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The demographics of water: A review of water ages in the critical zone

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This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1029/2018RG000633

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Key points:

- New tracer techniques now allow tracking water at high spatio-temporal resolution across the vastly varying water ages in the water cycle.
- Exchanges of water between hydrological compartments at key interfaces influence the water age distribution more than previously assumed.
- Variation from complete to nearly absent mixing of water at the interfaces in the critical zone affects the water ages in compartments.

Abstract

The time that water takes to travel through the terrestrial hydrological cycle and the critical zone is of great interest in Earth system sciences with broad implications for water quality and quantity. Most water age studies to date have focused on individual compartments (or sub-disciplines) of the hydrological cycle such as the unsaturated or saturated zone, vegetation, atmosphere, or rivers. However, recent studies have shown that processes at the interfaces between the hydrological compartments (e.g., soil-atmosphere or soil-groundwater) govern the age distribution of the water fluxes between these compartments and thus can greatly affect water travel times. The broad variation from complete to nearly absent mixing of water at these interfaces affects the water ages in the compartments. This is especially the case for the highly heterogeneous critical zone between the top of the vegetation and the bottom of the groundwater storage. Here, we review a wide variety of studies about water ages in the critical zone and provide (1) an overview of new prospects and challenges in the use of hydrological tracers to study water ages, (2) a discussion of the limiting assumptions linked to our lack of process understanding and methodological transfer of water age estimations to individual disciplines or compartments, and (3) a vision for how to improve future interdisciplinary efforts to better understand the feedbacks between the atmosphere, vegetation, soil, groundwater, and surface water that control water ages in the critical zone.

Plain language Summary

Investigating how long it takes for a drop of rainwater until it is either evaporated back to the atmosphere, taken up by plants, or infiltrated into groundwater or discharged in streams provides new understanding of how water flows through the water cycle. Knowledge about the time water travels further helps assessing groundwater recharge, transport of contaminants, and weathering rates. Often, such water age studies typically focus either on water in individual compartments of the water cycle such as soils, groundwater or stream runoff. But we argue, that the interfaces between these compartments can have an influence on the water age. Here, we present methods how water ages can be estimated using tracers and hydrological models. We further discuss the "demographics of water" (water age distribution) in the critical zone that spans from the tree canopy to the bottom of the groundwater. Our review highlights how water flows and mixes between plants, soils, groundwater and streams and how this interaction affects the water ages. This way, our work contributes towards a better understanding of vital resource water sustaining the life in the Earth's living skin.

Keywords: Travel times, Water ages, Tracer hydrology, Stable isotopes, Critical Zone, Terrestrial water cycle

Running head: Water ages in the critical zone

1 Introduction

Age-based concepts characterizing water in different **hydrological compartments** (see Glossary) have been used in hydrology for over 65 years as means to learn about the underlying hydrological processes of the water cycle. Starting with the works of Danckwerts (1953), Libby (1953) Begemann & Libby (1957), Eriksson (1958), and Buttlar (1959), these ideas have gained increasing attention in the Earth system science community in recent years. The time it takes for rainfall to travel through a **hydrological system** is, for example, highly relevant for weathering rates (Maher, 2010), groundwater quantity and recharge (Gleeson et al., 2016), biogeochemical processes (van der Velde et al., 2010), assessment of flow path characteristics (i.e., intrinsic groundwater vulnerability, Wachniew et al., 2016), and specific vulnerability of water bodies to contamination (Hrachowitz et al., 2016; Jasechko et al., 2017). Age concepts have been useful in hydrology because the ages of waters present in a landscape reflect those waters' **velocities** and flow paths, of which some are difficult to observe. Hydrologists assess how different flow paths contribute to **catchment runoff** and how these flow path contributions change over time (McDonnell et al., 2010; Tetzlaff et al., 2014; Rinaldo et al., 2015). Thus, accounting for **water ages** enables insights beyond hydraulic responses (e.g., rainfall-runoff or rainfall-soil moisture), helping to better understand hydrological processes and timescales of transport, and to improve the realism of hydrological models (Kirchner, 2006). Investigation of water ages has become increasingly important as hydrological research has broadened its focus from quantifying water fluxes towards understanding which specific waters are in flux and which are less mobile in storage (McDonnell & Beven, 2014; McDonnell, 2017).

Water age studies have often progressed independently within subfields of hydrology that study specific compartments of the hydrological cycle. Hydrogeologists have largely focused on groundwater, soil scientists on soil water, eco-physiologists on plants, and fluvial ecologists on stream water. These distinct research communities use different **tracers**, different analytical tools to interpret those tracers, and different concepts and terminology to describe the processes that they reveal. Based on the typically applied control volume approach in these subfields, input and output fluxes or water ages are generally defined, but usually not the interactions and interrelations among the compartments and the possible feedback loops. For example, recharge to groundwater may consist of different fractions of contrasting ages caused by the flow processes in soils. Yet, in many studies focusing on the groundwater compartment, age is set zero as water enters the groundwater system and does not include the age information during recharge. Consequently, reviews until now have dealt with water age estimates for individual compartments, such as the soil (Sprenger et al., 2016b) or the groundwater (Suckow et al., 2013; Suckow, 2014; Turnadge & Smerdon, 2014; McCallum et al., 2015; Cartwright et al., 2017; Jasechko, 2019), or focused on the catchment scale (McGuire & McDonnell, 2006; Birkel & Soulsby, 2015; Hrachowitz et al., 2016).

Knowing how, when, and why waters of different ages are connected within the water cycle is key for correctly interpreting age distributions within and between compartments and their connections in time and space. Here, we review the compartments and their connectivity to better understand the **demographics** of water (age distributions of water). We therefore focus our review on the **critical zone** between the top of the vegetation and the bottom of the groundwater storage.

The critical zone concept, as introduced by the National Research Council (2001), provides a useful framework for investigating the interplay of hydrological processes to understand water ages in the terrestrial water cycle, as the critical zone "extends from the top of the vegetation canopy through the soil and down to fresh bedrock and the bottom of the groundwater" (Grant & Dietrich, 2017). We first provide an overview of how water ages have been quantified in the critical zone. We then emphasize how potentially violated assumptions in water age estimates of the individual compartments are limiting the progress towards the understanding of water ages across the critical zone. We further discuss how different processes differentially transport water across hydrological interfaces, and how the distributions of water ages in associated storages can be used to infer and examine those transport processes. Our main objective is to synthesize cross-disciplinary water age information to support more integrative views in hydrology. A Glossary is provided to clarify less common terms, which are written in bold font when mentioned the first time.

2 Quantifying water ages in the critical zone

2.1 Definitions

Travel time (also called transit time) (τ) is the time between the moment (t_{in}) a water molecule enters a hydrological system or compartment and the time (t_{out}) that it flows out (Lewis & Nir, 1978):

$$\tau = t_{out} - t_{in} \qquad \text{(Equation 1)}$$

For catchment hydrologists, t_{in} is usually the moment when precipitation or meltwater enters a catchment (McGuire & McDonnell, 2006). In groundwater studies, t_{in} is usually the time when water enters the saturated zone and becomes groundwater (Bethke & Johnson, 2008). In atmospheric studies, t_{in} is often defined as the time water evaporates into the atmosphere (Läderach & Sodemann, 2016). Thus, these definitions have been adapted to different disciplines or compartments. Similarly, the time t_{out} depends on the compartment and process or point of interest. For example, t_{out} has been defined as the moment the water rains out for travel times in the atmosphere, is taken up by roots for estimating transpiration time (usually ignoring plant water storage; see section 3.2), evaporates from surfaces (evaporation time), or discharges into the outflow of the system (e.g., travel time to a spring or a catchment or lysimeter outlet). More generally, t_{in} and t_{out} can be defined with respect to any control volume or process within the hydrological continuum (e.g., specific soil depths or groundwater well) (McDonnell et al., 2010).

Mean travel times (T [T]) provide useful initial approximations of transport behavior and can be derived by dividing the stored mobile water volume (V [L^3]) by the flow rate (Q [L^3/T]) leaving the system (e.g., Kreft & Zuber, 1978; Leibundgut et al., 2009):

$$T = V/Q \qquad \text{(Equation 2)}$$

The mean travel time as defined through Equation 2 is sometimes referred to as turnover time (Bolin & Rodhe, 1973) and assumes steady state conditions.

While the mean travel time is helpful to characterize and compare different scales of water ages of different hydrological systems (section 2.3), its use has some limitations. Firstly, mean travel time is often difficult to quantify reliably, both using tracers (see 2.2) and using Equation 2 as the estimate of the mobile water storage V in the compartment is typically very uncertain. Then, in most cases, the mean value is extracted from a very skewed distribution (Kirchner et al., 2001), but for a number of scientific and environmental problems, the characterization of the entire travel time distribution (TTD) — rather than just its mean — is of greater importance (e.g., Wachniew et al., 2016). Different distributions or probability density functions (PDF) can be used to characterize the time water spends in a system and many alternative terminologies and definitions can be found in the literature (Bolin & Rodhe, 1973). In analogy to demography, one can track water molecules through a system in a forward mode ("**Forward travel time distribution**", Benettin et al., 2015c), thus addressing the molecules' "life expectancy" (Nir & Lewis, 1975), or in a backward mode ("**Backward travel time distribution"**, Benettin et al., 2015c**)**, thus focusing on their "age" or "**residence time**" (Bolin & Rodhe, 1973). Taking the case of a contaminated aquifer as an example, one can focus on when the contaminant has been introduced in the past (contaminant age distribution), or on when the contaminant will exit the aquifer in the future (contaminant life expectancy). The distinction between forward and backward distributions is relevant whenever the system under consideration is not in long-term **steady state** (Niemi, 1977). Besides their mathematical distinctions, however, the terms age, residence time and travel time are often used as synonyms in common language.

Figure 1 conceptualizes the relationship between the time-varying age distributions of the water stored in a hydrological system (see color code of S) and in the resulting stream discharge (color code of Q). The water age distributions of both the storage and flux will vary considerably depending on the wetness conditions (e.g., Harman, 2015). When storage is high, water ages tend to be younger than when the system dries out (black and red squares in Figure 1).

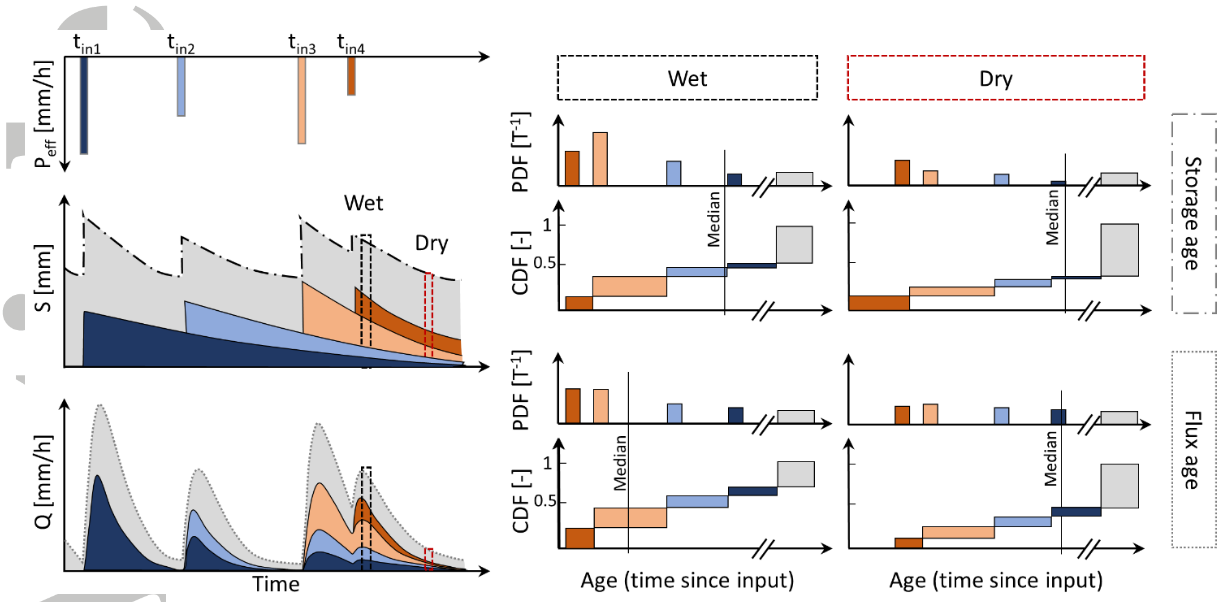

Figure 1 Relationship between input, storage and release in a hydrological system. Water age dynamics in the storage (S) and flux (Q) are visualized by colors that refer to the precipitation input, while grey indicates water older than t_{in1} (left). Storage and age distributions are reported as probability density functions, PDF, and cumulative density functions, CDF. Wet and dry conditions are indicated by black and red dashed boxes, respectively, in the storage and flux time series. Medians of the distributions are shown with vertical lines. The broken x-axis accounts for waters of age older than t_{in1}. P and Q time series were inspired by Botter et al. (2010).

2.2 How to estimate water ages?

As mentioned in Section 2.1, mean water ages can be estimated from water balance approaches (Equation 2). However, the components of the water balance are sometimes difficult to quantify, or we simply do not know the mean fluxes and mobile water volumes in the compartment of interest. Tracer data are usually essential for getting information on the flow paths and effective hydrological fluxes, which is required for disentangling the **celerity** (e.g., pressure wave propagation) and velocity (mass flux of the water) responses of hydrological systems (McDonnell & Beven, 2014). Several methodological developments in tracer hydrology, such as laser spectrometry (e.g., Berman et al., 2009) or atom trap trace analysis (e.g., Lu et al., 2014), which are discussed later, open up new insights into water fluxes in the critical zone. Still, the scales at which we can apply and observe tracers are limited due to a combination of logistical, financial and technological constraints. This in turn limits our ability to track the water through the hydrological cycle (Figure 2). While processes taking place in the soil-plant-atmosphere continuum tend to be studied with tracers at the plot scale and over relatively short periods of time (Dubbert & Werner, 2019), a meaningful characterization of the interactions between waters in the unsaturated and saturated zone requires larger spatio-temporal scales from hillslopes to catchments. Water age estimates are challenged by the natural multiscale heterogeneity of hydraulic conductivity (e.g., soil matrix versus macropores in the subsurface) (Troch et al., 2009; Bachmair & Weiler, 2011), which can lead to long tails of the water age distribution functions (Kirchner et al., 2000). Additionally, heterogeneity in infiltration and percolation results from vegetation (e.g., interception and throughfall (e.g., Molina et al., 2019), root water uptake volumes and depths (e.g., Dick et al., 2018)), snow accumulation and melt patterns (e.g., Garvelmann et al., 2015), and other spatially variable environmental characteristics.

Age distributions with long tails, resulting from heterogeneity of the flow and transport processes, variable flow path connectivity and/or mixing intensity (Hrachowitz et al., 2013) are challenging to assess, because the characteristic timescales of hydrological tracer inputs to the system will control which parts of the age distribution can be determined (Benettin et al., 2017a). Moreover, due to the age characteristics of some compartments, particular tracers are useful for one part of the critical zone, but cannot be applied for other parts. As a result, there is no single tracer that can be used to cover the wide range of spatial and temporal scales of water ages in the critical zone; instead, different tracers are needed to investigate different parts of the water age distribution (Figure 2).

2.2.1 Dating tracers

Temperature and ^{222}Rn are usually limited to processes related to several days (Petermann et al., 2018). Natural variation of **stable isotopes** of hydrogen (^{2}H) and oxygen (^{18}O) in water molecules can be used in the unsaturated zone to date water of up to 3 to 5 years, depending on the mixing and dispersion across the soil profile (Koeniger et al., 2016; Sprenger et al., 2016a). On the catchment scale, seasonal cycles of the stable isotopic composition in precipitation are most useful for inferring relatively short travel times (2-4 years) (McGuire & McDonnell, 2006; Stewart et al., 2010). Frisbee et al. (2013) showed that TTDs based on stable isotope data will underestimate the water ages, compared to approaches based on ^{14}C (see below) when old groundwaters contribute considerably to the runoff. It has been argued that the isotopic seasonality will be blurred by the heterogeneity of flow paths, which obscures the estimates of the long tails of TTDs (Seeger & Weiler, 2014; Kirchner, 2016a). Nevertheless, mean catchment travel times of up to 10 years have been reported, which were partly supported by tritium (^{3}H) data (Hale et al., 2016). ^{2}H and ^{18}O can also be used to identify paleo-groundwater, because the isotopic composition of precipitation (and thus groundwater recharge) was different during the Pleistocene (ending 11700 years ago) under a different climate (e.g., van Geldern et al., 2014; Rozanski, 1985). The time scale of artificially introduced tracers like Br^{-}, SF_6, dyes (e.g., brilliant blue), or isotopically enriched water ("deuterated" enriched in ^{2}H; enrichment in ^{18}O is also possible) during sprinkling or injection experiments mainly depend on the tracer breakthrough curve in the monitored flux and the observation limits in the studied compartment (e.g., groundwater in Becker &

Coplen, 2001; soil and lysimeter outflow in Koeniger et al., 2010; Evaristo et al., 2019; transpiration in Bachmann et al., 2015; Beyer et al., 2016; Volkmann et al., 2016a).

Water ages of up to about 60 years can be assessed with tracers whose concentrations were artificially increased in the atmosphere by nuclear bomb tests (tritium (^{3}H) and its decay product ^{3}He), nuclear power generation (^{85}Kr), or industrial emissions (SF_6, CFCs). Groundwater is also commonly dated based on the decay of radioisotopes, covering time scales ranging from 50 – 1000 years with ^{39}Ar, 1000 – 40,000 years with radiocarbon (^{14}C), and 50,000 to 1 million years with ^{36}Cl or ^{81}Kr (Aggarwal, 2013). ^{4}He, which is produced by α decay in rocks and accumulates in groundwater, allows qualitative age dating between 100 and 1 million years (Aggarwal, 2013). The principles, applications and limitations of these different tracer methods for groundwater age dating have been discussed in a large number of books and reviews (Clark & Fritz, 1997; Cook & Herczeg, 2000; Kipfer et al., 2002; Plummer, 2005; Bethke & Johnson, 2008; Newman et al., 2010; Suckow et al., 2013; Beyer et al., 2014). The most recent development in this field is the introduction of an analytical method from atomic physics (ATTA: Atom Trap Trace Analysis), which greatly facilitates the use of the noble gas radioisotopes ^{39}Ar, ^{81}Kr, and ^{85}Kr (Lu et al., 2014). This new method of groundwater dating is now increasingly being applied, making successful use of the advantageous properties of the noble gas radioisotopes (e.g., Ritterbusch et al., 2014; Aggarwal et al., 2015; Gerber et al., 2017; Matsumoto et al., 2018; Yechieli et al., 2019).

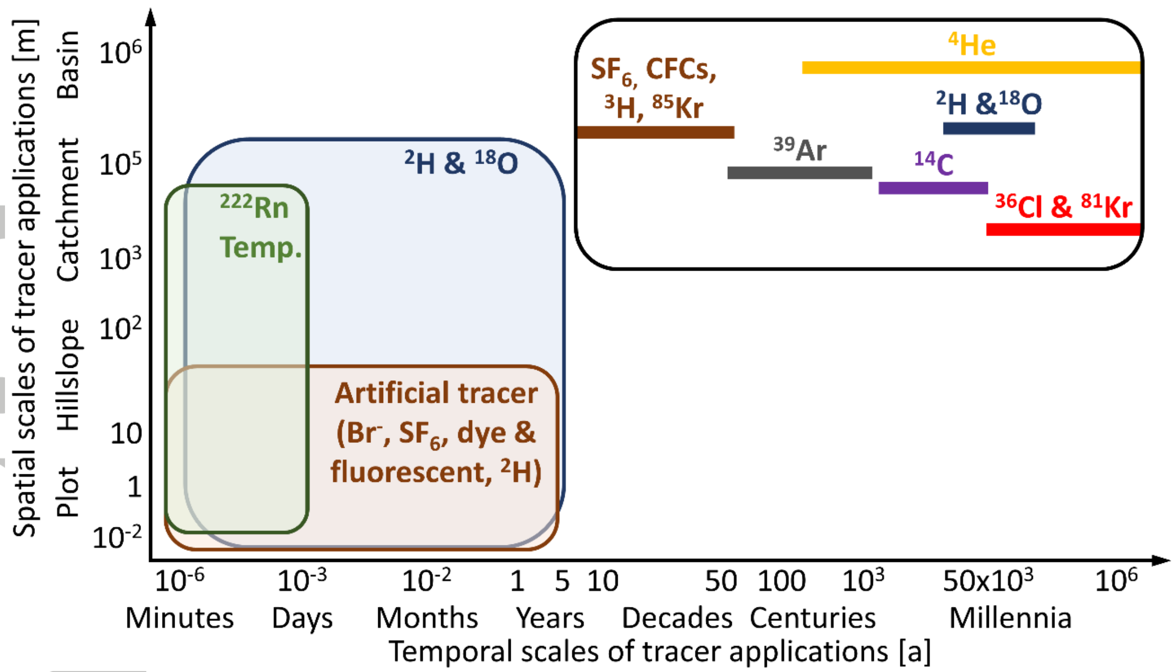

Figure 2 Spatial and temporal scales for use of different hydrological tracers (Newman et al., 2010; Aggarwal, 2013; Abbott et al., 2016). The black box represents groundwater age tracers applicable on scales from small catchments to large basins that span different temporal scales.

It should be noted that most of the tracers used for groundwater dating are gases (CFCs, SF_6), noble gas isotopes (^3He, ^4He, ^{39}Ar, ^{81}Kr, ^{85}Kr) or isotopes that enter the groundwater in gaseous compounds (^{14}C as $^{14}CO_2$). For these gas tracers, the system closure occurs – at least in a first approximation – at the groundwater table, so they only measure travel times in the saturated zone. Only the non-gaseous tracers (^3H, ^{36}Cl) reflect travel times from the time of precipitation, as discussed above for dating in surface and soil water hydrology. The issue of travel times through the unsaturated zone and its effects on tracer concentrations will be discussed in more detail in section 3.4.

2.2.2 Interpretation of tracer data

The interpretation of the results obtained from age-dating tracers can be challenging, since every water sample taken in the critical zone consists usually of contributions with various ages, as water does not move in isolated packets through hydrological systems. Thus, water ages derived from radioactive decay will underestimate the actual age of the water mixture due to diffusion or mixing with isolated water and therefore are “apparent ages” (Bethke & Johnson, 2008). Similar issues arise when matching historical tracer inputs like ^{3}H from the nuclear bomb peak, pollutants like CFCs and SF_6, or artificially introduced tracers like Br^-, deuterated water, dye or fluorescent tracers to a measured breakthrough curve of the corresponding tracer. Ages inferred from these historical tracers can also be strongly biased, if waters of different ages (and thus different concentrations) mix within the studied hydrological system. Differences between apparent water age and actual water age can also occur for tracer concentrations that increase nonlinearly with age (e.g., ^{222}Rn), while for tracers with linear increase (e.g., ^{4}He), the apparent age equals the actual water age of a mixed water sample (Bethke & Johnson, 2008).

Estimates of travel time distribution are often based on the change of or the damping of seasonally variable tracer inputs (e.g., stable isotope ratios in precipitation) observed in the output (e.g., stream, spring) of a hydrological system (Figure 3). The amplitude of such a seasonal tracer cycle typically decreases nonlinearly with mean water age, reflecting dispersion by the complex flow path distribution in a hydrological system (Kirchner, 2016b). Mixtures of waters that have undergone different amounts of dispersion can lead to biased estimates of mean age (Kirchner, 2016a), similar to the bias in ages inferred from radioactive tracers.

The TTD describes the transfer function between the input and output of an environmental tracer, which can be defined in the time domain with a convolution equation (Maloszewski & Zuber, 1982). Steady-state TTDs have been employed mostly in the early travel time studies (McGuire & McDonnell, 2006) (Figure 3a). They are assumed to not vary in time, and to be characterized by a particular shape, for example an exponential distribution (Maloszewski & Zuber, 1982) or a gamma distribution (Kirchner et al., 2000, 2001). In typical applications, the parameters of these distributions are calibrated to observed time series of concentrations of one or more tracers in system output fluxes (e.g., stream flow, springs, groundwater wells) via a convolution operation either in the time domain (Maloszewski et al., 2002; Corcho Alvarado et al., 2007; Speed et al., 2010; Soulsby et al., 2010) or the spectral domain (Kirchner et al., 2000, 2001). This approach is increasingly being used not only to determine the parameters of traditional TTD models, but to derive shape-free or nonparametric distributions (Massoudieh et al., 2012; Visser et al., 2013; Massoudieh et al., 2014; McCallum et al., 2014; Kirchner, 2019). Such flexible distributions can overcome possible biases introduced by choosing the TTD shape a priori, but are demanding with respect to the number of data points and different age tracers measured. Different flow components can be distinguished in these steady-state TTDs (compound TTDs; Weiler et al., 2003). The weights of the flow components are usually assumed to be constant and are deduced from mixing models (Maloszewski et al., 1983; Stewart et al., 2010). The steady-state assumption can be partly relaxed by using a flow-weighted time in the steady-state TTDs (Niemi, 1977; Rodhe et al., 1996), by modifying the input function (Grabczak et al., 1984; Weiler et al., 2003; Stumpp et al., 2009c; Soulsby et al., 2010), or by applying the steady-state TTDs to a shifting time window over the study period (Hrachowitz et al., 2009; Tetzlaff et al., 2014).

Nevertheless, rigorously accounting for non-steady-state conditions and thus for time-variance requires solving a balance equation that takes into account the observed variability in fluxes and storage of the considered hydrologic compartment, referred to as "age master equation" of travel times by Botter et al. (2011). For conceptualizations of a hydrological system as a single (or several discrete) reservoir(s), the age master equation has been solved by specifying a "StorAge Selection function" (SAS) of all outflows, which can be used to represent different mixing assumptions inside the hydrologic compartment (Bolin & Rodhe, 1973; Rinaldo et al., 2015) (Figure 3b). This approach can be applied to whole catchments (van der Velde et al., 2012; Harman, 2015; Benettin et al., 2017b), individual compartments (Benettin et al., 2015b; Rodriguez et al., 2018), and lakes (Smith et al., 2018). SAS functions are usually determined by assuming a functional form (e.g., a beta or gamma distribution) and calibrating the relevant parameters against observed tracer data, like stable isotopes (e.g., Benettin et al., 2017b), chloride (e.g., Benettin et al., 2015b), and recently also cosmogenic radioactive isotopes (Visser et al., 2019). A description of the SAS function approach can be found in Rinaldo et al. (2015).

Functionally equivalent to the SAS function approach is the use of mixing coefficients that are often implemented in conceptual catchment models that are calibrated with tracer data. The difference to the above is that these models do not directly and explicitly parametrize the SAS function but they rather specify the degree of mixing through a mixing coefficient which describes the storage selection in a given compartment (Hrachowitz et al., 2016; Knighton et al., 2017). The SAS function then emerges from the water storage and release dynamics of the system. These models can thus also be used to estimate time-varying TTDs by tracking water fluxes (McMillan et al., 2012; Hrachowitz et al., 2013; Klaus et al., 2015) (Figure 3c). Flux-tracking in spatially-distributed models was further shown to enable relating water age variability of storages and fluxes within catchments to assumed flow paths and mixing in the model setup (van Huijgevoort et al., 2016; Ala-aho et al., 2017b; Kuppel et al., 2018), to disentangle contributions of different flow paths to the catchment runoff.

Spatially distributed, continuum-based hydrological models (Hrachowitz & Clark, 2017) are also being increasingly used to simulate time-varying TTDs by tracking the age of particles of water as they flow through the catchment (Davies et al., 2013; Maxwell et al., 2016; Danesh-Yazdi et al., 2018; Remondi et al., 2018; Yang et al., 2018) (Figure 3d). In these models, mixing hypotheses can be formulated at smaller scales. Although usually much more computationally demanding and affected by the closure problem (Beven, 2006), these models offer the opportunity to simulate the physical redistribution of water within the system (Engdahl et al., 2016), which might allow linking travel times more specifically to hydrological processes. In numerical groundwater flow models, particle-tracking can be used to directly compare travel times and tracer ages (Sheets et al., 1998), to derive TTDs (Visser et al., 2009) and to compare them to tracer-derived TTDs (Eberts et al., 2012). An approach to overcome the restrictions of purely advective flow models and to correctly account for the effects of dispersion consists of the direct modeling of age using an advection-dispersion equation (Goode, 1996; Varni & Carrera, 1998; Ginn et al., 2009). The direct simulation of age can also be combined with reservoir theory to derive transit times of water at the outlet of an aquifer (Etcheverry & Perrochet, 2000; Cornaton & Perrochet, 2006). Ultimately, however, the most straightforward approach to make use of age tracer data in groundwater models may be the numerical simulation of the tracer mass transport to obtain spatially explicit tracer concentrations that can directly be compared to observations (Turnadge & Smerdon, 2014; Troldborg et al., 2008).

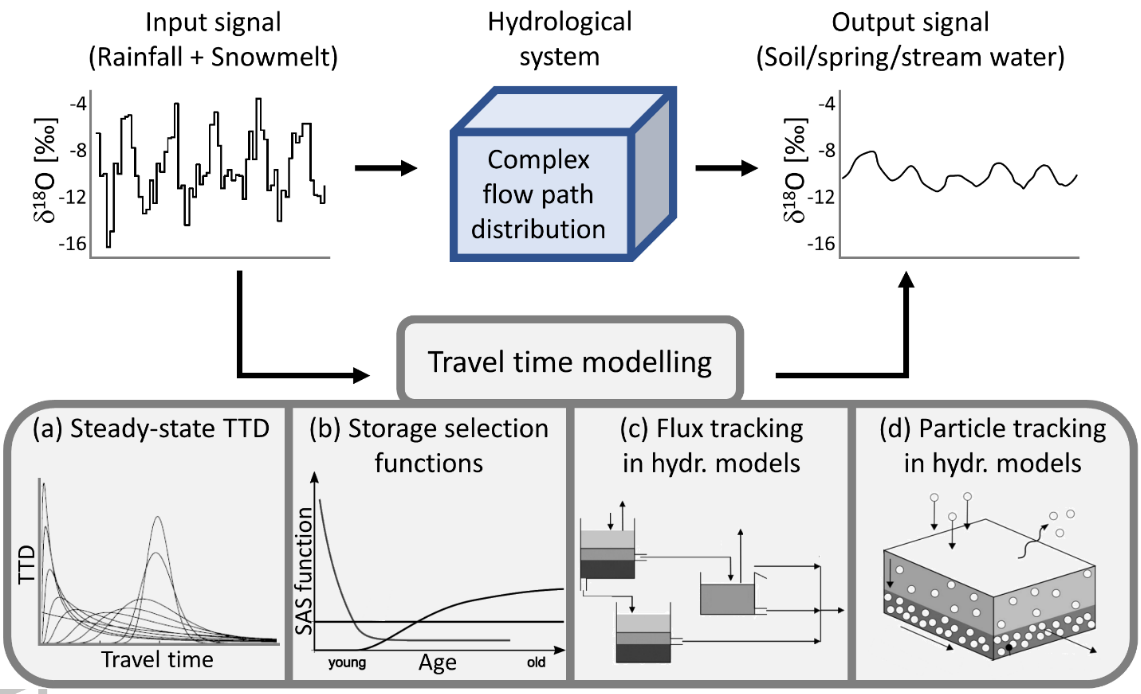

Figure 3 Travel time distributions (TTDs) estimated from tracer input – output relationships. Tracer input signals (e.g., ^{18}O) introduced via precipitation or snowmelt are damped, to different degrees on different time scales, due to dispersion by complex flow path distributions in hydrological systems (e.g., catchment, soil column). The resulting output signal, e.g., sampled in soil water, spring water or stream water, shows less variability (Graph based on Plummer et al., 2001; McGuire & McDonnell, 2006). The input – output relationship is used (a) to derive steady-state TTDs (reviewed by McGuire & McDonnell, 2006), (b) to calibrate storage selection (SAS) functions (e.g., Benettin et al., 2015c), and to calibrate hydrological models using (c) flux tracking (e.g., Hrachowitz et al., 2013) or (d) particle tracking (e.g., Davies et al., 2013) approaches.

2.3 Variability of water ages in the critical zone

Mean water ages in the different compartments in the hydrological cycle based on Equation 2 have been estimated since at least 40 years (Ambroggi, 1977; Korzun et al., 1978; Oki et al., 2004). According to these flux-based estimates, global average water ages in the water cycle range from several hundreds to thousands of years in the deep groundwater, thousands of years for waters stored in the ocean and glaciers to several years for wetlands, lakes and modern groundwater (Table 1). While such values suggest that water in soils, rivers, the atmosphere and vegetation have on average the fastest turnover due to either small storage volumes or high fluxes, not all of that storage equally contributes to outputs. Thus, these global average travel times are only rough estimates that do not account for temporal and spatial variability; they are also vulnerable to the considerable uncertainties in global estimates of storage volumes and fluxes. Especially for the relatively short residence times of vegetation, rivers and soils, the water budget approach over-simplifies the water age by providing a mean value of a possibly very broad and variable age distribution (Figure 4) and does not account for the effect that vegetation types and climate zones have on water storage and age.

Recent research indicates that a significant volume of groundwater (~350,000 km^3) is less than 50 years old (Gleeson et al., 2016). Although only a small fraction of total groundwater storage, this "modern groundwater" still represents around three times the volume of terrestrial surface water storage and soil water storage (~100,000 km^3 and ~16,000 km^3, respectively; Oki & Kanae, 2006). Being active in the hydrological cycle, the modern groundwater contributes to streamflow and thus could also alter stream water ages. In a survey of aquifers around the globe, 42-85% of total aquifer storage in the upper 1 km of the Earth's crust was older than roughly 12,000 years, but about 50% of the surveyed aquifers also contained water younger than 65 years (Jasechko et al., 2017). How much of the groundwater contributes to streamflow is yet unknown, as we currently lack adequate methods to detect relatively small proportions of old water in the streamflow (Frisbee et al., 2013).

Due to the limited information provided by the concept of mean water ages (because waters are typically mixtures of different ages), hydrological research has moved from calculating mean ages towards quantifying water age distributions in the atmosphere (e.g., van der Ent & Tuinenburg, 2017), evaporation and transpiration (e.g., Botter et al., 2010), soils (e.g., Queloz et al., 2015b), unsaturated sediments (e.g., Stumpp et al., 2007), groundwater (e.g., Bethke & Johnson, 2008), and streamflow (e.g., Kirchner et al., 2000; Kirchner, 2019).

2.4 Water ages within compartments

Dividing the hydrological cycle into compartments and fluxes between them is an obvious simplification of a more complex reality. Nonetheless, in-depth research often requires focusing on individual compartments of the hydrologic cycle and treating their connections to the rest of the water cycle as boundary conditions. Focusing on individual compartments often comes with strong assumptions. As an example, the output flux of one compartment is generally the input flux to another compartment and it is often challenging to assess the age distribution or tracer **flux concentration** (Kreft & Zuber, 1978) at the interfaces. For instance, the input to groundwater storage (i.e., the recharge flux and its tracer concentration or age distribution) is difficult to estimate and thus often assumed to be at steady state in groundwater age modeling (as reviewed in Cartwright et al., 2017). Strong assumptions are also often made when travel time modeling approaches developed for one compartment are transferred to another compartment. For example, while the steady-state assumption might be applicable for some groundwater systems, where the change in storage is relatively small (Table 1), using the steady-state assumption in hydrological systems with highly variable flow rates – like the unsaturated zone – can be problematic (Stumpp et al., 2009a). A common strong assumption is that compartments are well mixed; this assumption is often violated and can introduce bias for water age estimates (Kirchner et al., 2000; Fenicia et al., 2010; McMillan et al., 2012; van der Velde et al., 2015). A well-mixed compartment will have the same age distribution as its output flux, allowing one to be inferred from the other, but the same is not true of compartments that are not well mixed.

Thus, while there are good reasons to study the water ages of individual compartments, there are also limitations in doing so. Recent water age studies have highlighted that the forcing of hydrological systems through their boundary conditions strongly influence the time-variant character of water ages (e.g., Heidbüchel et al., 2013; Benettin et al., 2015a), and that the connections of these boundary conditions to other compartments need to be better understood (see also Staudinger et al., 2019).

Recently, McDonnell (2017) highlighted a compartmentalization within the terrestrial water cycle beyond the traditional compartments that represent the stores. For example, within the soil water storage, stable isotopic compositions of mobile and bulk soil water is often different (e.g., Brooks et al., 2010; Goldsmith et al., 2012; Sprenger et al., 2018b; Sprenger et al., 2019), which indicates that some part of the infiltrated precipitation recharges to groundwater and streamflow more quickly than others. The slower component of the subsurface flow (studied with bulk water isotopic compositions) was found based on stable isotope data to be transpired preferably over the fast flow (studied with suction lysimeters), resulting in so-called "ecohydrological separation" (Brooks et al., 2010; Evaristo et al., 2015) (section 3.3 and 3.4.1). Thus, the soil compartment appears to be compartmentalized and the interactions occurring at the present interfaces are not well understood (Berry et al., 2017; Vargas et al., 2017). However, this compartmentalization would have a great impact on water ages in the unsaturated zone (Table 1), as some travel time simulations under varying mixing assumptions indicate (McMillan et al., 2012; Hrachowitz et al., 2013; van der Velde et al., 2015). How these compartmentalized water stores influence the demographics of water in the critical zone will be discussed in the following.

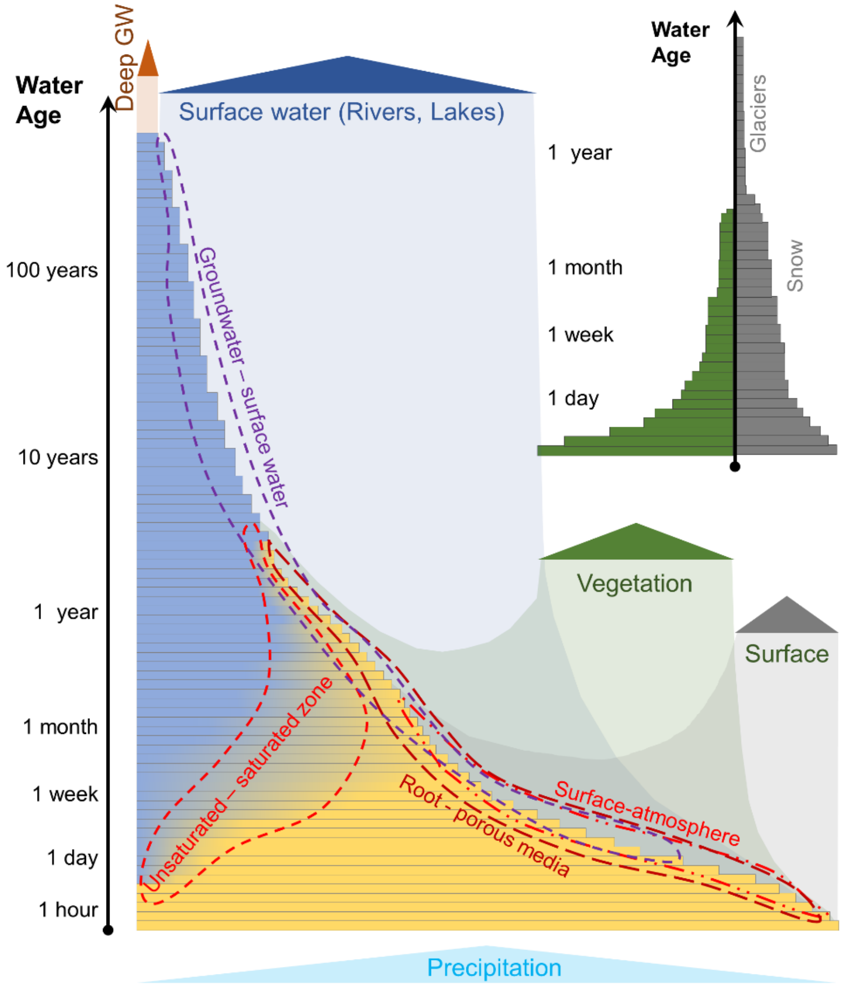

Figure 4 Conceptual diagram showing hypothetical demographics of water (age distributions) in the critical zone. Dashed lines indicate the mixing of water with different ages at the interfaces. The central demographics reflect the unsaturated (yellow) and saturated (blue) zone of the critical zone, the demographics of the vegetation (green) and additional stores on the surface (e.g., snow or glaciers) are shown separately.

Table 1 Hydrological compartments of the terrestrial water cycle (Antarctica excluded) and their global estimates of storage and flux volumes, derived average travel times using Equation 2, and estimated storage variability. *Note that the numbers given for global storage and flux are approximations and vary both in space (e.g., across various climates) and time (e.g., seasonally). Since storage variations cannot be accounted for using Equation 2, average water ages can only serve as rough estimates, while the water age is highly variable within the compartments as shown in the distributions in Figure 4.

Compartment		Storage [10^3 km^3]	Flux [10^3 km^3/y]	Global average water age*	Max. storage variation [%]
Atmosphere over land		3[†]	111[†]-116.5[ч]	10 days	< 5
Vegetation		1[†]	58[†]	6 days	< 10
Snow		12.5[†]	12.5[†]	1 year	100
Glacier and permanent snow		24,064[†]		1,600 years[‡]	< 5
Unsaturated zone	Mobile water	17[†]	18.6[ϕ]	11 months	100
	Bound water		11.4[ϕ]	1.5 years	30
Surface water	Lakes	175[†]		17 years[†]	30
	Wetlands	17[†]		5 years[†]	10
	River	2[†]	45.5[†]	16 days	40
Groundwater	Modern	347[ʊ]		<50 years[ʊ]	<5
	Old	23,090[ʊ]			<1

[†]Oki & Kanae (2006), [ч] Rodell et al. (2015), [‡]Korzun et al. (1978), [ϕ]Good et al. (2015), [ʊ]Gleeson et al. (2016)

3 How interfaces affect water age distributions

3.1 Surface – atmosphere

3.1.1 Precipitation input

Precipitation inputs to landscapes are the fundamental supply of "new water" (age zero). While this time of age zero often coincides with the time of infiltration into the soil, the storage of part of the precipitation in the canopy due to interception or as non-liquid precipitation on land surfaces is an important consideration, and is not consistently accounted for in travel time estimations (e.g., time of melt or time of precipitation as age = 0 days; Figure 4, Table 1). Snow can reside for months (as snowpack) or years (as glacier ice), altering the age, timing and chemistry of infiltrating waters. Snow is stored on the ground surface causing a delay of infiltration. During storage, the snow ages and also the isotopic composition in the snowpack changes over time due to diffusion and fractionation processes (Herrmann et al., 1981; Stichler & Schotterer, 2000). In cold regions, wind causes redistribution of snowpacks (Freudiger et al., 2017), which results in high spatiotemporal variability in snowpack height and isotopic composition (Dietermann & Weiler, 2013; Hürkamp et al., 2019). During snowmelt, early meltwater is isotopically lighter than later melt due to isotopic exchange between meltwater and the remaining ice (Taylor et al., 2001; Taylor et al., 2002; Feng et al., 2002). For catchment scale modelling, Ala-aho et al. (2017b) showed that snowmelt dynamics and their tracer signals (e.g., fractionation of stable isotopic compositions in snowpack, Ala-aho et al. (2017a)) were crucial for a realistic representation of the flow processes in northern catchments and influenced the estimated water age distributions of catchment runoff.

An accurate characterization of the input from the atmosphere should consider the lack of representativeness of the input tracer data. For instance, while the uncertainty of the input data used to run hydrological models is recognized (e.g.; Kavetski et al., 2006; Vrugt et al., 2008), uncertainties related to the input tracer data in water age modeling have not been systematically characterized (McGuire & McDonnell, 2006). To that end, a better knowledge of the tracer signatures of the water that effectively recharges the catchment is needed, because not every tracer signature contributes to the recharge as initially measured in precipitation. Generally, small-scale variation of the tracer signal can be high, which challenges sampling strategies, as for example highlighted by the spatial variability of stable isotopic compositions of water in the upper soil layers (Yang et al., 2016a; Goldsmith et al., 2019). Water and therefore tracer signatures can be lost or altered due to interception, sublimation, evaporation, or transpiration. For example, the interception and canopy storage of precipitation not only changes the spatial and temporal distribution of throughfall (Keim et al., 2005, 2006), but in the case of stable isotopes, it can also cause noticeable differences between precipitation, throughfall, and stemflow isotopic composition (Allen et al., 2014; Allen et al., 2017; Cayuela et al., 2018). These differences have been shown to affect the estimated water ages in catchment runoff (Stockinger et al., 2015). These demographic shifts further affect the inputs of age-zero water and tracer to the critical zone. Thus, precipitation input variability (e.g., induced by climate change) not only drives variations in water ages themselves (Wilusz et al., 2017), it also both facilitates and complicates the inference of water ages.

Tracer sampling resolution in time and space needs to be as fine enough to reflect the true variability of the hydrological forcing. Most water age studies in the past have relied on monthly or weekly water samples, while complex sub-hourly temporal patterns of tracer signatures in precipitation have been observed recently with high-frequency tracer measurement techniques (Berman et al., 2009; Munksgaard et al., 2012; von Freyberg et al., 2017; Herbstritt et al., 2018). Tracer measurement frequency in precipitation has been shown to affect the estimation of stream TTDs (Hrachowitz et al., 2011; Stockinger et al., 2016) and timing of the sampling also matters for calibration of tracer-aided water age models (Wang et al., 2018). Accounting for spatial variations in rainfall isotope ratios, even within small catchments, is as important to inferring flow and transport processes as accounting for temporal variations (Fischer et al., 2017; Cayuela et al., 2019). Accounting for spatial variations in precipitation inputs is especially important when comparing water sample isotopic compositions (e.g., from rivers, soil, plants, aquifers) that are collected across areas with spatially variable precipitation regimes (Bowen & Wilkinson, 2002; Bowen, 2008; Allen et al., 2018). Comparing those values to location-specific inputs allows for more accurately inferring how those precipitation patterns propagate through the system of interest (von Freyberg et al., 2018). However, mixing of spatial and temporal signals complicates interpreting tracer values in subsurface pools that integrate over large areas and durations (Kirchner, 2016a).

3.1.2 Evaporation

Before reaching soils, a large fraction of precipitation inputs are intercepted by and evaporated from canopies (e.g., often 10-50 %; Carlyle-Moses & Gash (2011)), or intercepted by and evaporated from litter (e.g., often 10-50%; Gerrits & Savenije (2011)). However, evaporation from non-soil surfaces in terrestrial environments is often lumped with soil evaporation in (eco)hydrological studies, despite having potentially different water ages. These small, ephemeral storages (e.g., interception in the canopy) typically dry quickly, implying that they rapidly return event water to the atmosphere with maximum water ages of a few days (Allen et al., 2014); thus, tracers are rarely used to focus on this process, because transit times are likely to always be short. The evaporative flux of these pools contributes varying amounts of very young water to the atmosphere, so the mean age of water evaporated from terrestrial environments is younger than estimates that only account for soil evaporation and transpiration. However, foliar uptake of fog, as revealed by stable isotope studies (Limm et al., 2009; Eller et al., 2013), would increase the return time of meteoric water into the atmosphere, but it will usually represent a relatively small share of the evaporative flux. When a larger fraction of atmospheric water demand is satisfied by interception (up to 50% of rainfall as reviewed by Carlyle-Moses & Gash, 2011), waters in soils will move more slowly and age more.

Evaporation of soil water takes place at the interface to the atmosphere and is thus often limited to the topsoil (Or et al., 2013). As the upper soil layers usually contain relatively young waters (see section 3.4.1), the soil evaporation flux should also contain young water. Soil physical simulations indicate that the mean ages of evaporative fluxes range between one and about 50 days at sites in northern latitudes (Sprenger et al., 2018a). Generally, the partitioning between evaporation and transpiration flux is challenging, but increasingly applied in situ stable isotope measurements were shown to allow distinguishing between both fluxes (Wang et al., 2010). Soil evaporation is generally likely to be of younger water age than transpiration (Sprenger et al., 2018a), since plant roots access water below the evaporation front (usually limited to the shallow soil, Or et al., 2013), where older water resides (Allen et al., 2019, Figure 5). If stable isotopes are used as tracers for water age simulations (Knighton et al., 2017), evapotranspiration partitioning into evaporation and transpiration is also important to account for evaporative isotopic fractionation of soil water (e.g., Sprenger et al., 2017a) or stream water (e.g., Sprenger et al., 2017b).

3.2 Plant – atmosphere

The age of water travelling to the atmosphere through plants is a function of the age of waters held in soils (section 3.4.1), the roots' access to those waters (section 3.3), and the travel time from root to the atmosphere. Here we discuss the travel time of water through plants, which is highly variable because plants vary by several orders of magnitude in both size (i.e., path length) and conductivity (e.g., Tyree & Zimmermann, 2002; Gleason et al., 2012). In many trees, although water occupies much of the pore space, only the outer fraction of the wood conducts water. Thus, most trees grow new conductive xylem vessels each year, while the inner area of conductive tissues decreases as xylem elements cavitate or become clogged over time and cease to transport measurable amounts of water (Zimmermann & Brown, 1971; Wullschleger et al., 1998). While the species specific exchange between the transpiration stream and water stored in the stem can affect the residence times (James et al., 2003), only a fraction of the water stored in plants may contribute to the transpiration flux (Zimmermann & Brown, 1971); for example, one study observed tree water use of 150-300 liters per day in Douglas fir, with only 25-55 liters being sourced from stored water (Cermák et al., 2007; also see studies reviewed by Landsberg et al., 2017). Travel times for isotopic tracer arrival from the soil to the tree crown can range from 2.5 to 21 days and sap velocity is reported as 2.4 – 5.4 m d^{-1} (Meinzer et al., 2006; Brandes et al., 2007). However, Meinzer et al. (2006) also noted preferential flows because isotope tracer velocities were nearly an order of magnitude higher than the sap flux (per sapwood area) rates inferred by thermal probes. Bulk metrics of flux are more often used; for example, stem hydraulic conductance is frequently measured and known to vary widely with plant functional type and age (e.g., spanning from 3-5x10^{-4} m^2 s^{-1} MPa^{-1} in coniferous wood to 500x10^{-4} m^2 s^{-1} MPa^{-1} in lianas, Larcher, 2003). Any fluxes from across a cross section of stem, and travel times inferred from whole-stem metrics (e.g., using Equation 2), are unlikely to approximate the velocity of water in stems and the water age transfers that occur across this interface. While extant evidence of heterogeneity in conductivity across conductive tissue in plants (e.g., Meinzer et al., 2006; James et al., 2003) has been presented, which results in water ages of plant water storage exceeding water ages of transpiration flux, empirical evidence of water ages and transit times remains limited.

Moreover, fluxes and thus transport velocities are strongly mediated at the leaf–atmosphere interface, because their driving forces are atmospheric water vapor deficit (VPD), turbulent mixing of the atmosphere, net radiation, and the plants' control of stomatal water loss. Transport is generally lower during times of drought-induced stomatal closure or low VPD, and higher during times of ample water supply and/or high VPD. Moreover, during prolonged high atmospheric demand (i.e., high VPD), when surface soils dry out, plants may shift their water uptake to deeper soil layers with potentially older water ages (e.g., Ehleringer et al., 1991; Bertrand et al., 2014; Barbeta et al., 2015; Barbeta & Peñuelas, 2017), and thus return different water ages to the atmosphere (section 3.3). Moreover, transport velocity, particularly during soil drying, depends on species-specific water use strategies (Larcher, 2003). For instance, "water saver" isohydric plants react to soil drying by effectively controlling transpiration losses due to structural (e.g., leaf morphology) and physiological adaptions (e.g., stronger stomatal control) and maintain stable water potentials in dry and wet conditions (Tardieu & Simonneau, 1998). In comparison, anisohydric "water spenders" sustain higher transpiration rates under soil drying and vary strongly in their water potentials even at a greater risks of cavitation failure (Sade et al., 2012). Species-specific water use strategies will affect not only the transit time through plants, but also water age at the entry point of plants, due to different plants' widely varying abilities to maintain low water potentials. For example, anisohydric plants can tolerate water potentials as negative as -12 MPa (Werner et al., 2002), thus being able to take up water from very dry soils. However, there is a broad range of anisohydric and isohydric behavior in plants, which can even be modulated by growth conditions (Hochberg et al., 2018) and will determine the transport time in the plants. Interestingly, the invasion of anisohydric species in isohydric dominated ecosystems can alter the transpirational water fluxes in these ecosystems (Rascher et al., 2011; Caldeira et al., 2015), and therefore the velocity by which soil water is returned to the atmosphere.

In contrast to effects of different source waters on plant water age, plant–atmosphere interactions influence plant travel times on much smaller temporal scales of days rather than months. Nonetheless, plant-water transport in plant ecophysiological studies is usually considered in the context of sap flux radial profiles or relative conductivities (Wullschleger et al., 1998; Thomas & Winner, 2002; Čermák et al., 2004), whereas transport velocities through plants are rarely calculated and thus plant water ages or transit times are largely under-described.

3.3 Root – porous media

The upper part of the unsaturated zone that supports vegetation rooting is called the root zone. Depending on the plant species, soil type, groundwater depth and climate, the root zone typically ranges from the soil surface to 0.4-2 m (Fan et al., 2017; Yang et al., 2016b), but can reach beyond several meters for individual plants (Stone & Kalisz, 1991; Canadell et al., 1996; Schenk & Jackson, 2005). Different plants take up waters of many different ages, depending on the different water ages that are available in soils on the waters they can access, as determined by their rooting depth. However, one would expect the distribution of the plant water uptake to be skewed towards younger water ages (green in Figure 4). Traditional conceptualizations of infiltration represent recent water as filling shallow soils, and either mixing with or displacing previously stored (older) waters. In this **translatory** flow model, in which new water displaces older water (Horton & Hawkins, 1965; Hewlett & Hibbert, 1967), shallower waters would be younger (Figure 5a). However, a key unknown is how infiltrating water displaces previously stored water, which provided the rationale for initial investigations into ecohydrologic separation (Brooks et al., 2010). Preferential flow allows water to bypass the matrix (Beven & Germann, 1982), resulting in young water infiltrating deeply into soils (Thomas et al., 2013), and rapidly contributing to streamflow or aquifers, rather than refilling the soil matrix. The consequences of translatory flow and ecohydrological separation for the water ages in soil storage, transpiration, evaporation, and recharge are visualized conceptually in Figure 5. While it is sometimes assumed that water in fine and coarse pores is fully mixed, pronounced differences between the stable isotopic compositions of mobile water and bulk soil water question this assumption (Brooks et al., 2010; Goldsmith et al., 2012; Geris et al., 2015; Hervé-Fernández et al., 2016; Sprenger et al., 2018b). These field studies show that subsurface flow can be non-uniform, with a faster flow component in coarser pores and macropores compared to finer pores and the soil's matrix. Because coarse soil pores or macropores allow young water to be transported through the soil quicker in the case of ecohydrological separation (Figure 5b) than for the translatory flow (Figure 5a), the distribution of ages in soil storage contains more younger water in the latter case. Due to the relationship between storage and flux ages (Sprenger et al., 2018a), water ages in the transpiration, evaporation, and recharge are also affected by the ecohydrological separation. For example, during wet conditions, bypass (preferential) flow leads to rapid percolation of young water, while under dry conditions, the water flow in coarse pores and preferential flow paths will cease resulting in older water ages in the recharge (and evapotranspiration) flux (Figure 5b).

Brooks et al. (2010) and subsequent observations of isotopic differences between plant xylem water and mobile soil water recharging groundwater and streams led to the hypothesis that plants may not access water that is less tightly bound to soils and thus of relatively young age (Sprenger et al., 2018b). However, xylem water will reflect the mixture of different water ages taken up by the plant. It has been shown that the uptake of a small proportion of highly evaporatively enriched water from the upper soil surface, i.e. often the soil layer with the highest nutrient concentrations, can markedly change the xylem water isotopic signature, even when bulk water uptake derives from deeper soil layers with higher water content (Dubbert et al., 2019). Moreover, it needs to be taken into account that root water uptake is a passive process following a water potential gradient. Thus, the same processes mediating hydraulic redistribution of water from wet root tips into the dryer soil will drive the water uptake of mobile water into the roots, as long as roots maintain connectivity with the soil matrix (Dubbert & Werner, 2019).

Understanding infiltration dynamics and rooting patterns supports progress towards estimating ages of waters in the subsurface, and conversely, characterizing water age patterns in soils supports understanding infiltration and flow processes.

Despite the role of preferential flow, rooting depth is a major factor determining the age of water uptake, because plants selectively access certain parts of the rhizosphere. If the distribution of ages of water in soils can be approximated, then the distribution of roots (density and maximum depth) together with the distribution of pore sizes may be a first useful approximation of the water age distribution accessible by plants. However, it should be noted that the soil water status (matric potential, hydraulic pressure) and the conductivity of the roots needs to be quantified as well to get an indication of the accessible ages of water in the soils (Werner & Dubbert, 2016). Up to now, little is known about rhizosphere water transport dynamics (Carminati et al., 2009; Carminati et al., 2017), which are technically challenging to capture in situ (Rudolph-Mohr et al., 2014). Root distributions have been largely identified with direct observations, whereas the depth of water uptake can be determined by analyzing soil moisture depletion, nutrient concentrations (Stone & Kalisz, 1991), or stable isotope tracers (see review by Rothfuss & Javaux, 2017). For example, root water uptake is governed by root distribution and the hydraulic conductivity of the roots during wet periods, whereas the soil water potential is the main driver during dry periods (Figure 5) (Asbjornsen et al., 2008; Hallett et al., 2003; Song et al., 2014; Ellsworth & Sternberg, 2015; Zarebanadkouki et al., 2016). Only recently, due to technological developments have stable isotopes become commonly used in studying small scale (10^0-10^1-cm scale; i.e. Volkmann et al., 2016a, 2016b, Rothfuss et al., 2015) or short-term (sub-daily timescale) (e.g., Volkmann et al., 2016a; Piayda et al., 2017) root–water interactions.

Depending on the climatic conditions (Gao et al., 2014) but also on topography (e.g., Fan et al., 2017) and nutrient or seasonal water availability (see below), plants have different strategies to allocate their roots and will thus access water of different ages (Figure 6). In arid regions, plants tend to either be shallow-rooted (e.g., as is common of succulents; Schenk & Jackson, 2002) to efficiently take up recent precipitation before it evaporates (Donovan & Ehleringer, 1994), or deep-rooted to access deeper unsaturated zones or the groundwater (often woody shrubs; West et al., 2012; Beyer et al., 2016; Fan et al., 2017). Grasses likely predominantly take up water from shallower soils, where they develop dense root networks (Scholes & Archer, 1997; West et al., 2012; Bachmann et al., 2015). Variations in depths of water uptake among trees (which likely correlate with age variations) are extensively investigated with stable isotopes (as compiled in Barbeta & Peñuelas, 2017; Evaristo & McDonnell, 2017). Studies have shown that trees are highly variable in their root patterns among locations and species, consistent with their life-history strategy that involves long lives and thus persisting through variable conditions (Stone & Kalisz, 1991; Schenk & Jackson, 2002). In cases where soils are deep, trees can grow very deep roots that may access very old waters (Zhang et al., 2017). In contrast, in cases where only the shallowest soils are hospitable, trees may exclusively use water from shallow soils (Ish-Shalom et al., 1992;

Hsueh et al., 2016), a source that must be frequently recharged to support vegetation, and thus must be young.

Only recently, soil hydrological simulations demonstrated that the age distribution of water taken up by trees during the growing period ranged from days (fresh precipitation) to several months and even precipitation originating from the previous growing seasons (Sprenger et al., 2018a; Brinkmann et al., 2018). Additionally, water age distribution of transpiration depends on species specific root distributions, for example being older on average in *Fagus sylvatica* than for *Picea abies* at a Swiss study site (Brinkmann et al., 2018) and older for *Pinus sylvestris* than for *Erica* species at a Scottish study site (Sprenger et al., 2018a). Such species specific differences in water ages of plant water uptakes were recently also observed by Allen et al. (2019), who found xylem water of beech and oak trees during mid-summer to be isotopically similar to winter precipitation, while the source water for spruce trees was not clearly related to precipitation of a specific season. Independent of the species, trees across Switzerland were generally taking up older water at drier sites, indicating the trees' response to drought (Allen et al., 2019) (Figure 5). It should be further considered, that frequency and intensity of precipitation strongly influence soil water and thus plant water ages.

In soils dominated by preferential flow, younger water is not always closer to the surface (Bachmair et al., 2009; Thomas et al., 2013), and thus to infer age of uptake, the complex subsurface age distribution should be considered. For example, in soils where water predominantly flows down macropores or cracks, and then infiltrates laterally into the soil matrix (e.g., identified with dyes in Weiler & Naef (2003)), roots were clustered along these preferential pathways that likely receive recent precipitation (Kazda & Schmid, 2009; Zhang et al., 2015). Similarly, roots may form sheaths surrounding macropores to opportunistically access precipitation as it infiltrates (Pierret et al., 1999; Stewart et al., 1999). Further focusing on pore-dependent variations of roots may be key to estimating the age of water uptake. However, it must also be considered that water could be redistributed via the root system from wetter to dryer soil layers, flowing along the water potential gradient. This hydraulic redistribution can transport younger rain water into deeper soil layers, or conversely lift older water from deeper soil or even ground water into shallow soil layers (e.g., Caldwell et al., 1998; Neumann & Cardon, 2012; Sardans & Peñuelas, 2014). Hydraulic redistribution can even be mediated by mycorrhizal fungi (Prieto et al., 2012) and may play an important role in nutrient uptake by plants (Sardans & Peñuelas, 2014).

Thus, although hydrologists often assume that root distributions are optimized for water uptake (e.g., Kleidon & Heimann, 1998), ecologists and ecophysiologists often attribute root architectural patterns to macronutrient distributions in the upper soil layers, competitive effects among neighboring plants (Dubbert & Werner, 2019), or barriers to root penetration (e.g., Robinson et al., 2003). For example, tighter pore spaces in aggregates of finer materials may contain older waters, but may not be exploited by the roots (e.g., conifers; Bauhus & Messier, 1999), even though fine mycorrhizal networks strongly expand the area accessible by the rooting system and aid water and nutrient uptake (Allen, 2007; Sardans & Peñuelas, 2014). In combination with soil water travel time modelling, the extensive, cross-disciplinary knowledge on root distributions will likely support predicting the ages of water exchanged at the root–soil interface. In order to understand the soil water sources from which plants take up their water, we need to have a solid understanding of the interactions between water (mobile and immobile water) and the overall soil compartment including weathered rock and bedrock fractures.

One pitfall for the application of water stable isotopes in ecohydrological and unsaturated zone studies is the lack of standard protocols for soil (and plant) water extraction for isotope analysis (Orlowski et al., 2018b; Orlowski et al., 2018a; Penna et al., 2018). Several laboratory- and field-based water extraction methods for isotope analysis have been developed (see review by Sprenger et al., 2015a). Orlowski et al. (2016) showed that the extraction technique can have a significant effect on pore water isotopic composition.

An alternative approach is the direct measurement of water vapor isotopologues in porous media (soils and woody tissue) by field-deployable laser spectroscopy, which can be coupled with soil and plant gas-exchange chambers (e.g., Wang et al., 2012; Dubbert et al., 2013; Dubbert et al., 2014). Moreover, recent development of in situ membrane-based probes for direct measurements of soil water isotopes (e.g., Rothfuss et al., 2013; Volkmann & Weiler, 2014) and plant xylem water isotopes (Volkmann et al., 2016b) allow for continuous observations along soil profiles or within trees. Such new in situ continuous measurement methods allow for new insights into processes at the soil–plant interface and at the same time highlight the need for research about stable isotopic variation in subsurface waters used by plants (Brantley et al., 2017).

The fractured bedrock as a potential source for root water uptake is relatively unexplored compared to the shallow soil. Rempe & Dietrich (2018) found up to 27% of the annual precipitation to be stored as "rock moisture" in the weathered bedrock sustaining the plant transpiration at the end of the dry season. However, little is known about the age distribution of the rock moisture and recent stable isotope measurements revealed potential impacts of subsurface isotopic fractionation, as mobile and bulk water in saprolite differed considerably (Oshun et al., 2016).

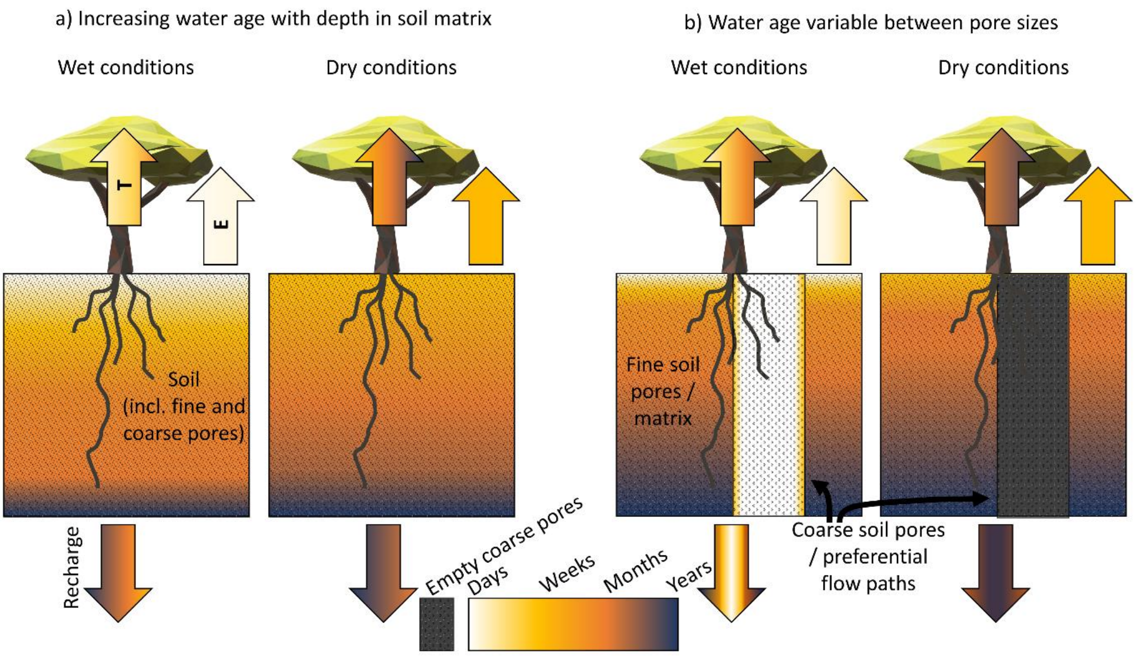

Figure 5 Water ages in soil storage (box) and transpiration (T), evaporation (E) and recharge fluxes (arrows) under wet and dry conditions. Dark blue represents old water (years), while brown (months) to yellow (weeks) and white (days) represent the younger water. Subplot a) assumes that soil water ages increase with soil depth (translatory flow), with fine and coarse pores comprising the same age. In subplot b), the subsurface is conceptually divided into coarse soil pores or preferential flow paths that result in fast flow and thus transport preferably young water and fine soil pores, or the soil matrix that results in slow flow and preferably stores old water. This visualization does not reflect realistic subsurface structures but represents a lumped representation of a dual-porosity system. Dark grey represents empty coarse pore space or macropores during dry conditions (in b).

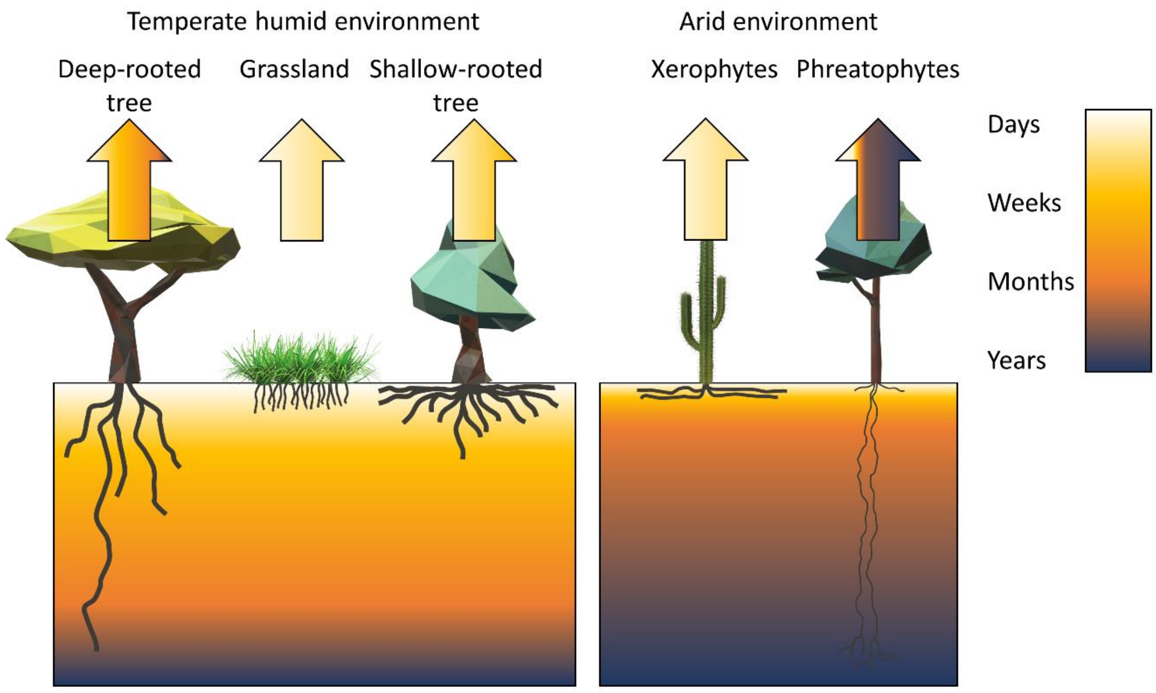

Figure 6 Examples of rooting strategies of different vegetation types in either temperate humid or arid environments. Color code indicates the water age in the soil storage (box) and the root water uptake (arrow).

3.4 Unsaturated zone – saturated zone

3.4.1 Unsaturated root zone

Through its unique physical position, linking land–atmosphere–vegetation exchange, the unsaturated root zone is the main interface and principal source of non-linearity in the response of terrestrial hydrological systems (Blöschl & Zehe, 2005). Through its roots, vegetation extracts water from the soil between field capacity and the species-specific permanent wilting point, which would otherwise not be available as this water is relatively tightly bound and cannot be drained by gravity alone. The dynamic water storage volume result in threshold behavior of runoff and percolation to rainfall or snowmelt (e.g., Zehe & Sivapalan, 2009), which is a major source of nonlinearity commonly found in soils. The role of the unsaturated root zone is reflected in its key function as the major partitioning point (e.g., Savenije & Hrachowitz, 2017) of water fluxes into downward (e.g., groundwater recharge) and lateral drainage (e.g., shallow, preferential sub-surface flow, overland flow) as well as upward (evaporative) fluxes (e.g., soil evaporation, plant water uptake and transpiration). The unsaturated root zone therefore regulates the dynamically changing pattern of how water is stored and released along different flow paths under different wetness conditions. In addition to its critical role for the movement of water, this compartment also hosts most of the terrestrial biogeochemical processes (Hinsinger et al., 2006), many of which are influenced by water through physical (e.g., transport), chemical (e.g., dissolution/weathering), and biological processes (e.g., decomposition through microbes) (Hinsinger et al., 2009). Thus, understanding the water transport capacity and contact time available for element cycling is important for understanding and quantifying solute (e.g., nutrient) budgets.

The role of the unsaturated root zone as an interface is illustrated by the individual water fluxes out of it, following the different upward, downward and lateral flow paths that typically occur at a wide range of timescales, spanning up to four orders of magnitude from hours to years (Figure 4). These distinct response timescales are largely the consequence of heterogeneity in soils: the sizes of soil pores can span several orders of magnitude. Figure 7 conceptually visualizes the variability of water ages in the heterogeneous subsurface and its relation to various processes taking place on the hillslope scale. The unsaturated root zone is characterized by a high level of discontinuities, caused by the pronounced dichotomy between the small pores of the soil matrix on the one hand and macropores on the other hand (see E, F, and G in Figure 7). Created by animal activity, roots, and drying cracks in the top soil, these large flow features are abundant in near-surface parts of the soil. The significantly higher water holding capacity and lower flow velocities in the matrix, as water is trapped in small pores due to capillary forces or by adsorption (H in Figure 7), together with the low water holding capacity and high flow velocities in macropore networks (Beven & Germann, 2013) result in highly heterogeneous and discontinuous spatio-temporal distributions of soil water storage. As a consequence and depending on where water is stored, and along which flow path it is released during different wetness conditions ("connectivity"), the ages of water stored in and released from the unsaturated zone can exhibit distinct differences and complex temporal patterns (compare a) and b) in Figure 7). The interactions between storage and release in soils have been observed and described both at small scales, i.e., plot to hillslope scale (e.g., Weiler & Fluhler, 2004; Anderson et al., 2009), as well as at the catchment scale (e.g., Brooks et al., 2010). The underlying concept is ecohydrological separation, which was discussed above. Flow-generating subsurface water fluxes mostly originate from water in the larger, drainable (macro-)pores, which can bypass the matrix with little exchange or mixing (Figure 5b). Such preferential flow were observed in lysimeter studies where younger water that bypassed older water were observed in the outflow via stable isotope measurements (Stumpp & Maloszewski, 2010; Benettin et al., 2019; Evaristo et al., 2019). The age of the percolating water can also vary with the redistribution of soil water into the soil matrix due to macropore–matrix interactions (Klaus et al., 2013) and due to soil heterogeneity (Danesh-Yazdi et al., 2018). The water ages of the subsurface fluxes are therefore largely controlled by the connectivity of and flow resistance in these pores. As mobile and matrix soil water can be of distinct isotopic composition over long periods spanning varying wetness conditions (Sprenger et al., 2019), one of the central questions is how much water can exchange (or mix) among the different pore spaces (conceptually shown in Figure 5b).

The inter-dependence between flows and moisture dynamics has been described through soil moisture balances (Rodriguez-Iturbe et al., 1999) and physically based formulations for example based on Richards' equation (e.g., Molz, 1981; Šimůnek, 2005) or random walks of water particles (Zehe & Jackisch, 2016). However, while moisture dynamics and soil–plant interactions have been explored extensively over the last 20 years, less attention has been devoted to travel times through the unsaturated zone (e.g., Sprenger et al., 2016b).

Experimental studies have mostly focused on either storage or outflow of the unsaturated zone. For example, stable isotope data from soil water extracted through tension lysimeters allows for the characterization of the age dynamics of the mobile water within shallow soil profiles (McDonnell et al., 1991; Asano et al., 2002; Muñoz-Villers & McDonnell, 2012; Timbe et al., 2014). Water age estimates can also be inferred from isotope measurements in water from soil cores (Sprenger et al., 2016a; Sprenger et al., 2016c). Tracer experiments in large lysimeters (Stumpp et al., 2012; Queloz et al., 2015a; Kim et al., 2016) allow measuring and collecting deep percolation and characterizing its age. Time series of water extracted from plant xylem samples (Brandes et al., 2007) allow estimating the age of transpiration (Kuppel et al., 2018). The direct estimation of evaporation age is instead more challenging due to the phase change of water and mixing within the atmosphere and has not been specifically addressed yet.

Evaporation is, at least in (sub-)humid climates, predominantly sourced by shallow soils (Or et al., 2013) and root density decreases with depth (Jackson et al., 1996). When sufficient water is available in the soil, rooting distribution correlates with water uptake (e.g., Asbjornsen et al., 2008; Ellsworth & Sternberg, 2015). Under this condition, the combined effect of evaporation and transpiration is the preferential withdrawal of the upper (and generally younger) soil water (limited to wet conditions, section 3.3). Therefore, deeper percolation is often produced by older water (Figure 5a) in regions where vertical preferential recharge to the groundwater is of minor importance. Water age dynamics in the different fluxes are not independent from one another, as they are mediated by the age balance within the unsaturated zone storage (Queloz et al., 2015b; Sprenger et al., 2018a) and thus by the temporal phase shift between atmospheric water supply and demand (i.e., annual evaporation cycle vs. annual precipitation cycle) and by the relative importance of these fluxes. The resulting pattern and temporal evolution of water ages in the individual fluxes can therefore exhibit distinct differences in different environments and climates (note the differences of water ages in the unsaturated zone in Figure 6). The integrated age dynamics can be described through a balance equation (Botter et al., 2010, 2011; Porporato & Calabrese, 2015) that takes into account how the different fluxes "sample" from the available pool of soil water ages.

Tracer hydrological experiments can provide important data for developing and calibrating transport models in the unsaturated zone (Stumpp et al., 2009b; Queloz et al., 2015b; Sprenger et al., 2015b; Groh et al., 2018). Such model approaches account for both celerities (e.g., by using soil moisture data) and velocities (e.g., by using stable isotope data) and, thus, enable an improved process representation through a multi-objective calibration. In order to advance our understanding of transport processes through the unsaturated zone, we need focused manipulation experiments where the soil storage and all the fluxes are monitored simultaneously, possibly with replicate measurements that allow characterizing local process variability (Penna et al., 2018). For example, recent tracer experiments at the hillslope (Scaini et al., 2017) and the lysimeter (Benettin et al., 2019) scale highlighted the effectiveness of tracer hydrological applications in disentangling velocity and celerity response of hydrological systems. However, given the ubiquitous heterogeneity of the natural environment, a major challenge lies in addressing larger landscapes characterized by diverse assemblages of vegetation.

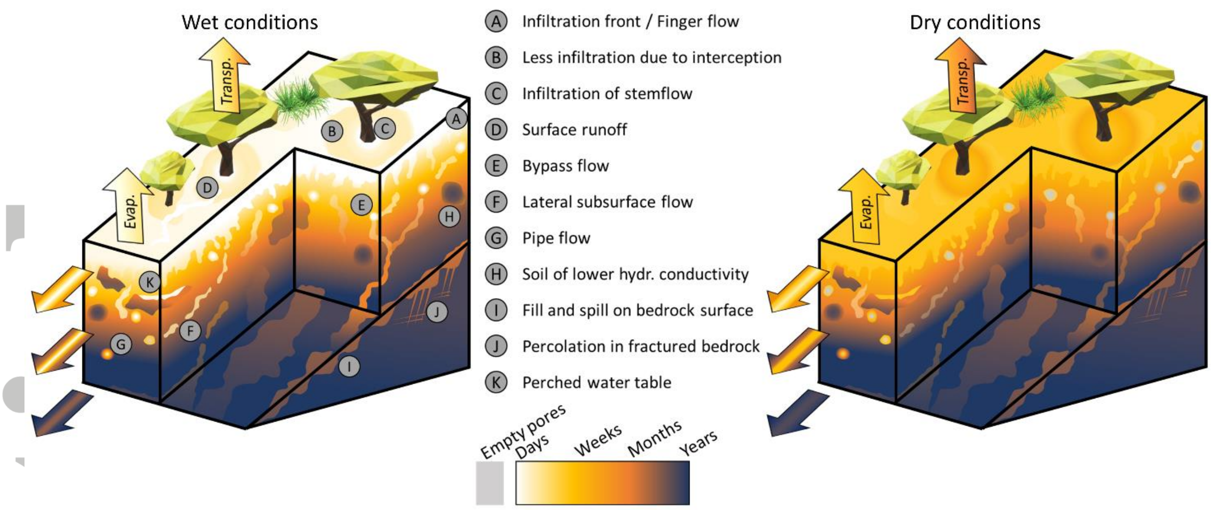

Figure 7 Water ages at the hillslope scale under wet (left) and dry (right) conditions with various processes resulting in high spatial heterogeneity. Colors indicate water age ranging from days (white) to weeks (yellow), months (orange), and years (blue) and arrows represent age distributions in evaporation (Evap.), transpiration (Transp.), and flow paths along the hillslope. Note that grey indicates empty pores, which are only shown in the dry conditions on the right.

3.4.2 Transition zone to groundwater

In systems with groundwater tables deeper than the root zone, soil water first percolates through the unsaturated zone below the root zone until it reaches the groundwater table and contributes to groundwater recharge. In this transition zone, there is no root water uptake and the influence of soil evaporation is low. Thus, the same water volume entering as percolation from the root zone above will eventually recharge the groundwater or directly drain to the stream following lateral flow paths (Figure 7). Therefore, this part of the subsurface only alters the water flowing to the groundwater or the streamflow. As a consequence of the reduced variability in water content compared to the root zone (Sturm et al., 1996), the temporal variability in water ages (as indicated by the dynamics of the soil water stable isotopic compositions; DeWalle et al., 1997) is less pronounced in this compartment than in the root zone (Sprenger et al., 2016b). It can be assumed that during percolation, the low flow velocities through the relatively small pores allow exchange (“mixing”) with resident water, averaging out some of the variability in the ages of water percolating from the root zone. More intense mixing occurs when the groundwater table rises and mixes with water stored in the unsaturated zone (Rouxel et al., 2011; Rühle et al., 2015). Depending on the soil water content, the air-filled pore space of the unsaturated zone will be filled with groundwater typically characterized by older water ages. However, little research has been explicitly devoted to understanding the age dynamics at the interface of the saturated and unsaturated zones (Weiler & McDonnell, 2004), mostly due to observational challenges (Gassen et al., 2017) and the absence of direct effects of unsaturated flow on streamflow. Recent work by Ameli et al. (2018) has combined tritium ages from groundwater at the water table with a semi-analytical free-surface integrated flow and transport model. That work explored the controls on the magnitude, age, and flow paths of groundwater near the unsaturated–saturated interface and showed how watershed slope, watershed active thickness, and recharge rate control the out-of-catchment groundwater subsidies to the parent watershed of small headwater systems.

The rise of the groundwater table into more transmissive layers or perched groundwater tables within the unsaturated zone has been identified in many studies as a key mechanism of streamflow generation at the catchment scale (Bishop, 1991; Weiler & McDonnell, 2004; Ali et al., 2011; Rinderer et al., 2017). Processes like the rise of groundwater into more transmissive soil layers, perched groundwater tables, or preferential flow will result in pronounced changes in the age distributions of the active flow paths contributing to catchment runoff (Figure 7). The TTDs of recharge to the saturated zone depend on the mobilization processes. Gabrielli et al. (2012) monitored bedrock groundwater dynamics in the M8 (Maimai, New Zealand) and WS10 catchments (H.J. Andrews Forest, USA), and concluded that the water table rise in these catchments was not sufficient for older bedrock groundwater to mobilize the younger soil water located above it. In that case, the soils only can provide young water to the bedrock groundwater during wet periods. Conversely, Legout et al. (2007) found in the Kerbernez catchment in France that during wet periods, a high water table was able to remobilize the water recharged in the soil matrix a few months before. In that case, the soils were able to provide both event (young) and pre-event (older) water to the groundwater. This may result in younger water entering the stream at high storage volumes and older water at low storage state, as also shown in an experimental hillslope study by Pangle et al. (2017). A comparison of these two mechanisms was made by Hale & McDonnell (2016) and Hale et al. (2016) where they showed how catchments within 200 km of each other in Oregon USA with strikingly similar rainfall-runoff dynamics and catchment topography and land use had large differences in stream water MTT and especially, MTT scaling relations. The catchments with poorly permeable bedrock, where transient water tables were largely perched, show young MTT and scaling relations where stream MTT followed topographic characteristics related to slope length and gradient (as shown originally by McGuire et al., 2005). Alternatively, the catchments with permeable bedrock and general transmissivity feedback behavior had much longer MTT and stream water MTT scaled with basin area—reflecting deeper flow path accumulation downvalley.

The role of the weathered bedrock in groundwater recharge is not yet well understood, partly due to challenges in observing rock moisture dynamics (Rempe & Dietrich, 2018). However, weathering products (e.g., total base cations and Na^+) were shown to serve as valuable age tracers, since they correlate with tritium-based spring water age estimates (Zapata-Rios et al., 2015). Uchida et al. (2006) found that the residence time of soil water was increasing vertically with soil depth at a Japanese site (Fudoji) with high bedrock permeability, while it increased laterally from the top to the bottom of a hillslope in the Maimai catchment, New Zealand with less permeable bedrock and therefore predominantly lateral subsurface flow. Katsuyama et al. (2010) showed for 6 nested catchments of the Kiryu Experimental Watershed, Japan that catchment residence times decrease with increasing bedrock permeability.

While the processes in the transition zone are accounted for in physically-based continuum models, few conceptual models based on SAS functions/mixing volumes (e.g., McMillan et al., 2012; Hrachowitz et al., 2015) explicitly attempt to estimate the storage (and thus mixing) volume of the transition zone, because insufficient data are typically available to meaningfully distinguish its effect on water ages from that of the groundwater below.

The transition from the unsaturated zone to the groundwater is where the concentrations of gaseous age tracers are set, before the water enters the saturated zone and groundwater flow is considered to start. Understanding the conditions at this location of “time zero” is therefore important for groundwater dating. Cook et al. (1996) showed that one needs to consider a substantial delay for the transport of transient gas tracers such as CFCs, SF_6, and ^{85}Kr to the water table in the case of thick unsaturated zones. Although water in the unsaturated zone exchanges gases with the soil air, the assumption that the resulting dissolved gaseous tracer concentrations correspond to atmospheric equilibrium at the time of entering the groundwater does not necessarily hold. The different behavior of gaseous tracers compared to the water-bound tritium can be used to separate the transit times in the unsaturated and the saturated zones by combined modeling of the water and tracer transport in both compartments (Zoellmann et al., 2001; Rueedi et al., 2005).

3.4.3 Subsurface contributions to stream TTDs

A number of recent studies calculating TTDs from catchment scale conceptual models have explicitly distinguished the unsaturated and saturated zones (e.g., Hrachowitz et al., 2013; Benettin et al., 2015a; Benettin et al., 2015b; Birkel & Soulsby, 2016; Rodriguez et al., 2018). The conceptualization of the unsaturated zone and groundwater compartment was introduced to account for nonlinearity in the flow response, as the soil determines the temporally varying partitioning between storage, evaporation, transpiration, and recharge/drainage. Such a model setup reveals that the soils usually contain more younger water than the groundwater (Benettin et al., 2013; Hrachowitz et al., 2015; Kirchner, 2016b; Remondi et al., 2018; Kuppel et al., 2018). Yet the tails of the age distribution of soil water can in certain cases be long (Sprenger et al., 2016c), indicating that water can be held for years in the soils depending on the soil type and on the dynamics of evapotranspiration (Sprenger et al., 2016c; Sprenger et al., 2018a; Brinkmann et al., 2018). In arid environments, zero or very small downward fluxes might occur over centuries, as for example observed by Sandvig & Phillips (2006) using chloride depth profiles. This recharge to groundwater can thus contain noticeable fractions of "old" water. The interactions of saturated and unsaturated zones are generally responsible for hysteresis in the stream water ages when plotted against catchment wetness (Hrachowitz et al., 2013; Benettin et al., 2017a; Rodriguez et al., 2018; Yang et al., 2018).

3.5 Groundwater – surface water

With an estimated volume of around 22 million of km³, groundwater represents the largest storage of non-frozen terrestrial water (Gleeson et al., 2016). Aquifer areas range from several km² up to several millions of km² (BGR/UNESCO, 2008), and their permeability spans more than twelve orders of magnitude (Huscroft et al., 2018). If not influenced by groundwater extraction and not discharged directly into the oceans (e.g., Taniguchi et al., 2002), groundwater will eventually reach the land surface, either re-entering the atmospheric cycle through root water uptake (Fan et al., 2017), discharging into lakes or wetlands (Kluge et al., 2012; Ala-aho et al., 2015) or providing the base flow that feeds streams during dry periods (Cuthbert, 2014; Zipper et al., 2018).

The timing and rate of groundwater discharges into streams depends on groundwater recharge, topography, hydraulic gradient, hydraulic conductivity and river bed properties. Groundwater flow is not homogeneous. Heterogeneity and anisotropy of the hydraulic properties greatly affects the flow and discharge rates of aquifers (Freeze & Cherry, 1979). This heterogeneity and anisotropy is created by (1) different sediment layers in unconsolidated aquifers or sedimentary rock aquifers, (2) fractures and fault structures in igneous or metamorphic rock aquifers, and (3) dissolution processes in soluble rock (carbonates, gypsum, halite) aquifers. Groundwater recharge zones often differ from the topographic catchment (Domenico & Schwartz, 1998).

Methods to quantify the contributions of groundwater to streams include graphical methods (Dingman, 2015), filter methods (Eckhardt, 2005; Beck et al., 2013), recession and base flow analysis (Beck et al., 2013; Stoelzle et al., 2013; WMO, 2009) and tracer methods (Kirchner, 2003; Klaus & McDonnell, 2013) that rely on differences between the hydrochemical signatures of groundwater and other sources of streamflow.

Groundwater discharging into streams has been used to gather information on the hydrodynamic properties of the surrounding aquifers, guided by the idea that groundwater flow paths naturally converge at gaining streams, which then act as flow-weighted integrators of transit times. Stolp et al. (2010) showed that the effect of gas exchange on the concentrations of gaseous groundwater dating tracers measured in stream water can be accounted for in order to derive the age of the inflowing groundwater. Solomon et al. (2015) also analyzed groundwater dating tracers in samples collected from base flow of a gaining stream, whereas Gilmore et al. (2016) sampled streambed water using piezometers and seepage blankets, both achieving useful estimates of mean transit time and transit time distributions for the groundwater.

Groundwater ages span wide ranges due the aquifers' intrinsic heterogeneity and anisotropy (Bethke & Johnson, 2008). Early approaches accounted for the distributions of groundwater age by assuming analytical travel time distribution functions that reflect the age structure of a given location within the aquifer (Section 2.2, Maloszewski & Zuber, 1982). Stronger heterogeneities were taken into account by assuming separate age distributions for slow and fast flow paths as, for instance, for the ^{18}O and ^{3}H based estimation of travel time distributions of the karstic aquifer that is the main drinking water resource for the city of Vienna, Austria (Maloszewski et al., 2002). Using gamma distributions of streamflow ages, Berghuijs & Kirchner (2017) showed that stream waters can be much younger than the groundwaters that they are derived from, implying that a small, faster-flowing part of the aquifer is contributing disproportionately to streamflow. Their findings are consistent with the relatively high fractions of young stream water found in a large sample of global rivers by Jasechko et al. (2016).

More recently, more detailed models have been developed to calculate water ages. Using an integrated transport model, Benettin et al. (2015a) calculated ^{2}H ratios and dissolved silica and sodium fluxes at a humid catchment in the north-western USA. Compared to lumped parameter models, this integrated model separately considers soil, groundwater and riparian storages, and calculates travel time distributions separately for all of them using simple analytic formulations (Botter et al., 2011). Comparing wet and dry periods, Benettin et al.

(2015a) provide clear evidence that stream water ages shift to older values after prolonged recession during drier periods. With a similar modelling approach, Hartmann et al. (2016) calculated travel time distributions separately for soil, unsaturated zone (epikarst) and groundwater using virtual tracer injections (Weiler & McDonnell, 2004) to assess the release and transit of carbon and nitrogen through a dolostone system in Austria after windthrow disturbances. They concluded that the slow pathways will dampen and delay the transfer of disturbance to the stream, while the fast flow paths through the groundwater will pass the signal more rapidly.

Groundwater of riparian zones can play a major role for stream water ages, because the riparian zone connects the hillslope to the stream at the catchment scale (Jencso et al., 2009). Thus, the riparian zone is often conceptualized as a buffer storage where hillslope and groundwater mix before recharging into the stream (e.g., Birkel et al., 2011; Birkel et al., 2014; Benettin et al., 2015a), leading to a dampening of the tracer signal. The seasonal dynamics of this hydraulic connectivity between the water in free-draining hillslopes and peaty riparian zones in the Scottish Highlands was found to contribute to the time variance of catchment travel times, as travel times for the riparian zone were generally longer than for the hillslope (Soulsby et al., 2015). Due to riparian zones' key role in tracer dynamics and water ages of stream runoff in the Scottish catchment, Tetzlaff et al. (2014) described them as "isostats" that integrate travel times from different flow paths coming together in the valley bottom. As riparian zones often remain hydraulically connected to the stream during dry periods and become quickly activated during wet periods, Stockinger et al. (2014) found for 15 investigated catchments that travel times decreased with increasing riparian zone cover. Similar relationships were found in an alpine valley by Holocher et al. (2001), who used the ^{3}H-^{3}He method and hydrochemical data to show that the shallow groundwater in the floodplain was connected to the stream and younger than the underlying groundwater, which was not hydrologically connected. Burns et al. (2003) also used ^{3}H-^{3}He data and found increasing water ages in a riparian groundwater along a 500 m stream spanning from zero to one year in the headwaters, to six to seven years mid-way, and up to 27 years further down valley.

The examples from the previous paragraphs show that groundwater can alter observed stream water ages significantly as groundwater storages generally represent large mixing volumes and they are able to hold recharging waters for times long enough to alter their hydrochemical composition. It can be expected that larger groundwater contributions to a stream will shift water ages to larger values, particularly during dry periods when shallow flow paths with younger ages do not provide water to the stream any more. It is also possible that heterogeneous aquifers transfer water rapidly to the stream, which may counteract the increasing influence of groundwater on streamflow ages to some extent. However, a first-order estimate of streamflow ages by Jasechko et al. (2016) showed that approximately two thirds of global streamflow is more than 1.8 – 3 months old, pointing out that the slower pathways provide the larger fraction of global streamflow.

Along the interface between groundwater and rivers, the hyporheic zone is a very dynamic and intensively studied interface. Recently, several studies have developed models to predict travel times through the hyporheic zone, considering the relevant spatial scale of groundwater–surface water exchange (Cardenas, 2008; Wörman et al., 2007; Boano et al., 2014). The vertical exchange due to in-channel features such as bars and bed forms with dimensions of centimeters to meters results in travel times between minutes to days (Salehin et al., 2004). Flows through the hyporheic zone across sinuous channel deposits and bars at scales of meters to kilometers increase the water age in the river by days to months (Alley et al., 2002). Boano et al. (2014) have recently reviewed the different regimes of hyporheic flow for which certain physical processes are associated with specific fluvial and geomorphic conditions, and they also determined the wide span of the corresponding travel times. As the fraction of discharge in the river interacting with the hyporheic zone can also vary over a wide range in space and time, the resulting change on the age distribution of stream water by processes in the hyporheic zone cannot be well quantified so far.

4 Conclusions

Water ages estimated based on hydrological tracer applications are increasingly used in Earth system sciences for characterizing flow paths and transport processes. However, we argue that until recently, water ages have been studied mainly within sub-disciplines that have often neglected transport of water and the effects on its tracer concentrations across interfaces among different compartments of the terrestrial water cycle in general and the critical zone in particular. Our review of the demographics of water (i.e., the ages of the compartments that comprise the terrestrial water cycle) describes how travel times have traditionally been estimated within specific hydrological compartments using empirical tracer approaches and numerical and conceptual modeling. We also presented how recent studies have started to consider cross-boundary and feedback effects of water transfer between compartments.

Nonetheless, empirical water age data remain scarce. With improving technology, we are gaining insights into the diversity of water ages within pools that have been elsewhere treated as well-mixed buckets. For example, tracer data regularly demonstrate that some waters can have extremely long residence times even in parts of the terrestrial water cycle with frequent turnover. Such water age insights can assist in developing, calibrating, and validating realistic integrative models. We therefore recommend to further develop sampling designs and new measurement techniques for process investigations at specific interfaces of the critical zone. Given the intense spatio-temporal dynamics of hydrological systems, increasing measurement frequencies in time and space (e.g., due to in situ measurements or high frequency sampling in the field) is promising. However, optimizing cost and labor efficiency requires a better understanding of where, when, and how often to take samples in tracer hydrological investigations. Additionally, methodological uncertainties have to be addressed, and technological developments have to be nurtured. By synthesizing those insights, we provided diverse background information on the demographics of water in the critical zone and propose directions for further research to improve our current incomplete understanding of hydrological tracer data for their application in water age studies.

Glossary

Backward travel time distributions (= age distributions) describe the probability distribution of water that entered the system in the past and that is leaving the system at a given moment (Benettin et al., 2015c).

Catchment is an area having a common outlet for its surface and subsurface runoff.

Catchment runoff is the precipitation which flows towards a recipient water body (e.g., river/stream) on the ground surface or within the subsurface.

Celerity is the speed with which a perturbation to the flow propagates through the flow domain (e.g., pressure wave propagation) (McDonnell & Beven, 2014).

Compartments (hydrological compartments) are conceptualized water storages (soil, groundwater, river, ocean) within the hydrological cycle. Water is moving within and between these compartments (Pinder & Celia, 2006).

The **critical zone** “includes the land surface and its canopy of vegetation, rivers, lakes, and shallow seas, and it extends through the pedosphere, unsaturated vadose zone, and saturated groundwater zone” (National Research Council, 2001), it is the “fragile skin of the planet defined from the outer extent of vegetation down to the lower limits of groundwater“ (Brantley et al., 2007).

Demographics are statistical data relating to populations and particular groups within them (en.oxforddictionaries.com/definition/demographics).

Forward travel time distributions describe the distribution of how long water entering the system at a given moment (i.e., a precipitation pulse) will spend transiting through the system before it reaches the outlet (Benettin et al., 2015c).

Flux concentration is defined as the mass of a hydrological tracer per unit volume of water passing through a cross section at a given time (Kreft & Zuber, 1978).

Hydrological system comprises a water storage (e.g. hydrological cycle, catchment, soil column), into which water enters (input) and from which water leaves (output) according to physical laws (Dooge, 1973). The system approach can be expanded to environmental or artificial tracers entering and leaving a storage volume (Leibundgut et al., 2009).

Residence time is the time a water molecule spends (resides) within a hydrological system.

Residence time distributions (RTD) describe the age distribution of water volumes that entered the system in the past and that are still stored in the system at a given moment (Hrachowitz et al., 2016).

Steady state of a hydrological system is when state variables describing the system (e.g., energy, mass, or the TTD) do not vary in time.

Stable isotopes of hydrogen (^{2}H) and oxygen (^{18}O) occur naturally in water molecules. Their abundance is described by **isotope ratios** (or **isotopic compositions**) $^{2}H/^{1}H$ and $^{18}O/^{16}O$, often expressed as ‰ relative to the Vienna Standard Mean Ocean Water (Craig, 1961).

Tracers (or hydrological tracers) are dissolved, suspended or floating substances detectable in the hydrological cycle (Leibundgut et al., 2009). One can distinguish between **environmental tracers** that are inherent components of the hydrological cycle (e.g., stable isotopic compositions of water) and **artificial tracers**, brought actively into hydrologic system (e.g. fluorescent dyes) (Leibundgut et al., 2009).

Translatory flow is defined by Hewlett & Hibbert (1967) as rapid displacement of stored water by new rain (as illustrated by column experiments by Horton & Hawkins (1965)).

Travel time (or **transit time**) is the time elapsed between water entering a system (e.g., infiltration of precipitation into ca catchment) and leaving it (e.g., stream discharge) (McDonnell et al., 2010).

Velocity (compare with celerity, above) is the speed with which water travels through a system (McDonnell & Beven, 2014).

Water age describes the time elapsed since a water molecule has entered a hydrological system.

Acknowledgements

This review is based on discussions at the workshop on Water Ages in the Hydrological Cycle, held in the Black Forest in October 2017 and funded by the Wassernetzwerk Baden-Württemberg. We thank the attendees of the workshop R. Bäumle, T. Gebauer, D. Gooddy, P. Königer, M. Loschko, V. Maurer, R. Purtschert, S. Seeger, and H. Wang. MS thanks Wassernetzwerk Baden-Württemberg and the Deutsche Forschungsgemeinschaft (DFG) – Project no. 397306994 – for funding.

Author contributions

Conceptualization, M.W., C.S., and M.S.; Funding acquisition, M.W. and C.S.; Visualization, M.S. and M.W.; Writing – original draft: M.S., S.T.A., P.B., M.D., A.H., M.H., N.O., N.R., C.S., M.W.; Writing – review & editing, J.W.K., J.J.M, D.P., S.P., M.R., C.S., M.W., C.W, M.S., S.T.A., W.A., M.Sch., P.B., M.D., A.H., M.H., N.O., and N.R..

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