemi, 1977) and made use of the flow-weighted time approach (Rodhe et al., 1996; Roth et al., 1991; Zuber, 1986). This technique replaces the calendar time with the accumulated flow, effectively shortening periods with low flows and expanding periods with high flows. If flow variability is the only source of temporal variability (i.e., the storage and the flow paths remain constant), the TTD expressed in the new flow-weighted variable is time-invariant and can be parameterized with a fixed pdf and used in the convolution integral. Another simple approach to assess some degree of variability in age distributions while keeping a fixed TTD shape has been to calibrate the TTD parameters separately over different time periods (Stumpp et al., 2009) or over moving windows (e.g., Heidbuechel et al., 2012; Hrachowitz, Soulsby, Tetzlaff, Dawson, Dunn, et al., 2009; Tetzlaff et al., 2014). As an alternative to time-domain convolution approaches, data-based spectral and wavelet methods were also developed for TTD estimation (Kirchner et al., 2000, 2001; Kirchner & Neal, 2013). These have the advantage that they do not require continuous inputs, and the shape of the spectrum can help to constrain the shape of the TTD (Shaw et al., 2008); however, they have not been widely adopted.

3.2. New Approaches Based on the Water Age Balance

Some of the new theoretical approaches to TTDs are different from the approaches in Section 3.1 because the shape of the TTD is not assumed a priori but is instead computed based on mass conservation over time and age. These approaches have seen significant theoretical developments in the last 10 yr, but progress has been heterogeneous and there is now the need to homogenize the existing literature. For this reason, a sizable part of this review focuses on the harmonization of the water age balance approaches. Other and more recent approaches, like the ensamble hydrograph separation (Section 3.4), do not suffer from this heterogeneity because their development can be tracked to just one or two scientific papers.

3.2.1. The Population Balance

Conservation of age and mass can be easily seen in the human population example of Figure 3. The storage age distribution (i.e., the age distribution of the resident population in this case) changes from 2010 to 2018 because of: (a) addition of new individuals (particularly newborns); (b) departure from the system by some former residents; and (c) aging, which is visible in the rightwards shift of the distribution, as each surviving individual is 8 yr older after 8 yr. So how can this population conservation over age be related to our original problem of water age distributions? If we consider a simple hydrologic system (e.g., a catchment) as described in Section 2.2.1, then the two major water outputs (ET and Q) are analogous to the two major population outputs and precipitation J is effectively equivalent to newborns. The storage of individuals with different ages becomes the storage of water with different ages. A mathematical expression for water conservation over time and age is:

$$\frac{\partial s(T,t)}{\partial t} = j(T,t) - et(T,t) - q(T,t) - \frac{\partial s(T,t)}{\partial T} \tag{10}$$

The storage term $s(T, t)$ denotes the water storage with age T at time t. This is dimensionally a density and has units of volume/age. The flux $j(T, t)$ is the precipitation input and is concentrated in $T = 0$ (the mathematical expression using a Dirac delta is $j(T, t) = J(t)\ \delta(T)$). The terms $et(T, t)$ and $q(T, t)$ indicate the outflow of water of age T leaving the catchment via ET and Q, respectively. The total output fluxes are obtained by integration over all ages $\int_0^\infty et(T,t)dT = ET(t)$ and $\int_0^\infty q(T,t)dT = Q(t)$. Aging appears as the derivative of $s(T, t)$ over age (last term on the r.h.s of Equation 10) and can be seen as an advection process over age, with celerity equal to 1. Overall, Equation 10 is a mass balance applied to each water parcel (rather than to the entire water storage) and its evolution depends on inputs and outputs, as in any mass balance, but in this case also on aging.

The demographic analogy is useful to make age distributions intuitive, but it also has limitations that need to be overcome. The population balance is usually carried out annually with annual fluxes, while the hydrologic balance is often needed at daily and subdaily scales. At these scales, precipitation is highly erratic and the input to the system becomes very discontinuous with gaps corresponding to dry periods. Moreover, when dealing with populations one can sample individuals and measure their age, as well as measure the total population storage; by contrast, water parcels cannot be sampled individually, their age cannot be measured, and the total water storage is very difficult to estimate (Carrer et al., 2019; Pfister et al., 2017).

Besides these practical considerations, there is one structural limitation that prevents the direct use of Equation 10 in real-world water age problems. The term $q(T, t)$ incorporates both the outflow amount $Q(t)$ and its age distribution $p_Q(T, t)$. This means that the flow and transport problems cannot be decoupled, while we typically want to treat these two terms separately because they are controlled by different system properties (sensu the "old water paradox", Section 2.1).

3.2.2. The Water Age Balance

The first form of water-age balance equation where the flow and transport problems are decoupled was introduced by Botter et al. (2011, Equation 3) as the "Age master equation". Though with a different notation, the water age outputs were expressed as the product between a water flux (which can be determined through measurements or hydrologic modeling), and its relevant age distribution:

$$q(T,t) = Q(t)p_Q(T,t) \tag{11}$$

$$et(T,t) = ET(t)p_{ET}(T,t) \tag{12}$$

This effectively enables the decoupling between the flow and transport problem. Additionally, the storage age distribution was expressed as the product between the total storage $S(t)$ and its age distribution density $p_S(T, t)$. In the same work, Botter et al. (2011) introduced the StorAge Selection functions $\omega(T, t)$ (Equation 7, called "age mixing" functions at the time) to relate the age distributions of an outflow to that of the storage: $p_Q(T, t) = \omega_Q(T, t)\, p_S(T, t)$. This implies that outflowing water can only be a subsample of the existing stored water and for example, there cannot be any storage of age 10 days if no rain fell 10 days ago, and thus no streamflow can be 10 days old. The introduction of ω had fundamental implications in transport hydrology because, by providing closure to the water age balance, it enabled consistency between transit times and mass conservation. After decoupling the problem of flow and transport (Equations 11 and 12) and introducing the SAS functions (Equation 7), the water age balance equation after Botter et al. (2011) reads:

$$\begin{aligned}\frac{\partial\left(S(t)p_s(T,t)\right)}{\partial t} &= J(t)\delta(T) - Q(t)\omega_Q(T,t)p_S(T,t)\\ &-ET(t)\omega_{ET}(T,t)p_S(T,t) - \frac{\partial\left(S(t)p_s(T,t)\right)}{\partial T}\end{aligned} \tag{13}$$

Equation 13 is equivalent to the population balance (Equation 10), but age distributions now appear explicitly and the SAS function is used to describe how the current water storage, which comprises a distribution of past precipitation inputs, contributes to current discharge or evaporation.

As mentioned above, Equations 11 and 12 allow decoupling flow from transport, but the price to pay is a nonlinear constraint enforcing that an outflow must be equal to the sum of all the stored parcels that contribute to it per unit time: $Q(t) = \int_0^\infty q(T,t)dT = \int_0^\infty Q(t)\omega_Q(T,t)p_S(T,t)dT$. This translates into the constraint:

$$\int_0^\infty \omega_Q(T,t)p_S(T,t)dT = 1 \tag{14}$$

A convenient way to deal with this constraint is reasoning in terms of a different variable, as proposed by van der Velde et al. (2012), who introduced a transformed SAS function (termed STorage Outflow Probability STOP function at the time), and by Harman (2015), who reformulated the problem in terms of "rank storage" rather than absolute age. In both cases, the transformed problem is based on a mapping from age to the cumulative storage age distribution:

$$T \mapsto S_T(T,t) = S(t)P_S(T,t) \tag{15}$$

This transformation is explained in more detail in Benettin, Rinaldo, et al. (2015), Harman (2015), and van der Velde et al. (2012) and the different mappings are discussed in Section 3.2.3. The general idea behind these approaches is to shift the focus from the absolute age of a water parcel to the rank of the parcel with respect to all other parcels. A "low" rank, for example, means that a parcel is younger than most of the water storage, regardless of its actual age. Just like age, the rank position also serves as identifier of a water parcel and this identifier is a function not just of the precipitation event that originated the parcel, but also of all subsequent (and thus younger) parcels. The rank storage can be thought of as a virtual water column where parcels are stacked on top of each other from old to young, such that the depth in the column indicates the rank (see. Harman, 2015, Figure 1). By expressing the SAS functions in terms of rank storage (or normalized-rank storage, as done by van der Velde et al., 2012), Equation 14 is automatically verified whenever the SAS function $\omega(S_T, t)$ is a pdf. After integrating Equation 13 over age, we obtain the evolution of the rank storage over time and age (Harman, 2015, Equation 3):

$$\frac{\partial S_T(T,t)}{\partial t} = J(t) - Q(t)\Omega_Q\left(S_T,t\right) - ET(t)\Omega_{ET}\left(S_T,t\right) - \frac{\partial S_T(T,t)}{\partial T} \tag{16}$$

with initial condition $S_T(T, t=0) = S_{T_0}$ and boundary condition $S_T(T = 0, t) = 0$. The symbol Ω indicates the cumulative SAS function. Once again, the age balance Equation 16 is a statement of mass conservation over time and age, which can be visualized in Figure 4: the rank storage (i.e., the storage volume younger than age T) changes over time because new storage with age 0 is introduced through precipitation, storage of different ages is released to evapotranspiration and streamflow, and all storage volumes get older with time. To help visualize how

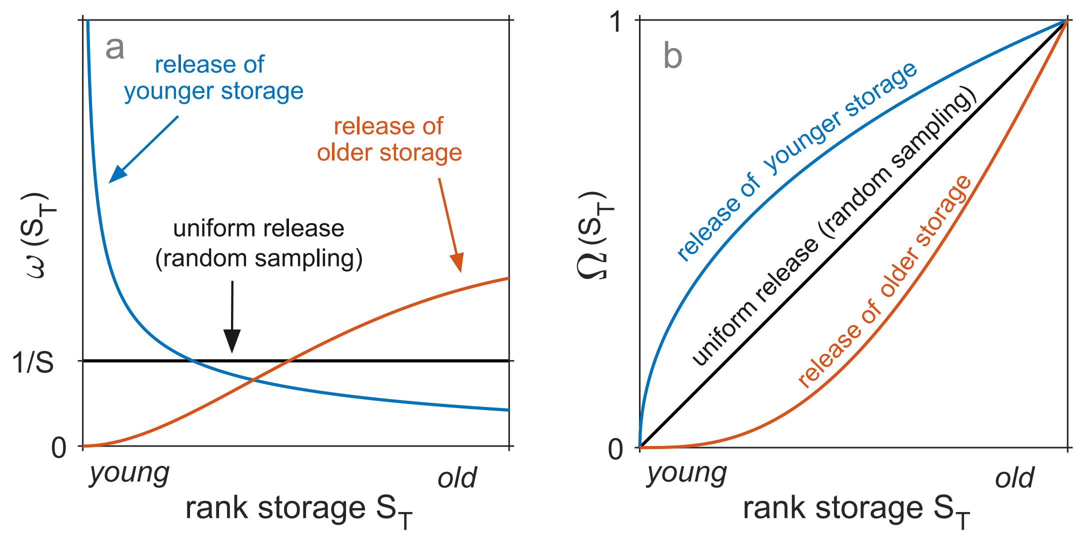

Figure 5. Illustration of the three main conceptual shapes of StorAge-Selection (SAS) functions when expressed as (a) probability density functions $\omega(S_T)$ or (b) cumulative frequencies $\Omega(S_T)$.

the water age balance evolves over time, we have created an educational video available in Harman (2022) and accessible online at https://www.youtube.com/watch?v=WBYy_iDPRv0 (October 2022).

The age balance equation, being a reformulation of mass conservation, is not a "model" by itself, but solving this equation requires a model for the SAS functions. As SAS functions need to satisfy the properties of a probability distribution, it makes sense to model them as pdfs (e.g., a gamma distribution, see Section 3.2.3), with one or more parameters that need to be assigned or calibrated. When the SAS parameters are set for both $\Omega_Q(S_T, t)$ and $\Omega_{ET}(S_T, t)$, and hydrologic fluxes (J, Q, ET) are given, the mathematical problem framed in Equation 16 can be solved. A numerical implementation is usually required except for special cases of uniform sampling and perfect piston flow (see. Botter, 2012). Numerical solutions are usually based on the method of characteristics (see. Benettin & Bertuzzo, 2018; Harman, 2015; Harman & Fei Xu, 2022, for open software implementations), but in certain cases, it may be desirable to uncouple time and age numerically, depending on data requirements and simulation needs (Rodriguez & Klaus, 2019).

Solution to the age balance equation allows one to simulate, at any time, the rank storage S_T and, through the SAS functions, the outflow age distributions:

$$P_Q(T,t) = \Omega_Q\left(S_T(T,t),t\right) \tag{17}$$

$$p_Q(T,t) = \frac{\partial P_Q}{\partial T} = \frac{\partial \Omega_Q\left(S_T(T,t),t\right)}{\partial T} \tag{18}$$

Equation 18 can be used to feed the time-variant convolution integral (Equation 8) and compute tracer concentration in each outflow. Thus, all this theory that started from a mass balance equation ultimately leads to a problem that can be solved numerically and can be confronted with tracer data.

3.2.3. On SAS Functions

The SAS function can be seen as a statistical summary of the transport behavior of a hydrologic system. It quantifies the release of waters of different ages from the storage to an outflow (Rinaldo et al., 2015). This function may have three main conceptual shapes (Figure 5): preferential release of relatively younger storage volumes (decreasing function), uniform release of all volumes (constant function), or preferential release of older storage volumes (increasing function). These behaviors can be modeled through probability distributions such as the beta (van der Velde et al., 2012), power function (Queloz, Carraro, et al., 2015) or gamma (Harman, 2015) distributions. By making the parameters of these distributions vary over time, the SAS functions can also be made time variable. The SAS functions can be parametrized as a function of the rank storage S_T ("rank" SAS functions, rSAS), or as a function of the normalized rank storage $S_T/S(t)$ ("fractional" SAS functions, fSAS). The main difference is that the function domain is the variable interval [0, $S(t)$] for rSAS functions and the fixed interval [0, 1] for fSAS functions. While there are practical differences in using one parameterization over the other (Harman, 2015), and both approaches are used in the literature, these different approaches are not in contrast with each other and they fundamentally express the same transport behaviors.

The particular case of uniform storage selection implies that the water storage is uniformly (or randomly) sampled by an outflow (Benettin, van der Velde, van der Zee, Rinaldo, & Botter, 2013). In this special circumstance, the age distribution of the storage and the outflow are identical and the discharge tracer concentration is equal to the average storage tracer concentration. This is equivalent to the behavior of a completely mixed reservoir, but with the important difference that it does not require any physical full mixing and water parcels are simply selected proportionally to their abundance, regardless of where they are (in fact, space is not involved at all in a lumped approach). Prior to the development of the SAS-function concept, many modeling studies have also generated TTDs using "mixing coefficients" (Birkel et al., 2015; Dunn et al., 2007; Fenicia et al., 2010; Hrachowitz et al., 2015, 2013; McMillan et al., 2012; Soulsby et al., 2015). The mixing coefficient (C_M) quantifies the fraction of input water that is "mixed" with the resident water, while the remaining fraction ($1 - C_M$) bypasses the storage entirely. In spite of the differences in terminology and the practical procedure to calculate the TTDs, the method is functionally and mathematically equivalent to a piece-wise linear SAS-function (Hrachowitz et al., 2016).

Estimating SAS functions quantitatively (i.e., not just their shape but also the actual value that they may take) in a real-world catchment is perhaps the greatest challenge in SAS approaches. SAS functions cannot be measured directly (except under special circumstances, see Harman & Kim, 2014), they may not be regular, and they likely change over time. Current approaches to estimate SAS functions rely on the calibration of SAS parameters to tracer data. This faces the issues of model parameter calibration through a convolution integral, which is only partly alleviated by the use of formal calibration techniques. The use of different SAS functions may induce different model performances and water age estimates and only few studies addressed this issue explicitly (Borriero et al., 2022). Moreover, there is great uncertainty related to the SAS function of ET fluxes because of the lack of tracer data in ET (see Sections 4.2 and 4.5 for a discussion), which makes it difficult to evaluate the convolution integral for ET. This certainly influences the estimated SAS function of Q. However, one can use the water age balance to test different assumptions on the SAS functions of ET and see how/if they impact the estimated SAS function of Q (and related transit times, see Visser et al., 2019). More generally, estimating the "true" SAS function of a real-world catchment may be difficult, but one can formulate competing hypotheses (e.g., is a given SAS function more plausible than random sampling? Is it necessary to use time-variant SAS functions to adequately reproduce a given tracer time series?) and use formal model comparison methods to test them. The last 15 yr of research provide some guidance about the shapes that these functions are expected to take (see Section 4.2).

3.2.4. Practical Ways to Apply the Age Balance Equation

The water age balance can be applied to any hydrologic control volume as long as input/output fluxes and SAS functions are provided. We can differentiate two practical ways to construct catchment-scale transport models using this approach. They are distinguished on the basis of whether they partition the watershed into conceptual compartments (sometimes referred to as "buckets") or not (see Benettin, Soulsby, et al., 2017, Figure 1). Approaches that do compartmentalize the catchment can be seen as an extension of conceptual hydrologic models, where a water age balance is solved for each compartment. The alternative is a more "pure" application of the SAS approach, in which the entire catchment is treated as a single control volume, and internal compartmentalization is replaced by a catchment-scale SAS function.

The use of multiple conceptual compartments provides great model flexibility. The simplest case is that of two compartments, typically interpreted as soil and groundwater storage, but many more compartments can be introduced such as canopy interception, hillslope and riparian zone compartments (see Hrachowitz et al., 2013). Such an approach requires knowledge of the internal fluxes from/to all compartments. As these usually cannot be measured, they need to be modeled as well and so these models need to integrate both flow and transport processes. This application also requires a suitable SAS function for each storage component, such that the number of parameters quickly increases with model complexity. Thus, a careful testing procedure is generally required to limit parameter uncertainty. Following progress in our conceptual understanding of transport processes, we expect that storages preferentially release relatively young water to streamflow (see Section 4.2). Various studies explicitly modeled an unsaturated root zone compartment with preferential release of younger ages, using either piece-wise linear (e.g., Cain et al., 2019; Fenicia et al., 2010; Hrachowitz et al., 2015, 2013; McMillan et al., 2012) or beta distributions (Hrachowitz et al., 2021). Berkowitz and Zehe (2020) argue that the preferential release of younger water can be highly relevant also in the groundwater environment and should therefore be reflected by the use of suitable SAS functions. Yet, many studies (Benettin, Bailey, et al., 2015; Rodriguez et al., 2018), opted for a simpler uniform sampling scheme (often termed complete or uniform mixing in those studies) in each storage component. While physically unrealistic, this simplifying assumption provided satisfactory results in terms of tracer simulation with a much-reduced computational effort. Indeed, it can be shown (Benettin, Kirchner, Rinaldo, & Botter, 2015) that, in well-mixed cases or those with constant mixing coefficients, TTDs are not needed to compute tracer concentrations (they can be computed a posteriori) and computational times are drastically reduced.

In the "pure" SAS application (e.g., Lapides et al., 2022; Lutz et al., 2017; van der Velde et al., 2015; Visser et al., 2019; Wilusz et al., 2017; Z. Zhang et al., 2021), the age balance equation is solved using observed catchment-scale inflows and outflows (or best estimates of them obtained from some auxiliary model, as is typically required for snowmelt and ET). This solution does not aim to simulate flow and generally requires fewer parameters. As there is not much flexibility with the model structure, the ensemble of catchment-scale transport processes are all aggregated into a catchment-scale SAS function. The SAS function itself is commonly allowed to vary in time to account for the rate at which waters of different ages are mobilized into the outflows. The time variability is usually achieved by linking one or more SAS parameters to some observed catchment state variable (see Harman, 2015). This implementation has the advantage that inferences about transport processes are not artifacts of the watershed compartmentalization. However, they may still contain artifacts of the chosen SAS function and its coupling to state variables. There is no general rule as to when a single control volume is better than a catchment compartmentalization and the choice usually depends on whether one wants to model water fluxes along with tracer transport or not.

A somewhat hybrid and spatially distributed approach has been proposed by Nguyen et al. (2021); Nguyen et al. (2022) through the mHM-SAS model. In such a model, water flow and transport in the top soil layers is simulated using a grid-based model under a random sampling assumption, while transport in the subsurface component (either spatially distributed or not) is tracked through a SAS function approach. The mHM-SAS model has been tested and applied to nitrate circulation in mesoscale catchments (Nguyen et al., 2021, 2022).

3.2.5. Other Applications of the Age Balance

While the theory described here addresses the water age balance equation in the general time-variant case, there are similar equations that can be used for different purposes. The water age balance equations can be solved at steady state (i.e., with water fluxes, storages, and age distributions that are constant over time) to provide unique, long-term relationships between storage and flux age distributions (Berghuijs & Kirchner, 2017; Bolin & Rodhe, 1973; Harman, 2015). In case the decoupling between flow and transport is not necessary, Equation 10 can be treated as a simple population balance and it takes the form of the McKendrick-Von Foerster (MKVF) equation (see Lewis & Nir, 1978; Trucco, 1965). The MKVF equation makes use of the "loss function" λ, which is functionally equivalent to the SAS function, but it is not bound to nonlinear constraints like Equation 14. Thus, it supports closed-form solutions that have been used to explore the probabilistic structure of water age (Calabrese & Porporato, 2015; Porporato & Calabrese, 2015). Equations similar to 13 and 16 have also been developed and used in other contexts, including: carbon age and residence times (Metzler et al., 2018), bird migration (Drever & Hrachowitz, 2017), solute transport in lakes (A. A. Smith et al., 2018), solute transport in green biofilters (Parker et al., 2021) and reach-scale stream-hyporheic transport (Harman et al., 2016).

3.3. New Approaches Based on Spatially Distributed Models and Water Age Tracking

While this review does not specifically address the variety of existing spatially distributed transport models, it is worth mentioning that such models can be calibrated on tracer data and coupled to water age tracking algorithms to provide catchment-scale water age distributions. Physically based models, in particular, may help identify the physical controls on the shape of lumped functions such as TTDs and SAS functions.

A simple 1-D advection-dispersion model was used by Kirchner et al. (2001) as a mechanism to explain fractal scaling in stream tracer concentrations and to identify the Péclet (Pe) numbers that produce TTDs similar to gamma distributions with shape parameter $\alpha < 1$. 1-D advection and dispersion was similarly used by Benettin, Rinaldo, and Botter (2013) to relate the shape of a SAS function to the Pe number. Other examples of age distributions and SAS functions computed from process-based models and tracer data include: stationary two-dimensional groundwater flow problems (van der Velde et al., 2012), non-stationary 1-D and 2-D flow through unsaturated porous media (Asadollahi et al., 2020; Pangle et al., 2017; Sprenger et al., 2018), non-stationary groundwater flow (Kaandorp et al., 2021), and fully coupled catchment-scale flow and transport models (Kim et al., 2022; Kuppel et al., 2018; Remondi et al., 2018; Smith, Tetzlaff, & Soulsby, 2020; Wilusz et al., 2020; Yang et al., 2018). Recently, Kim and Harman (2022) used hydraulic groundwater theory to derive analytical expressions for the TTD and SAS functions of hillslope subsurface flow under steady recharge.

These approaches usually compute TTDs through virtual flux tracking or particle tracking. Virtual flux tracking refers to the virtual application of a fully conservative tracer in precipitation. The model is run as many times as there are rainfall events and the tracer is applied each time to a different event. At each run, the transport model computes the tracer breakthrough curve of the applied virtual tracer. The curve is then multiplied by the relevant outflow flux and normalized by the tracer input to provide the (forward) TTD associated with a rainfall event. Further details and formulas for this approach can be found in Asadollahi et al. (2020), Pangle et al. (2017), and Sprenger et al. (2018). This approach is simple and applies to any type of model (physics-based or conceptual), but it is computationally expensive because it requires the model to run for a potentially large number of times. Particle tracking is usually based on the introduction of virtual water "particles", whose number or mass is proportional to precipitation inputs, on top of the model domain. These particles are then typically moved through the domain according to advective fluxes (driven by water potential gradients between adjacent cells, under the assumption that dispersion is negligible), and they can be partly lost to evapotranspiration or removed when they reach the boundaries of the system. These particles are typically identified with water of a single age, but may also be identified with an evolving population of ages (see Benson et al., 2019). Tracking the position and mass of the particles allows one to reconstruct water trajectories and transit times (e.g., de Rooij et al., 2013; Wilusz et al., 2020). The Multiple Interacting Pathways approach (Beven & Davies, 2015; J. Davies et al., 2013) provides additional flexibility by assigning particles a velocity distribution that may account for preferential flows and bypassing.

3.4. New Data-Based Approaches

Recent methodological advances have aimed at estimating water age distributions (or at least some water age statistics) from tracer data directly, without prior assumptions on the TTD or SAS function.

3.4.1. Direct Estimates in Controlled Experiments

In some special and controlled experimental settings, an individual (forward) TTD can be directly computed from the breakthrough of an artificially applied tracer (Benettin et al., 2021; Evaristo et al., 2019; Mennekes et al., 2021; Queloz, Bertuzzo, et al., 2015). While this approach is the only one that can measure and isolate individual distributions, it has the obvious limitation that it cannot go beyond one realization (or just a few of them), within a small and typically disturbed experimental setup. A larger number of direct TTDs observations can be obtained using the PERTH (PERiodic Tracer Hierarchy) method (Harman & Kim, 2014), where the tracer is introduced to an experimental system whose fluxes and storage vary in a periodic steady state. Breakthrough curves that each encompass multiple cycles of the periodic system can be folded together in a way that allows the direct estimate of the time-varying age distributions and SAS functions (Kim et al., 2016, 2022; Pangle et al., 2017).

3.4.2. Young Water Fractions

The right tails (older water) of TTDs, which are inherently difficult to constrain with tracer data, exert strong leverage on the mean transit time. As a consequence, estimates of mean transit times are highly sensitive to the assumed shape of the TTD (e.g., Kirchner et al., 2010; Seeger & Weiler, 2014). Even if the TTD shapes of individual compartments or subcatchments were knowable a priori, this will not be the case for the TTD shapes of heterogeneous combinations of those compartments or subcatchments (mixtures of exponential distributions are not exponentially distributed; mixtures of gamma distributions are not gamma-distributed, and so on). This directly implies that mean transit times cannot be reliably determined for spatially heterogeneous catchments. Instead, mean transit time estimates for heterogeneous catchments—which is to say, all catchments—will be strongly biased low, because the compartments or subcatchments with shorter mean transit times will have greater influence on the result (see. Kirchner, 2016a, Figures 5 and 7).

A rational response to this aggregation bias is to search for transit time metrics that are much less vulnerable to it. One such metric is the young water fraction F_{yw}, defined by Kirchner (2016a) as the fraction of streamflow younger than a threshold τ_{yw}. Using the notation of Sections 2.3.1 and 2.3.3, this metric can be seen as the marginal cumulative age distribution $<P_Q(T)>$ evaluated in $T = \tau_{yw}$. It was demonstrated by Kirchner (2016a) that F_{yw} can be calculated from the ratio between the seasonal isotopic cycles in streamflow and precipitation (or, more generally, the input and output from any control volume). Across a very wide range of TTD shapes, F_{yw} quantifies the fraction of streamflow that is younger than a threshold τ_{yw} of roughly 2–3 months (or roughly 1/6–1/4 of the wavelength of the dominant cycle, which could potentially be something other than a seasonal cycle). Furthermore, even in nonstationary catchments, F_{yw} accurately estimates the marginal (i.e., time-averaged) fraction of young water (Kirchner, 2016b). F_{yw} has the additional practical advantage that it can be accurately estimated from infrequently and unevenly sampled isotope data, and thus can be much more widely applied (e.g., Jasechko et al., 2016) than methods that require continuous or high-frequency isotope measurements. Because it can be estimated from discontinuous time series, F_{yw} can be calculated separately for individual ranges of discharge, thus mapping out how F_{yw} varies with catchment wetness (Kirchner, 2016b).

3.4.3. Ensemble Hydrograph Separation

Ensemble hydrograph separation (Kirchner, 2019) is based on correlations between fluctuations in input and output tracer time series, rather than on mass balances or age balances. Ensemble hydrograph separation yields estimates of the new water fraction F_{new}, averaged over ensembles (hence the name) of either precipitation or discharge time steps, chosen to reflect conditions of particular interest, such as different ranges of discharge, antecedent wetness, or precipitation intensity. Thus catchment response to precipitation can be mapped out, directly from data, as a function of ambient conditions and external forcing. The "new" in F_{new} refers to precipitation that has fallen since the previous stream water tracer sample; thus weekly sampling yields weekly new water fractions, daily sampling yields daily new water fractions, and so forth. Extending these methods to multiple time lags directly yields (ensemble-averaged) TTDs, which again can be estimated for different ensembles of time steps, to map out how TTDs respond to catchment conditions and external forcing. TTD shapes are not assumed a priori, but instead estimated directly from the data. Both new water fractions and TTDs can be expressed as "backward" fractions of streamflow, or "forward" fractions of precipitation, with or without volume-weighting. The calculations are conceptually straightforward but may be somewhat tricky to implement correctly, so user-friendly scripts are available for both R and Matlab (Kirchner & Knapp, 2020). Perhaps most importantly, the methods have been extensively benchmark tested (Kirchner, 2019), and demonstrated with chloride and isotope data from Plynlimon, in a proof-of-concept illustration of how F_{new} values and TTDs vary seasonally, with flow regime, and under varying precipitation intensity (Knapp et al., 2019).

Subsequently, Kim and Troch (2020) have suggested a somewhat similar approach that estimates TTDs in flow-weighted time. The flow-weighted time in their approach is different from the traditional flow-weighted time approach (e.g., Rodhe et al., 1996) in that multiple fluxes are considered explicitly. They showed that the use of flow-weighted time is advantageous in estimating TTDs because TTDs are less nonstationary in flow-weighted time. The estimated TTDs can be transformed back to calendar time using inflow and outflow data. Similar to the estimation of the ensemble-averaged TTDs described above, the approach can be used to estimate the ensemble-averaged TTDs in flow-weighted time. Kim and Troch (2020) showed the applicability of the dynamic multiple linear regression as an alternative way of tracking TTD time-variability, which allows for tracking time-variant TTDs or state-dependent TTDs without decomposing the data set. However, a user-specified hyperparameter controls how fast the TTDs can evolve over time, potentially affecting the interpretation of time-varying TTD behavior.

4. Implications and Lessons Learned

4.1. Timescales and Variability of Water Age Distributions

By solving the water age balance at fine temporal resolution (e.g., daily), the variability of the hydrologic fluxes naturally generates water age distributions with irregular and often discontinuous shapes (e.g., van der Velde et al., 2012, Figure 4). Besides being irregular, stream water age distributions are also naturally time-variant because they reflect the history of past meteorological events. While this has been known for a long time, no mathematical formulation was able to fully take this into account before the introduction of the water age balance (Section 3.2).

Most modeling applications based on tracer data suggest that transport mechanisms are very different during wet vs. dry periods. This diversity comes from the presence of multiple physical mechanisms of runoff generation (surface runoff, interflow, groundwater) and the change in their relative contributions as modulated by variable water storage and source area dynamics. Streamflow typically has higher proportions of young water during wet periods (when young water is abundant and near-surface processes dominate) and lower proportions of young water under low-flow conditions (when young water is scarce and poorly connected to the stream, and groundwater contributions prevail; e.g., Birkel et al., 2015; Hrachowitz et al., 2015; Knapp et al., 2019; Soulsby et al., 2015; Tetzlaff et al., 2014; von Freyberg et al., 2018; Wilusz et al., 2017).

The time variability of water age distributions can be virtually decomposed into two main components: (a) the temporal variability of the hydrologic input and output fluxes alone and (b) the variability of subsurface flow paths (e.g., Botter, 2012). These have also been referred to as "external" and "internal" transport variability, respectively (Kim et al., 2016). For example, when shifting from dry to wet conditions, streamflow age distributions will reflect the new water additions brought in by precipitation (external variability), but also the activation of quick flow paths that were previously inactive (internal variability; Heidbüchel et al., 2013). The variability of hydrologic fluxes causes any "instantaneous" age distribution to be very irregular and discontinuous (see conceptual example in Figure 2). This external variability is ubiquitous and it is often necessary to explain measured tracer observations (e.g., Harman, 2015). However, when we want to characterize the ability of catchments to store and release waters of different ages, it is desirable to use distributions that are less affected by the hydrologic variability. The external variability of age distributions is canceled out by taking an average distribution over time (see Section 2.3.3) and using "ensemble" approaches like ensemble hydrograph separation. It is also largely mitigated by considering TTDs in flow-weighted time (Kim & Troch, 2020). SAS functions are not affected by the external variability because they aim to describe transport processes independently of water flow rates.

Streamflow age distributions typically have significant contributions from both a narrow range of young (days to months) waters and from a very large range of old (>1–2 yr) waters (see Figure 2 and Benettin, Bailey, et al., 2017; Kirchner et al., 2000). This means that, for many environmental tracers like chloride and water stable isotopes, the bulk tracer signature of old water is almost constant over time, while the tracer signature of young water is variable, reflecting event and seasonal variability in the tracer inputs. Thus, young water has a disproportionate effect on streamflow tracer composition for the main environmental tracers and, in turn, these tracers can help quantify the contribution of old vs. young streamflow but not *how old* the old water is (see also Knapp et al., 2019). A more refined characterization of the old water components is better achieved through tracers with larger characteristic timescales like ^{3}H (see M. K. Stewart et al., 2010, 2012). The large uncertainty associated with old water requires careful selection of summary statistics. Water age metrics like the median transit time and the young water fraction (Kirchner, 2016a) are much less affected by the old water uncertainty than the mean transit time and thus they appear to be more desirable.

In the light of the complexity of the theoretical apparatus underlying time-variant TTDs (Section 3), one might wonder if this effort is actually worthwhile and all this complexity is really needed for practical purposes. Our claim is that, while time-variance might not be needed a priori to characterize transport processes in a catchment, it directly affects tracers and solute signals in stream water and plant water. Therefore, acknowledging and incorporating this time variance may be necessary to capture and explain both high-frequency and long-term tracer dynamics. Approaches that are capable of accounting for it (either through a time-varying water age balance or through data-based analyses carried out separately over different hydrologic conditions), have a fundamental advantage over those that do not.

4.2. On the Coevolution of Storage and Outflow Age Distributions

The new TTD frameworks based on the water age balance (Section 3.2) address a somewhat new scientific question. While early, pre-2006 work mainly focused on rainfall and streamflow by asking "How long does rainfall take to become streamflow?", the new approaches highlight the central role of the water storage by asking "How do water storages release waters of different ages to streamflow and evapotranspiration?" (see McDonnell et al., 2018). This goes toward a more holistic view of the transport process (Rinaldo et al., 2015) but it also faces the challenge of working with the water storage, which is difficult to quantify (Carrer et al., 2019; McNamara et al., 2011; Pfister et al., 2017; Staudinger et al., 2017) and sample, as measurements are necessarily local and not representative of the entire subsurface volume.

The transit time studies carried out in the past few years provide insight into the relationships between storage and outflow age distributions. The general expectation in catchments is that "Streams are generally younger than the water storage that they drain" (Berghuijs & Allen, 2019; Berghuijs & Kirchner, 2017). This behavior originates from subsurface velocity contrasts (induced by subsurface heterogeneity) and results in SAS functions that generally decrease with age. Declining hydraulic conductivity with depth also results in the preferential release of younger water because a large portion of young water is stored above old water (Ameli et al., 2016; Kim & Harman, 2022). Modeling work based on tracer data has usually confirmed this expectation, at least under wet conditions (Benettin, Kirchner, Rinaldo, & Botter, 2015; Benettin, Soulsby, et al., 2017; Harman, 2015; Heidbuechel et al., 2012; Hrachowitz et al., 2015, 2013; Kaandorp et al., 2018; Klaus et al., 2015; Lapides et al., 2022; Pangle et al., 2017; Remondi et al., 2018; van der Velde et al., 2012). The preferential release of young water is also often more marked during wetter conditions. This behavior has been termed the "inverse storage effect" (Harman, 2015; Pangle et al., 2017) to indicate that a larger storage promotes an increase in young-water release and thus shorter transit times.

When looking at finer temporal dynamics, models suggest that the general trend of younger water release may be inverted during low flows and dry periods (Rodriguez et al., 2018; Visser et al., 2019; Yang et al., 2018; Z. Zhang et al., 2021). This can occur if enough young water is retained in the vadose zone and streamflow is mainly fed by relatively old groundwater. The systematic release of older storage to streamflow (which corresponds to a SAS function that increases with age) appears to be unlikely in catchments, but it may occur in soils and hillslopes when flow advection is significantly larger than dispersion (high Péclet numbers, similar to piston flow). This behavior was identified in large experimental soil columns (Asadollahi et al., 2020; Queloz, Carraro, et al., 2015) and in some northern latitude soils (Sprenger et al., 2018), although in this case, the low-frequency (monthly) sampling strategy could not exclude the occurrence of short-term preferential flow. The SAS functions estimated for the Landscape Evolution Observatory hillslopes also indicate that those hillslopes mainly drain the older stored water (Kim et al., 2022), due to the high hillslope Péclet number and the convergent topography. The relationship between outflow and storage age distributions may in principle be more complex, for example, multimodal (Rodriguez et al., 2020; Wilusz et al., 2020) and irregular (Danesh-Yazdi et al., 2018; Yang et al., 2018), but this level of complexity is difficult to assess and validate from tracer behavior at the catchment outlet.

The relationship between stored and evapotranspired waters remains uncertain because of the fundamental lack of tracer data in ET fluxes at the appropriate scale. Preliminary work where xylem isotope data were used to calibrate the SAS function of ET showed some potential to characterize the ET age distribution (Asadollahi et al., 2022; Knighton et al., 2020, 2019; Smith, Tetzlaff, & Soulsby, 2020; Sprenger et al., 2022). A reasonable expectation is that ET mainly removes the relatively younger water stored in shallow, root-accessible soil layers (Sprenger et al., 2019), as also suggested by Thaw et al. (2021) using stable and radioactive isotope data. But plant strategies are complex and experimental work has shown that in many cases individual trees may take up relatively old water (Allen et al., 2019; Evaristo et al., 2019) stored in smaller soil pores, including, in some extreme cases, water several decades old (Z. Q. Zhang et al., 2017). The use of large-scale water balances can provide a lower bound to distributed ET age and it showed that ET must be at least several months old across large areas of the western continental United States (Hahm et al., 2022). Models that attempted to determine the SAS function of ET solely based on stream tracer data typically resulted in uncertain ET age estimates (Asadollahi et al., 2020). The lack of tracer data in evaporation and transpiration fluxes is also the reason why SAS approaches have not yet been used to separate the transit times of evaporation from those of transpiration, although these fluxes are likely to sample different water age pools. Indeed, soil hydraulic models that implement this separation suggest that water evaporated from soils is typically younger than water taken up by vegetation (Smith, Tetzlaff, & Soulsby, 2020; Sprenger et al., 2018).

4.3. Implications for Catchment-Scale Reactive Transport

The theory and approaches presented in Sections 2–3 address ways to use water age and TTDs to connect input and output tracer concentrations for conservative solutes. The question remains whether the same approaches can be useful to understand and simulate reactive transport processes at the catchment scale.

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Water age is expected to be an important control on biogeochemical processes because it approximates the time water is in contact with reactive materials. Water age is clearly neither the only nor the most important factor, because many others such as pH, redox potential, biological sinks, and the spatial heterogeneity of reactive material distribution may be more relevant (Li et al., 2021). Examples of processes that have a direct link with transit time are radioactive decay (see. Małoszewski et al., 1983, for tritium) and mineral weathering (Maher, 2011). Other transport processes may correlate well with transit time because water age can be a good proxy of deep vs. shallow flow paths. Different subsurface layers may be characterized by minerals and biogeochemical conditions that can drive specific chemical reactions. Thus, longer/shorter transit times may correspond to the chemical signature of reactive materials from deeper/shallower layers. As a result, relationships can often be found between reactive compound concentrations and water age metrics in stream water. For example, Kirchner (2016b) found strong correlations between young water fractions (computed from tracer cycle damping under different flow ranges) and the concentrations of reactive solutes (calcium, aluminum, and nitrate) at Plynlimon, UK. Similarly, Clow et al. (2018) found strong correlations between the young water fraction and sodium and silicon (but not nitrate) concentrations at 11 headwater catchments in mountains of the western United States. Work by Jutebring Sterte et al. (2021), based on 3-D transient flow simulations in MIKE SHE, showed a good correlation between simulated mean transit times and observed base cation concentrations across 13 boreal sub-catchments in Krycklan, Sweden.

Starting from these considerations, one possible approach is to develop chemical reaction equations (e.g., Maher, 2011) for each water parcel transiting through the catchment storage, which would determine $c(T, t)$ in Equation 8. Water age distributions then quantify which parcels—with their reactive tracer composition—reach the stream at any time. It is reasonable to expect that during low flows (when water tends to be older and more dominated by groundwater contributions) there will be a higher concentration of solutes that are associated with longer transit times and deeper subsurface layers (e.g., typical weathering products like silicon), while the opposite is expected during high flows (Neal et al., 1990; B. Stewart et al., 2022). Models that account for the variability of water age have the potential to explain the variability of reactive solute concentrations during the different phases of the hydrologic response. Following this approach, van der Velde et al. (2012) showed that a time-variant water age model coupled to chemical kinetics was able to simulate the same dynamics as those measured at high frequency for nitrate in a lowland catchment in the Netherlands. Similarly, Benettin, Bailey, et al. (2015) computed time-variant water age distributions based on deuterium data and then implemented first-order chemical kinetics to simulate a 14 yr record of fortnightly silicon and sodium concentration data at the Hubbard Brook Experimental Forest, US. Bertuzzo et al. (2013) implemented a linear decay equation to model the transport of atrazine to the stream in an agricultural catchment in Switzerland. Their work also highlighted the need to account for the age of evapotranspiration and the resulting effect on solute transport (typically, evapoconcentration of solutes). Water transit times, together with nutrient accumulation and removal processes, were shown to be important when predicting nutrient legacies in anthropogenic landscapes (Dupas et al., 2020; Meter & Basu, 2015). The relationship between nitrate and water transit times was also investigated by Yang et al. (2018), who used an advanced transport model and nitrate data from an agricultural catchment in Germany to show that nitrate export was anti-correlated with median streamflow age, mainly because of denitrification occurring over longer flow paths.

More advanced and fully integrated models of water flows and chemical reactions such as HPx (Jacques et al., 2018) offer many more opportunities to model reactive solute transport. However, they typically require large setup efforts and high computational times, and they are often data-demanding (e.g., parameterization). Catchment-scale models based on reservoirs and TTDs offer a promising alternative (Hrachowitz et al., 2016) to account for reactions and/or exchange between water and soils that depend directly and indirectly on water transit times.

4.4. Overview of Existing Applications

The Supporting Information (Text S1–S2 in Supporting Information S1, Tables S1–S2, Figures S1–S4 in Supporting Information S1) describes over 80 applied studies that estimated water age distributions using post-2006 methods based on tracer data. As much of the theory was consolidated between 2011 and 2016, the number of applications started to grow around 2015 (Figure S1 in Supporting Information S1). Most applications are based on SAS approaches, well/partially mixed compartments and spatially distributed models with virtual

Table 1
Summary of Requirements, Assumptions and Suitability of Different Transit Time Methods

	pre-2006		data-based		SAS-based	
	General steady-state lumped convolution	**Flow weighted time**	**Young Water Fraction**	**Ensemble Hydrograph Separation**	**Time-invariant SAS**	**Time-variant SAS**
Can be used to estimate	Time-invariant TTD distribution	Time-variant TTD distribution	Fraction younger than 2-3 months	Average TTD distribution	Time-variant TTD distribution	Time-variant TTD distribution
Distribution assumptions	TTD is an invariant parameterized distribution	TTD is an invariant parameterized distribution	TTD approximately a gamma distribution with shape parameter 0.2-2	No distribution assumption	SAS function is an invariant parameterized distribution	SAS function is a time-variant parameterized distribution
Accounts for time variability?	No	External variability only, with limitations	Can account for dependence on discharge	Can account for dependence on discharge	External variability only	External and internal variability
Requires flux or water balance data?	No	Discharge only	No	No	Yes, full water balance	Yes, full water balance
Accounts for effect of multiple fluxes (e.g. ET)?	No, except through "effective precipitation" input weighting	No, except through "effective precipitation" input weighting	No	Not needed	Yes, explicitly	Yes, explicitly
Auxillary choices needed	Choice of TTD distribution form	Choice of TTD distribution form	None	None	Choice of SAS function form	Choice of SAS function form; coupling to state variables
Useful if you have						
≥ 2-3 years of monthly observations	Maybe	Maybe	Yes	Maybe	Maybe	Maybe
≥ 2-3 years of weekly observations	Yes	Yes	Yes	Yes	Yes	Yes
<1 year of sub-daily observations	Maybe	Maybe	No	Yes	Maybe	Yes
sub-daily observations over a few events	No	No	No	Maybe	Maybe	Yes
incomplete data inputs	Maybe	Maybe	Yes	Yes	Maybe	Maybe
significant time-variable transport	No	No	Maybe	Maybe	Maybe	Yes

Note. The usefulness of an approach for given data set properties is marked with "Yes/No" if there is general evidence that the approach is suitable/unsuitable, while it is marked as "Maybe" when there is no general guideline and additional factors have to be taken into consideration to choose that approach (see Section 4.5)

tracer tracking. In some cases, multiple approaches are combined together. Applications were usually carried out on relatively small catchments between 0.5 and 5 km^2 (Figure S3 in Supporting Information S1), with just a few catchments larger than 100 km^2. Most of these studies were carried out on temperate and continental wet climates (Figure S4 in Supporting Information S1), essentially because tracer data has been collected more often at mid-latitudes in Europe and in the United States. Some intensively monitored sites (particularly Plynlimon and Bruntland Burn, both in the UK) stand out for the number of applications, which makes them ideal locations to test and compare different approaches. The data used to estimate the TTDs in these studies mainly include tracers like water stable isotopes and chloride concentrations. Sampling frequency and duration vary substantially from site to site, ranging from fortnightly over multiple years to daily and subdaily over shorter periods.

4.5. Advantages and Disadvantages of the Different Approaches

The approaches introduced in Section 3 differ in terms of purpose, data requirements, and types of output they can provide (Table 1). For simplicity, the approaches are here classified as: pre-2006, including the standard and flow-weighted lumped convolution approaches; data-based, including the young water fraction estimated from tracer cycle damping and ensemble hydrograph separation; and SAS-based approaches, making use of the water age balance coupled to a time-variant or time-invariant SAS function.

The pre-2006 and the data-based approaches generally aim to infer the long-term average streamflow age distributions or some portions or statistics of this distribution. Data-based approaches can also compute these outputs for different periods or flow regimes (if enough data is available). By design, these approaches are not meant to characterize TTDs during any particular storm event and should not be used for that purpose. SAS approaches aim to estimate the instantaneous age distributions of all the water outflows and storage. In terms of assumptions, pre-2006 approaches require that the average streamflow age distribution can be approximated by an analytical distribution. This is a reasonable assumption because smooth shapes naturally emerge when the variability of instantaneous distributions is averaged out. Moreover, long-term transport in catchments is typically compatible with age distributions that have sharp early peaks followed by a long right tail, such as the gamma distribution with shape parameter $\alpha < 1$ (Godsey et al., 2010; Hrachowitz, Soulsby, Tetzlaff, Dawson, & Malcolm, 2009). Data-based approaches do not require an analytical approximation of the TTD. The young water fraction simply requires that the TTD's shape is not piston-flow-like, which is reasonable in catchments (but not in soil columns), while the ensemble hydrograph separation requires no particular assumption. SAS approaches currently assume that the shape (either time-variant or not) of the SAS functions, rather than the shape of the streamflow TTD, can be approximated by an analytical function (though approaches for relaxing this assumption are in development (Harman, 2019b)). There is, however, a difference between *what* these approaches aim to estimate and *how* they can do it in practice. Data-based approaches make more parsimonious assumptions but depend more on the characteristics of the tracer data. For example, young water fraction calculations can become uncertain if the tracer input does not exhibit a clear seasonal cycle. Modeling approaches (both pre-2006 and SAS-based) need to estimate parameters that cannot be measured and they must be calibrated on available tracer data. They also need to assume a-priori some functional form (either for the TTD or for the SAS function and its possible coupling with state variables). While pre-2006 approaches use the average system state to fit the tracer data measured under varying hydrologic conditions, SAS approaches can take at least part of the dynamic system conditions into account.

All the approaches need tracer data in a catchment's input (precipitation and snowmelt) and output (at least streamflow). Methods based on convolutions or mass balances (including SAS approaches) require continuous input tracer data, meaning that any data gaps must be filled. This requirement does not apply to young water fractions or the ensemble hydrograph separation approach. Additionally, the flow-weighted time approach requires a discharge time series, while SAS approaches require an estimate of all terms in the water balance (e.g., precipitation, evapotranspiration, streamflow). While precipitation and streamflow are often measured in catchments, ET estimates are more data-demanding and so some hydrological modeling is required. Data-based approaches do not require estimating ET fluxes. They only need streamflow data to compute flow-weighted statistics or when focusing on different hydrologic periods/regimes. However, since the number of observations available is typically fixed, there is a trade-off between the number of distinct hydrologic regimes that can be investigated and the number of tracer observations available for each regime (which affects the uncertainty in ensemble-averaged TTD estimates).

Given all these considerations, we attempt to summarize which approaches may be useful depending on the user's needs and the available data. With low-frequency (monthly or longer) tracer data over multiple years (say, at least 2–3), the only approach that can robustly estimate some age statistics is the data-based young water fraction. Also, if there are extensive gaps in the tracer input data, these can be more easily accommodated in data-based approaches. When medium-frequency (weekly) data are available over a few years, tracer data can be suitable to estimate the long-term TTD. In this case, all approaches are likely to be viable, though each will still provide different estimates that reflect different aspects of the system's behavior. However, if tracer transport is substantially influenced by ET and there are significant water balance effects (e.g., large storage variability), the pre-2006 approaches are expected to be less reliable. When high-frequency (daily or sub-daily) tracer data is available but just for short periods (single events or seasons) the long-term average TTD cannot be estimated and SAS approaches may account for the variability of water age (and its effect on the measured tracer concentration) during these short periods.

One may wonder whether, moving from pre-2006 convolution approaches to SAS approaches, we simply shifted the problem from estimating the parameters of a TTD to estimating the parameters of a SAS function. While in terms of procedure (calibration on tracer data) the approaches may appear similar, the goals and especially the outputs are very different. Contrary to what is sometimes thought, SAS approaches do not need higher-resolution tracer data. SAS models can leverage high-frequency data if available and use it to estimate the variability of age distributions, otherwise, they can simply run at lower frequency (and provide lower-frequency variability) or even at hydrologic steady state. They are fundamentally more robust because they can explicitly account for the presence of ET (rather than using an "effective precipitation") and the variability of the water storage, and they always conserve mass. SAS approaches are generally expected to fit tracer data better than standard convolution approaches not because they have more parameters but because they are structurally more suited to deal with hydrologic variability. A barrier to the use of SAS approaches may be the more involved model implementation, but open code in different programming languages already exists (see Section 3.2.2).

Despite the differences among all these approaches, comparisons among them can be useful to test the consistency of the estimated water ages. The instantaneous age distributions estimated by SAS approaches are typically jagged and irregular, but when these are averaged out, they typically take a smooth shape that can be compared to steady state or data-based approaches. For example, the marginal TTD computed by Benettin, Kirchner, et al. (2015) at Plynlimon was shown to be very similar to a gamma distribution, as previously found for Plynlimon by Kirchner et al. (2000); Kirchner et al. (2001) using spectral methods. Spectral analyses may also support model-data consistency. For example, the $1/f$ fractal scaling observed in many tracer time series (e.g., Aubert et al., 2014; Kirchner et al., 2000; Kirchner & Neal, 2013) have been reproduced by some SAS models (Harman, 2015; Hrachowitz et al., 2015; Shaw et al., 2008). The young water fraction is a metric which has great potential for model-data intercomparisons, particularly when evaluated under various discharge regimes as done by Gallart, von Freyberg, et al. (2020), Kirchner (2016b), and von Freyberg et al. (2018), because it can be computed independently using either tracer cycle damping or models. Ensemble hydrograph separation can also be used to test the shapes of marginal distributions computed by models, as suggested by Knapp et al. (2019).

5. Pending Challenges

5.1. Unresolved Issues From the Past

The last review by McGuire and McDonnell (2006) laid out several challenges in transit time research. It is worth highlighting how six specific issues it identified have influenced the development of new work or have continued to challenge us: (a) the input characterization issue, (b) the assumption on the recharge flux, (c) the data record length problem, (d) the stream sampling issue, (e) the TTD selection problem, and (f) the model evaluation process.

Three of these challenges (1, 3, and 4) relate to tracer measurements used to estimate transit times. As already mentioned, tracer analytical capability has improved significantly in recent years, with laser spectrometers allowing for less expensive and more accessible analysis—including near real-time observation (e.g., Berman et al., 2009; von Freyberg et al., 2017) in streamflow and precipitation. But to improve transit time estimation, we still require accurate measurements of the inputs and outputs for catchments over long periods of time and at a high enough frequency to characterize dynamic flow paths and TTDs. However, tracer inputs are usually based on one precipitation sampler despite the known spatial variability in precipitation and in its tracer composition, and the spatial interpolation technique may affect the transit time estimates (see Borriero et al., 2022). We often do not have long enough records of tracer data. Likewise, there are only a few catchments (see SI) where streamflow tracers are sampled at high frequencies for the identification of the youngest water component (e.g., timescales of hours to days). Reliable tracer data are the pillar of any transit time estimation and it is impossible to think of progressing in transit time research without progressing in tracer data collection. And in turn, this is a problem of providing adequate incentives for funding agencies and researchers to do the difficult and costly work of collecting those data sets.

The new approaches have helped us overcome aspects of the recharge assumption (which was really one of estimating effective precipitation) and selection of appropriate TTD (challenges 2, 5). SAS approaches embed the recharge assumption into the water age balance and go beyond the concept of effective precipitation because they allow the ET fluxes to have a full age distribution instead of being just made of event water. Thus, both these challenges are integrated into the water age balance and are now replaced by the selection of the right SAS functions. Ensemble hydrograph separation does not require estimating ET fluxes (there is no need for a recharge assumption) and it does not require selecting a TTD, as the TTD is estimated directly from the tracer data fluctuations. Thus, these challenges have been solved or transformed through the new approaches.

The model evaluation challenge (Equation 6) has seen significant progress. Model parameter estimation has evolved markedly through the extended use of calibration approaches (see. Beven & Binley, 1992, 2014), including efficient Markov Chain Monte Carlo techniques (e.g., ter Braak & Vrugt, 2008; Vrugt et al., 2009). These Bayesian calibration techniques have often revealed that at least some model parameters are correlated and not easily constrained by the information content of typical calibration data sets. Indeed, one has to keep in mind that estimating TTDs from tracer data through the convolution integral (Equation 8) is an inverse problem that may be ill-posed, yielding results with large uncertainties. In data-driven approaches such as young water fractions and ensemble hydrograph separation, water age uncertainties are calculated directly from the input and output tracer data. The evaluation of model structure, which is a broader issue in hydrological modeling, still needs to be addressed in transit time approaches so that we can properly test hypotheses and include uncertainty in our estimates of age distributions (Beven, 2010; Borriero et al., 2022). This challenge is certainly still open.

5.2. New Challenges

Besides the unresolved issues highlighted in Section 5.1, the new advances in transit time research highlight several new challenges, which either did not exist or were less relevant before.

1. *The age of ET fluxes*
   Flow, solute transport, and water age are strongly controlled by evapotranspiration in many hydrological systems and climates (Maxwell & Condon, 2016). Explicitly including ET fluxes in transit time investigations now appears as a compelling opportunity, because estimating the age of transpiration is equivalent to understanding the temporal origin of water used by the vegetation. Work in this direction would help us understand the seasonal partitioning of precipitation between discharge and ET (Kirchner & Allen, 2020), the seasonal origin of water used by trees (see Allen et al., 2019) and related problems like whether plants make substantial use of water from summer storm events and irrigation. However, the relationship between stored and transpired water is poorly understood and we are currently not able to characterize the age of evapotranspired water sufficiently well (see Section 4.2) because there is a fundamental tracer data limitation. Measuring tracers at high-resolution in more than 2–3 plants is very demanding and vegetation exhibits temporal and spatial variability of water uptake, relying on different mixtures between groundwater and soil water that can vary between species (Allen et al., 2019; Barbeta & Peñuelas, 2017; Goldsmith et al., 2019; Penna et al., 2018). Models can of course provide estimates of the ET age distributions, but these estimates will always remain uncertain and difficult to validate in the absence of tracer data in ET. In fact, this ET age challenge is the challenge of producing new, high-resolution data sets that target the tracer composition of the ET fluxes.
2. *Incorporating stream hydrochemical data*
   The use of additional hydrochemistry data has great potential for transit time research because different chemicals can be used to probe different hydrologic flow paths (see Section 4.3 and Abbott et al., 2016). High-resolution multi-tracer data sets in streamflow (Aubert et al., 2014; Neal et al., 2013) are increasingly available and many water quality parameters can be measured continuously through sensors (Rode et al., 2016). However, these chemicals and water quality parameters are usually non-conservative and their reactivity must be accounted for. The integration of chemical reactions into transport modeling (Li et al., 2021) has often been carried out in spatially distributed models (which can explicitly account for the spatial distribution of minerals and subsurface properties), but it is challenging in lumped models (Hrachowitz et al., 2016), where effective catchment-scale chemical properties need to be defined. Thus, it is not surprising that there are currently few multi-tracer studies (Benettin, Rinaldo, et al., 2015; Kirchner & Neal, 2013; Knapp et al., 2019; van der Velde et al., 2010; Visser et al., 2019) in the literature. Research questions that could help us make progress include: can continuous measurements such as electrical conductivity or pH be used to inform transit time models? How can we develop meaningful catchment-scale models of reactive transport, and use them to compare water age estimates from stable isotopes against estimates from tracers like for example, nitrate, silicon, or sodium?
3. *Incorporating local tracer measurements*
   TTDs are commonly estimated from observed tracer data in precipitation and streamflow. Stable isotopes and hydrochemistry are also often observed locally (i.e., in soil, groundwater, and xylem water) at different spatio-temporal scales (e.g., Goldsmith et al., 2019; Hissler et al., 2020; Mennekes et al., 2021; Quade et al., 2019; Sprenger et al., 2018). While these data are increasingly available and used to test spatially distributed flow tracking models (e.g., Smith, Tetzlaff, Kleine, et al., 2020), they are also very localized and there are no clear methodologies for using them to estimate transit times in lumped approaches. We, therefore, pose the question of whether these measurements can potentially be interpreted as a subsample of a catchment water storage, and be characterized by a TTD or a SAS function. Which assumptions are needed to use the

new data-based approaches on these local data? Assessing the value of these additional data sets seems like a key challenge for upcoming research.

4. *Upscaling the lessons we learned*
   Understanding how processes emerge/change with scale is a relevant question not just in transit time research but in hydrology and science more generally. The key question here is how the lessons we learned from new data and approaches (see Section 4) change with scale. For example, how do the timescale and temporal variability of water age change from a headwater catchment to a mesoscale catchment to a large drainage basin? Theoretical research (e.g., Davies & Beven, 2015) is necessary to guide our expectations, but we need to avoid simply falling into more complicated and likely overparameterized models. The main challenge is perhaps that of using the few available data sets collected at multiple scales (e.g., Laudon & Sponseller, 2017; Nguyen et al., 2022) to test our theoretical expectations.
5. *Rigorously testing our methods*
   There is an urgent need for all transit time estimation methods, including SAS approaches, to be rigorously tested against synthetic benchmark data sets (e.g., Kirchner, 2016b; Kirchner, 2019) with realistic degrees of complexity and nonstationarity, including realistic distributions of measurement errors (with realistic degrees of serial correlation). It is not necessary for such benchmark models to be realistic analogs of any particular real-world field site. It is essential, however, that they do not embody similar assumptions as the methods that they are used to test (Kirchner, 2019). Otherwise, spurious success is virtually guaranteed, because the benchmark model and the methods under test will be performing essentially the same calculations (one forward, and the other backward). Benchmark tests can also help in assessing the value of longer and more detailed tracer time series—or, conversely, in revealing the uncertainties that are inherent in conclusions drawn from the limited data that are currently available. As the new TTD approaches are more complex than the pre-2006 approaches, the testing procedures should also be further developed.
6. *Which of our traditional assumptions should we challenge next?*
   As research and technology evolve over time, traditional assumptions (like flow stationarity or "well mixing" inside storage volumes) have gradually been relaxed. It is thus worthwhile to think about what other traditional assumptions may be relaxed in transit time research. For example, TTD estimation is influenced by the very definition of a hydrologic system. Catchments are typically delineated laterally through topographic boundaries and vertically through some "impermeable" bedrock layer. However, many studies have shown that significant volumes of water can cross the boundaries of the control volume as unobserved additional inputs or outputs (Bouaziz et al., 2018; Frisbee et al., 2012). These fluxes and their tracer concentrations are difficult to estimate for multiple reasons, but they have the potential to introduce a bias in TTD estimation, for example, if water source with an isotopic composition that is different from rainfall is transferred into the catchment. Getting to grips with where the bottom of a watershed is (Condon et al., 2020) seems essential to ultimately dealing with the catchment control volume effectively. Other hidden flux exchanges can occur due to anthropogenic activities that extract or introduce water for drinking, irrigation, or hydropower generation. As pristine, undisturbed catchments are increasingly rare, making steps in this direction seems like an important research path.

6. Going Forward

The challenges outlined above in Section 5 are meant to inspire new research related to transit time. Here, we provide concrete directions in terms of theoretical, modeling, experimental, and community work that can help address those open questions.

6.1. Outstanding Theoretical Advancements

Theoretical work is fundamental for inspiring new research questions and data collection efforts. New theoretical work could, for example, investigate the existence of age-concentration relationships in streamflow and develop reactive transport equations for catchment-scale problems that can help us interpret reactive tracer data. Other examples could be theoretical investigations of how the separation of a catchment into compartments (e.g., canopy, shallow soil, groundwater, riparian area, stream network), and the connectivity across these compart-

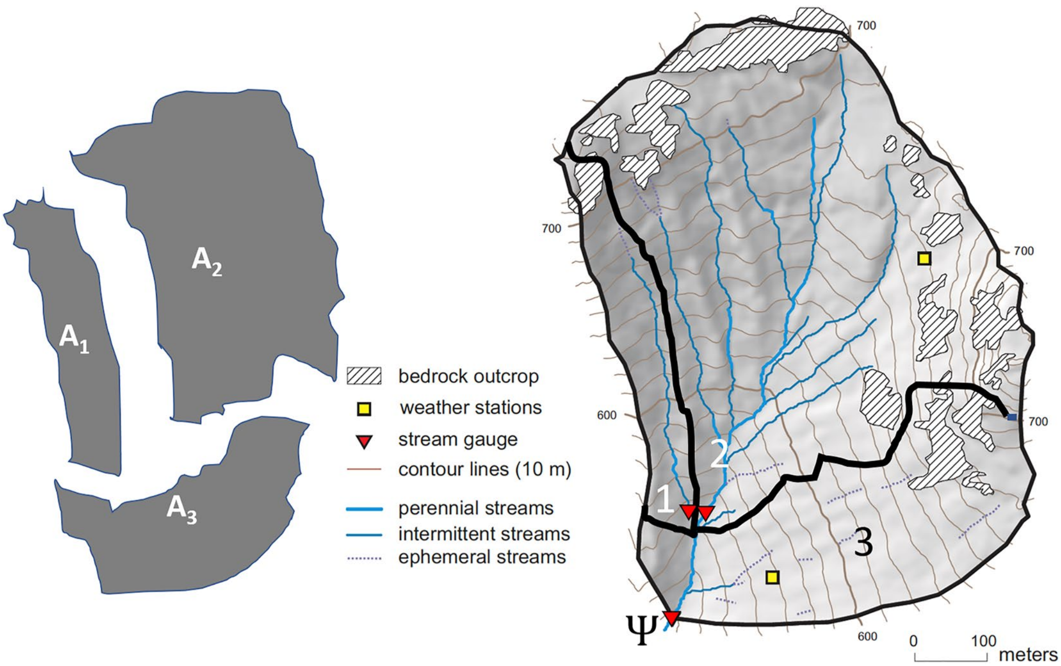

Figure 6. Sketch of a simple catchment (here an arbitrary modification of Hubbard Brook watershed 3, NH, US), with three hypothetical gauging stations that partition the catchment into three diverse source areas. We assume that hydrologic and tracer data are available at each station and age distributions can be estimated using the methods from Section 3.

ments, control the shape, scale, and variability of TTDs. Here, we provide a further and more detailed example addressing geomorphic effects on stream water age.

We aim to describe the water age distribution $p_Q^{\Psi}(T,t)$ at the outlet Ψ of a basin, as a function of the age distributions $p_Q^k(T,t)$ of the k subcatchments—identifiable geomorphic units (Figure 6) whose arrangement and connections may be remotely measured and objectively manipulated. A special interest is placed on geomorphic effects (Rigon et al., 2015; Rinaldo et al., 1991; Rodriguez-Iturbe & Valdes, 1979) on water age distributions. One example is mixing ages from tributary subcatchments of very different sizes. In this example of future research directions, we make the simplifying assumptions that instream processes (such as hyporheic flow and fluvial recharging of underlying aquifers) are negligible. Selective relaxations of the above constraints may certainly be possible, and perhaps even instructive. The example of Figure 6 shows three clearly identified source areas. Hydrologic and tracer data would be available at the outlet of each of them, such that one could estimate age distributions using the methods discussed in Section 3. The question here is: what would be the relation among the TTDs estimated locally (at the source areas) and globally (for the whole catchment)? In the simplest case, the tracer concentration at the outlet Ψ can be computed as a weighted average of the concentration at each source area outlet:

$$C_Q^{\Omega}(t) = \sum_{k=1}^{n} w^k(t) C_Q^k(t) = \sum_{k=1}^{n} w^k(t) \int_0^{\infty} c^k(T,t) p_Q^k(T,t) dT \tag{19}$$

where the weight w^k is the path probability computed as $Q^k(t)/Q^{\Omega}(t)$ and $c^k(T, t)$ and $p_Q^k(T,t)$ are the storage age concentration and streamflow age distribution at each source area k.

The set of all media involved in catchment transport processes may be seen as a hierarchical, gravity-driven collection of naturally heterogeneous states. Thus, any attribute of a water particle traveling through the catchment sees a path determined by topographic gradients in its journey to a control section. Heterogeneity—whether due to the nature of advection fields in natural soils or porous formations endowed with preferential flow paths, macropores or fractures, or due to material properties of the media involved—occurs throughout a range of spatial scales. It may therefore be necessary to link the descriptions at various scales to decode the role of the river network in integrating contributions from different source areas. *In silico* experiments may be a useful guide to test the robustness of features like the young water fraction (see benchmark tests by Kirchner, 2016b) but also other properties of the water age distribution.

6.2. What We Need From Our Models

Models allow us to formalize hypotheses and (partly) test them with data. They also help in interpreting data and filling data gaps. Irrespective of their temporal, spatial, and process resolution, each model is based on simplifications and assumptions. Tracer transport and water age emerge from many interacting processes. Yet observations typically provide information only about the integrated response of the overall system or large parts thereof. As a consequence, models are typically only tested as sets of multiple interacting hypotheses, instead of confronting the individual model components with suitable data (Clark et al., 2011). Given these premises, what can we reasonably do to advance our capacity to model water ages in catchments? Specifically for transit time models, one of the major challenges is to isolate functionally distinct storage components of the system, such as the unsaturated soil or the groundwater, and to estimate the potentially different shapes of the transit time distributions that are associated with different fluxes from these components, such as evapotranspiration or groundwater recharge. Progress in transit time models therefore requires the availability of suitable data and depends on our ability to devise experiments to test individual parts of our models and, in particular, to determine water ages for individual fluxes.

As for any hydrological model, such data will need to include hydrological variables to constrain the modeled magnitudes of the individual water storage volumes and fluxes, such as, for example, time series of soil moisture (Hrachowitz et al., 2021) or sap-flow (Nehemy et al., 2021). In addition, and perhaps even more importantly for transit time models, detailed tracer data will be invaluable for model development and testing. More specifically, data of the tracer compositions of at least some of the individual storage volumes and fluxes, such as soil moisture (Sprenger et al., 2016) or sap-flow (Knighton et al., 2020), have the potential to narrow down the spectrum of plausible shapes of the respective TTDs in individual fluxes (Smith, Tetzlaff, Kleine, et al., 2020; Smith et al., 2021). Importantly, this may eventually also enable us to identify, parametrize and quantify processes that have rarely been accounted for in models but that may in fact play key roles in controlling mass fluxes of water and solutes in terrestrial hydrological systems, thereby challenging "traditional" assumptions of catchment functioning. From that perspective, models featuring transit time formulations may become invaluable learning tools for the analysis of new hydrological and tracer/solute data. For example, the use of spatially distributed (grid-based) approaches (Section 3.3) can help relax the typical assumption that each landscape's pixel is fully mixed, especially when such pixels have a large size (e.g., > 1 km^2). However, this would come at higher computational expenses and would require additional model parameters. Transit time-based models may prove to be useful to better conceptualize and quantitatively describe the largely unknown individual water (age) balances of different evaporative fluxes, such as interception evaporation, soil evaporation or transpiration (e.g., Coenders-Gerrits et al., 2014; Jasechko et al., 2013). As these fluxes all sample water from different pools in different parts of the system, they are likely to interact with and affect the hydrological system in different ways. Because integrated modeling approaches that simulate the continuum soil-plant-atmosphere—and not only the hydrologic response—are increasingly available (e.g., O'Neill et al., 2021; Tubini & Rigon, 2021), they can be used to improve transit time estimates. A very specific class of processes that has remained elusive to quantification at larger scales is vertical or lateral hydraulic redistribution (Domec et al., 2010; Hafner et al., 2021) of water through root systems and mycorrhizae (Prieto et al., 2012; Sardans & Peñuelas, 2014). Another process which is often overlooked is that of groundwater import to or export from catchments (Ameli et al., 2018; Bouaziz et al., 2018; Condon et al., 2020).

Overall, the iterative process of exploring new data and testing alternative model hypotheses, including but not limited to alternative parametrizations of SAS-functions, is a strategy to eventually converge towards more trustworthy descriptions of hydrological transport processes. In this pursuit, it will be beneficial to embrace the complementary merits of different classes of models and to let different models learn from each other. While largely data-driven approaches (e.g., Kirchner, 2016a; Kirchner, 2019) rely on fewer assumptions and may provide robust estimates, they largely remain process-agnostic and do not explicitly represent the internal processes of a system, making it difficult to directly use observations of these processes in these models. As emphasized elsewhere (e.g., Beven, 2006; Kirchner, 2006; Kirchner et al., 1996), more detailed and/or spatially explicit models that aim to explicitly represent a spectrum of individual processes, may accommodate observations more readily, but due to a lack of sufficient data (or knowledge of their spatial covariance fields) they will

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be difficult to test (e.g., Maxwell et al., 2019). While output from simpler approaches can then be valuable to constrain more detailed models (e.g., Lutz et al., 2018), process detail from the more complex models may be helpful to guide the identification of processes emerging at larger scales in simpler models (Loritz et al., 2017).

6.3. What We Need From New Field Work and Tracer Techniques

The need for reliable hydrologic and tracer data has emerged from basically all the challenges outlined in Section 5. Besides the obvious solution of collecting *more* data from *more* locations, how can we practically improve our field work and come to better estimates of water ages?

Multi-tracer approaches that provide different information about shorter and longer transit times are promising in view of the wide range of water ages in the different hydrological compartments (Sprenger et al., 2019). For example, Visser et al. (2019) combined cosmogenic radioactive (^{3}H, ^{22}Na, ^{35}S) and stable (^{18}O) isotope ratios of stream water samples, which enabled the quantification of both the old and young water ages in the catchment's runoff. Notably, while tritium analyses are more costly than stable isotope analyses, the required sampling frequencies are also different, which can make tritium a cost-efficient tracer (Rodriguez et al., 2021). To understand the rapidly changing dynamics of young streamflow, we need tracer data at high frequency. In situ stream sampling systems (Floury & Roubaty, 2022; Sahraei et al., 2020; von Freyberg et al., 2017) are currently the only way to produce sub-daily, multi-tracer data over prolonged periods. But these systems also require significant effort and resources. For many researchers, it is not feasible to sample at high frequencies over long time spans. One alternative may be to develop efficient sampling techniques, such as the event-triggered and discharge-dependent stream water sampling with autosamplers (Gallart, Valiente, et al., 2020; Rodriguez et al., 2021). Even less systematic approaches, which involve for example, regular weekly samples and occasional subdaily campaigns, have potential for capturing some young water dynamics while keeping the sampling effort limited. These issues are similar to issues faced in discharge measurement in terms of where best to place one's efforts (Seibert & Beven, 2009; Seibert & McDonnell, 2015). In addition to a better representation of the short tail of the TTD, the long tails of TTD pose a challenge—mainly due to the limitations of stable isotopes for long transit times (Kirchner, 2016a; Seeger & Weiler, 2014). While the above-mentioned multi-tracer approaches (Visser et al., 2019) were promising with regard to an improved representation of long transit times, such tracer combinations are under-explored. Especially extending the age range that can be sampled in catchment runoff tracer concentrations would allow for an improved representation of deep groundwater contributions to the stream water. As reviewed in Abbott et al. (2016) and Sprenger et al. (2019), introducing tracers that are more commonly used in groundwater age dating, like CFCs, SF_6 or ^{85}Kr, can constrain the parameter space accounting for the long tails in transit time modeling (i.e., old water contributions to stream discharge). New developments of in situ noble gas measurements (e.g., Ar, Kr, He) via mobile mass spectrometry (Brennwald et al., 2016) provide opportunities for improved hydrological process understanding as recently outlined by Popp et al. (2021). The usefulness of high-frequency gas tracer measurements for transit time estimates has not yet been explored, but examples assessing the snowmelt contribution in a mountainous catchment show their feasibility (Schilling et al., 2021).

The increasing interest in ET age distributions (see Section 5.2) demands new data from transpiration and evaporation fluxes. The benefits of xylem stable isotope data based on cryogenic extraction of tree cores for conceptual transit time analyses were recently shown for the plot scale (Smith, Tetzlaff, & Soulsby, 2020), hillslope scale (Evaristo et al., 2019), and catchment scale (Knighton et al., 2019; Sprenger et al., 2022). The potential need to account for transport within the tree has also emerged (Knighton et al., 2020). However, to make progress, there is a need to ramp up sampling frequency in the field and improve the number of trees sampled to enable a better representation of the temporal and spatial dynamics. The highest plant water isotope sampling frequency is reached via in situ measurements, which were shown to provide continuous sub-daily isotope data over several weeks to months without the need for field visits (Seeger & Weiler, 2021). Since these in situ isotope probes can also sample soil water isotopes in parallel, storage-ET flux tracer dynamics can be monitored at sampling resolutions that reveal short-term soil-plant feedbacks (see Beyer et al., 2020).

The need for transit time modeling stems from the inability to directly measure TTDs. Experimental work with labeled (e.g., deuterated) water has the capability to target a specific flux or landscape unit and can provide information on transit times through tracer breakthrough curves (see Section 3.4.1). Tracer experiments at the scale of a whole watershed—as uniquely done by Rodhe et al. (1996)—are logistically challenging and they are currently out of reach. Still, even at much smaller scales, tracer experiments can provide valuable information about transport and transit times of hillslope flow paths (McGuire & McDonnell, 2010; Scaini et al., 2017) and root water uptake (Benettin et al., 2021; Beyer et al., 2016; Evaristo et al., 2019; Volkmann et al., 2016). Our understanding of feedbacks between different compartments of the terrestrial water cycle will benefit from new targeted tracer experiments. For example, there is a need for experiments with multiple tracers that interact differently with vegetation (e.g., deuterium and bromide). This would help partition the subsurface storage into transpiration and recharge fluxes and quantify the effect of vegetation on tracer transport.

6.4. What We Need as a Research Community

Many research advances are better achieved by a research community rather than by individual groups. With hydrometric and tracer data becoming more widely available for various research catchments, there is increasing potential for synthesizing water age studies across a wide range of environmental drivers to allow comparisons along large hydro-meteorological, geological, pedological, and ecological gradients. However, to do so, there needs to be a community effort to foster the inter-comparability and re-usability of our data sets, as outlined in the FAIR Guiding Principles (Wilkinson et al., 2016). A data base, similarly to the Catchment virtual Observatory for Sharing flow and transport models outputs (COnSOrT) introduced by Thomas et al. (2016), covering input data and model results of water age dynamics would open up great opportunities for catchment and/or model comparison studies. For example, public availability of water age simulations for various research catchments would enable their use to test physically based model results based on particle tracking. With regard to software, many codes are already freely accessible and well documented (Benettin & Bertuzzo, 2018; Harman, 2015; Harman & Fei Xu, 2022; Kirchner & Knapp, 2020). There are currently many initiatives to enhance the exchange among scientists working at different research catchments (see Brantley et al., 2017). A similar community effort toward a global network of water age studies, bringing together data, concepts, and model implementations would be very timely. In such synergistic efforts, the current lack of research catchments on the African continent (see SI and Burt & McDonnell, 2015, Figure 2 for location bias) and in large parts of South-East Asia should be tackled and overcome to allow for a global assessment of water age dynamics spanning various climates and geologies.

Water age characteristics have long been seen as one of the meaningful metrics in catchment classification (McDonnell & Woods, 2004) and the mean residence time was used for catchment inter-comparisons in several studies. However, because of the shortcomings of mean transit times (discussed in Section 4.1), there is a need to converge on different metrics. Among the many statistics explored in this review, two seem more suitable than others and we encourage future research to include them in their analyses: the ensemble-averaged (or "marginal") TTD and the young water fraction F_{yw} with a young water threshold of 2–3 months. A key advantage of both of these statistics is that they can be estimated using different methods (i.e., lumped models, physics-based models and data-based models) and they can be estimated on an entire data record but also on different periods and flow conditions to capture some of the temporal variability in water age. The young water fraction, owing to its low data requirements, has already been used in comparison studies with 254 catchments on a global scale (Jasechko et al., 2016), with 22 catchments across Switzerland (von Freyberg et al., 2018), and with 24 sub-catchments within a mesoscale catchment in Germany (Lutz et al., 2018).

Most transit time studies are done at well instrumented research (often head water) catchments that span a few square kilometers (see Section 4.4 and SI material). However, water management often takes place at much larger scales. It is not yet clear how applicable tracer-aided transit time analyses are on large scales that are often operationally more relevant than headwater catchments. With the availability of large-scale isotope data bases such as the Global Network of Isotopes in Precipitation and the Global Network of Isotopes in Rivers, data are at hand for large-scale applications (e.g., Jasechko et al., 2016). Recently, Stadnyk and Holmes (2020) showed that including stable isotope information for calibration of a semi-distributed model resulted in more constrained model parameter ranges and improved the long-term water balance simulation of large-scale (up to 1,000,000 km^2) catchments. But developing research at larger scales also requires bigger efforts and this is where working as a research community may help make progress.

We are convinced that there is still much to gain from transit time research. While many opportunities and challenges still exist, here we have highlighted key advances in transit time estimation of the past 15 yr. Future devel-

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opment, testing and implementation will no doubt yield exciting new findings. We hope that this current review helps to organize and synthesise the recent progress and lay a foundation for future work.

Data Availability Statement

This is a review paper and no data availability statement is applicable. Figure 4 was generated using the code by Harman and Fei Xu (2022). An interactive and maintained version of the SI material can be found at https://github.com/pbenettin/TTDstudies.

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