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A Review of Water Ages in the Critical Zone

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DOI

[10.1029/2018RG000633](https://doi.org/10.1029/2018RG000633)

Publication date

2019

Document Version

Final published version

Published in

Reviews of Geophysics

Citation (APA)

Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S. T., Benettin, P., Dubbert, M., Hartmann, A., Hrachowitz, M., & More Authors (2019). The Demographics of Water: A Review of Water Ages in the Critical Zone. *Reviews of Geophysics*, 57(3), 800-834. <https://doi.org/10.1029/2018RG000633>

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Reviews of Geophysics



REVIEW ARTICLE

10.1029/2018RG000633

Key Points:

- New tracer techniques now allow tracking water at high spatiotemporal 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

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Citation:

Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S. T., Benettin, P., et al. (2019). The demographics of water: A review of water ages in the critical zone. *Reviews of Geophysics*, 57. <https://doi.org/10.1029/2018RG000633>

Received 25 NOV 2018

Accepted 3 MAY 2019

Accepted article online 20 MAY 2019

The Demographics of Water: A Review of Water Ages in the Critical Zone

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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 subdisciplines) 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. 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 toward a better understanding of vital resource water sustaining the life in the Earth’s living skin.

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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 and Libby (1957), Eriksson (1958), and von 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; Rinaldo et al., 2015; Tetzlaff et al., 2014). 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 toward understanding which specific waters are in flux and which are less mobile in storage (McDonnell, 2017; McDonnell & Beven, 2014).

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, Leistert, et al., 2016) or the groundwater (Cartwright et al., 2017; Jasechko, 2019; McCallum et al., 2015; Suckow, 2014; Suckow et al., 2013; Turnadge & Smerdon, 2014), or focused on the catchment scale (Birkel & Soulsby, 2015; Hrachowitz et al., 2016; McGuire & McDonnell, 2006).

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 toward 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):

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

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):

$$T = \frac{V}{Q} \quad (2)$$

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. First, mean travel time is often difficult to quantify reliably, both using tracers (see section 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 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, Rinaldo, & Botter, 2015), thus addressing the molecules' "life expectancy" (Nir & Lewis, 1975), or in a backward mode (**backward travel time distribution**; Benettin, Rinaldo, & Botter, 2015), 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).

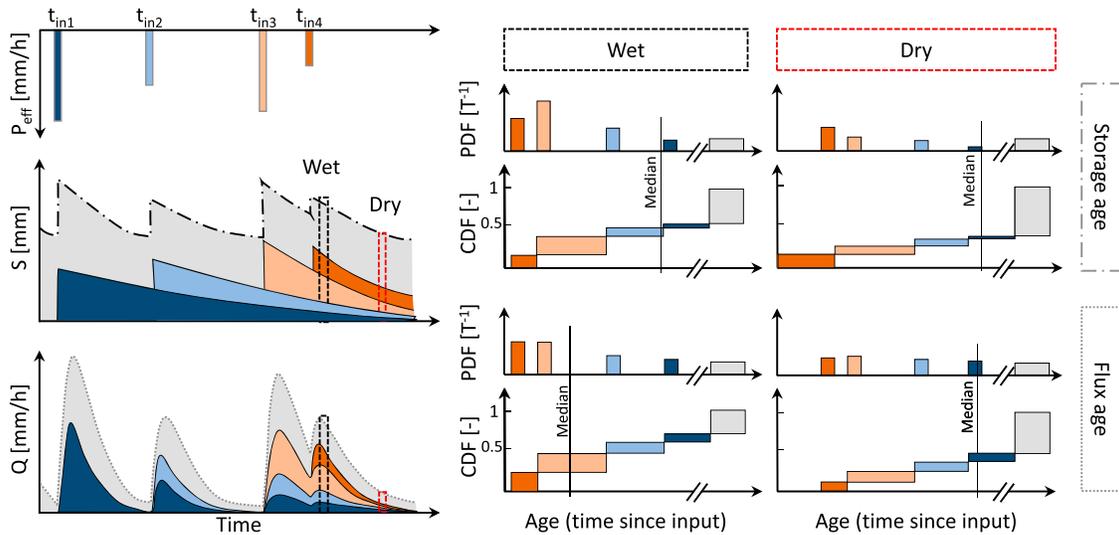


Figure 1. Relationship between input, storage, and release in a hydrological system. Water age dynamics in the storage (S) and flux (Q) are visualized by colors that refer to the precipitation input (P_{eff}), while gray indicates water older than t_{in1} (left). Storage and age distributions are reported as probability density functions (PDFs) and cumulative density functions (CDFs). 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

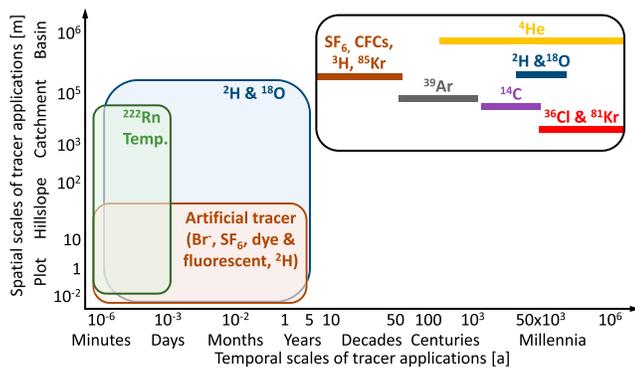


Figure 2. Spatial and temporal scales for use of different hydrological tracers (Abbott et al., 2016; Aggarwal, 2013; Newman et al., 2010). The black box represents groundwater age tracers applicable on scales from small catchments to large basins that span different temporal scales.

interactions between waters in the unsaturated and saturated zone requires larger spatiotemporal scales from hillslopes to catchments. Water age estimates are challenged by the natural multiscale heterogeneity of hydraulic conductivity (e.g., soil matrix vs. macropores in the subsurface) (Bachmair & Weiler, 2011; Troch et al., 2009), 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—and 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, Bailey, et al., 2017). 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 (^2H) 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, Erhardt, et al., 2016). 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 (^3H) data (Hale et al., 2016). ^2H 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 11,700 years ago) under a different climate (e.g., Rozanski, 1985; van Geldern et al., 2014). The timescale of artificially introduced tracers like Br^- , SF_6 , dyes (e.g., brilliant blue), or isotopically enriched water (“deuterated” enriched in ^2H ; enrichment in ^{18}O is also possible) during sprinkling or injection experiments mainly depends 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, Haberer, et al., 2016).

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 (^3H) and its decay product ^3He), nuclear power generation (^{85}Kr), or industrial emissions (SF_6 , CFCs). Groundwater is also commonly dated based on the decay of radioisotopes, covering timescales ranging from 50 to 1,000 years with ^{39}Ar , 1,000 to 40,000 years with radiocarbon (^{14}C), and 50,000 to 1 million years with ^{36}Cl or ^{81}Kr (Aggarwal, 2013). ^4He , 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 (Bethke & Johnson, 2008; Beyer et al., 2014; Clark & Fritz, 1997; Cook & Herczeg, 2000; Kipfer et al., 2002; Newman et al., 2010; Plummer, 2005; Suckow et al., 2013). The most recent development in this field is the introduction of an analytical method from atomic physics (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., Aggarwal et al., 2015; Gerber et al., 2017; Matsumoto et al., 2018; Ritterbusch et al., 2014; Yechieli et al., 2019).

It should be noted that most of the tracers used for groundwater dating are gases (CFCs and SF_6), noble gas isotopes (^3He , ^4He , ^{39}Ar , ^{81}Kr , and ^{85}Kr), or isotopes that enter the groundwater in gaseous compounds (^{14}C as $^{14}\text{CO}_2$). 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 nongaseous tracers (^3H and ^{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

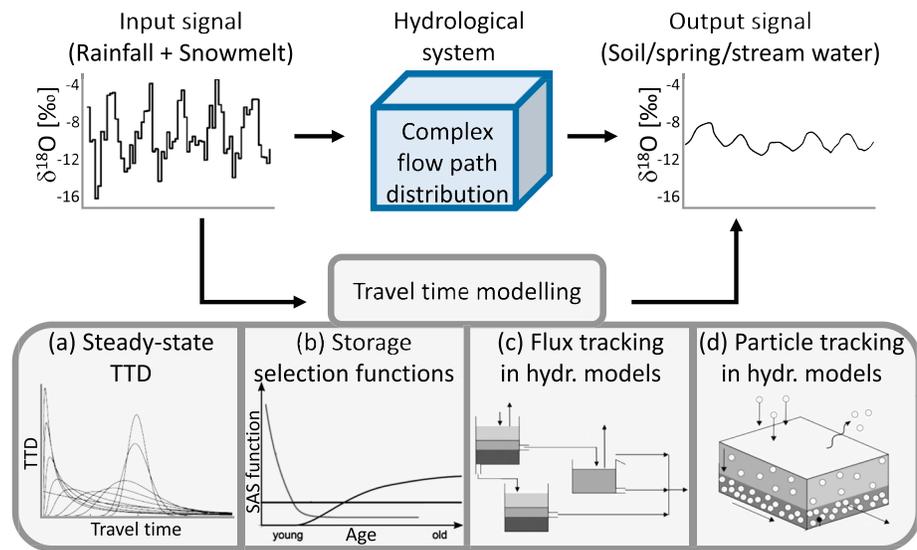


Figure 3. Travel time distributions (TTDs) estimated from tracer input–output relationships. Tracer input signals (e.g., ^{18}O) introduced via precipitation or snowmelt are damped, to different degrees on different timescales, due to dispersion by complex flow path distributions in hydrological systems (e.g., catchment and soil column). The resulting output signal, for example, 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 SAS functions (e.g., Benettin, Rinaldo, & Botter, 2015), 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.

^3H 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., ^4He), the apparent age equals the actual water age of a mixed water sample (Bethke & Johnson, 2008).

Estimates of TTD 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 and 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 3 a). 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., streamflow, springs, and groundwater wells) via a convolution operation either in the time domain (Corcho Alvarado et al., 2007; Maloszewski et al., 2002; Soulsby et al., 2010; Speed 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 (Kirchner, 2019; Massoudieh et al., 2012; Massoudieh et al., 2014; McCallum et al., 2014; Visser et al., 2013). 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; Soulsby et al., 2010; Stumpp, Stichler, & Maloszewski, 2009; Weiler et al., 2003), 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 (SAS) function” 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 (Benettin, Soulsby, et al., 2017; Harman, 2015; van der Velde et al., 2012), individual compartments (Benettin, Kirchner, et al., 2015; 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, Soulsby, et al., 2017) chloride (e.g., Benettin, Kirchner, et al., 2015), 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 (Ala-aho, Tetzlaff, McNamarra, Laudon, & Soulsby, 2017; Kuppel et al., 2018; van Huijgevoort et al., 2016), 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 (Ginn et al., 2009; Goode, 1996; Varni & Carrera, 1998). The direct simulation of age can also be combined with reservoir theory to derive transit times of water at the outlet of an aquifer (Cornaton & Perrochet, 2006; Etcheverry & Perrochet, 2000). 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 (Troldborg et al., 2008; Turnadge & Smerdon, 2014).

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

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

Compartment	Storage (10^3 km^3)	Flux ($10^3 \text{ km}^3/\text{year}$)	Global average water age ^a	Max. storage variation (%)
Atmosphere over land	3 ^b	111 ^b -116.5 ^c	10 days	<5
Vegetation	1 ^b	58 ^b	6 days	<10
Snow	12.5 ^b	12.5 ^b	1 year	100
Glacier and permanent snow	24,064 ^b		1,600 years ^d	<5
Unsaturated zone	Mobile water	17 ^b	11 months	100
	Bound water		1.5 years	30
Surface water	Lakes	175 ^b	17 years ^b	30
	Wetlands	17 ^b	5 years ^b	10
	River	2 ^b	45.5 ^b	16 days
Groundwater	Modern	347 ^f	<50 years ^f	<5
	Old	23,090 ^f		<1

^aNote 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. ^bOki and Kanae (2006). ^cRodell et al. (2015). ^dKorzun et al. (1978). ^eGood et al. (2015). ^fGleeson et al. (2016).

years for wetlands, lakes, and modern groundwater (Table 1). While such values suggest that waters 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 oversimplifies 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 ($\sim 350,000 \text{ km}^3$) 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 ($\sim 100,000$ and $\sim 16,000 \text{ km}^3$, 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 toward 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., Quéloz et al., 2015), unsaturated sediments (e.g., Stumpp et al., 2007), groundwater (e.g., Bethke & Johnson, 2008), and streamflow (e.g., Kirchner, 2019; Kirchner et al., 2000).

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

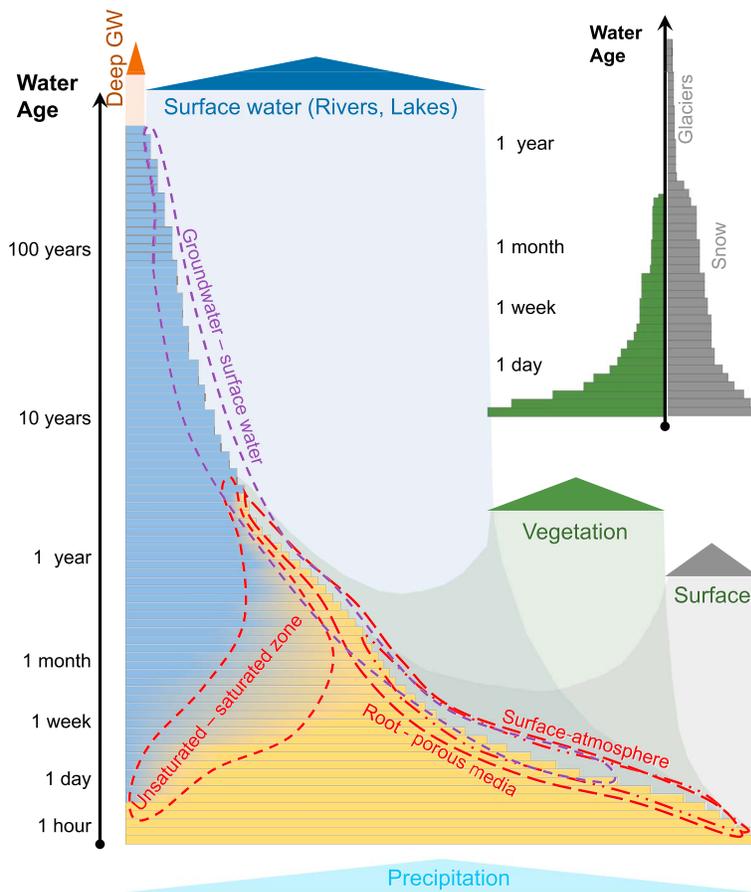


Figure 4. Conceptual diagram showing hypothetical demographics of water (age distributions) in the critical zone. Dashed lines indicate the mixing of water with different ages at the interfaces. The central demographics reflect the unsaturated (yellow) and saturated (blue) zone of the critical zone;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

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, Maloszewski, et al., 2009). A common strong assumption is that compartments are well mixed; this assumption is often violated and can introduce bias for water age estimates (Fenicia et al., 2010; Kirchner et al., 2000; 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., Benettin, Bailey, et al., 2015; Heidebüchel et al., 2013) 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 are often different (e.g., Brooks et al., 2010; Goldsmith et al., 2012; Sprenger, Tetzlaff, Buttle, Laudon, Leistert, et al., 2018; 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; sections 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 (Hrachowitz et al., 2013; McMillan et al., 2012; 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.

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 0). While this time of age 0 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 nonliquid 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 and 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 change 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 (Feng et al., 2002; Taylor et al., 2001; Taylor et al., 2002). For catchment scale modeling, Ala-aho, Tetzlaff, McNamara, and Soulsby (2017) showed that snowmelt dynamics and their tracer signals (e.g., fractionation of stable isotopic compositions in snowpack; Ala-aho, Tetzlaff, McNamara, Laudon, Kormos, et al., 2017) 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 (Goldsmith et al., 2019; Yang, Chen, et al., 2016). 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) but 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 subhourly temporal patterns of tracer signatures in precipitation have been observed recently with high-frequency tracer measurement techniques (Berman et al., 2009; Herbstritt et al., 2018; Munksgaard et al., 2012; von Freyberg et al., 2017). 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 (Cayuela et al., 2019; Fischer et al., 2017). Accounting for spatial variations in precipitation inputs is especially important when comparing water sample isotopic compositions (e.g., from rivers, soil, plants, and aquifers) that are collected across areas with spatially variable precipitation regimes (Allen et al., 2018; Bowen, 2008; Bowen & Wilkinson, 2002). 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 nonsoil 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 (Eller et al., 2013; Limm et al., 2009), 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 1 and about 50 days at sites in northern latitudes (Sprenger, Tetzlaff, Buttle, Buttle, Laudon, & Soulsby, 2018). 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, Tetzlaff, Buttle, Laudon, & Soulsby, 2018), 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, Tetzlaff, & Soulsby, 2017) or stream water (e.g., Sprenger, Tetzlaff, Tunaley, et al., 2017).

3.2. Plant-Atmosphere

The age of water traveling 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., Gleason et al., 2012; Tyree & Zimmermann, 2002). 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 (Wullschleger et al., 1998; Zimmermann & Brown, 1971). 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 L per day in Douglas fir, with only 25-55 L 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/day (Brandes et al., 2007; Meinzer

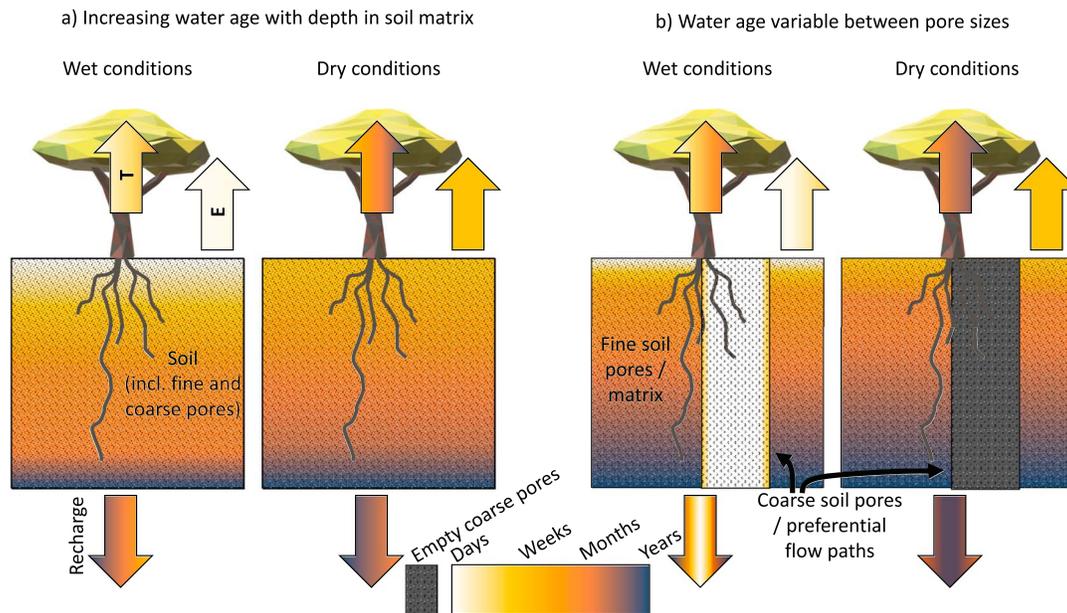


Figure 5. Water ages in soil storage (box) and transpiration (T), evaporation (E), and recharge fluxes (arrows) under wet and dry conditions. Dark blue represents old water (years), while brown (months) to yellow (weeks) and white (days) represent the younger water. Subplot (a) assumes that soil water 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 gray represents empty coarse pore space or macropores during dry conditions (in b).

et al., 2006). 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 $3\text{-}5 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{MPa}^{-1}$ in coniferous wood to $500 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{MPa}^{-1}$ 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., James et al., 2003; Meinzer et al., 2006) 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., Barbeta et al., 2015; Barbeta & Peñuelas, 2017; Bertrand et al., 2014; Ehleringer et al., 1991) 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 adaptations (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 (Caldeira et al., 2015; Rascher et al., 2011), 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 (Čermák et al., 2004; Thomas & Winner, 2002; Wullschlegel et al., 1998), whereas transport velocities through plants are rarely calculated and thus plant water ages or transit times are largely underdescribed.

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, Donohue, & McVicar, 2016) but can reach beyond several meters for individual plants (Canadell et al., 1996; Schenk & Jackson, 2005; Stone & Kalisz, 1991). 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 toward 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 (Hewlett & Hibbert, 1967; Horton & Hawkins, 1965), 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; Geris et al., 2015; Goldsmith et al., 2012; Hervé-Fernández et al., 2016; Sprenger, Tetzlaff, Buttle, Laudon, Leistert, et al., 2018). These field studies show that subsurface flow can be nonuniform, 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, Tetzlaff, Buttle, Laudon, & Soulsby, 2018), 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, Tetzlaff, Buttle, Laudon, Leistert, et al., 2018). 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, that is, 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 (Dubbart 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 (Dubbart & Werner, 2019).

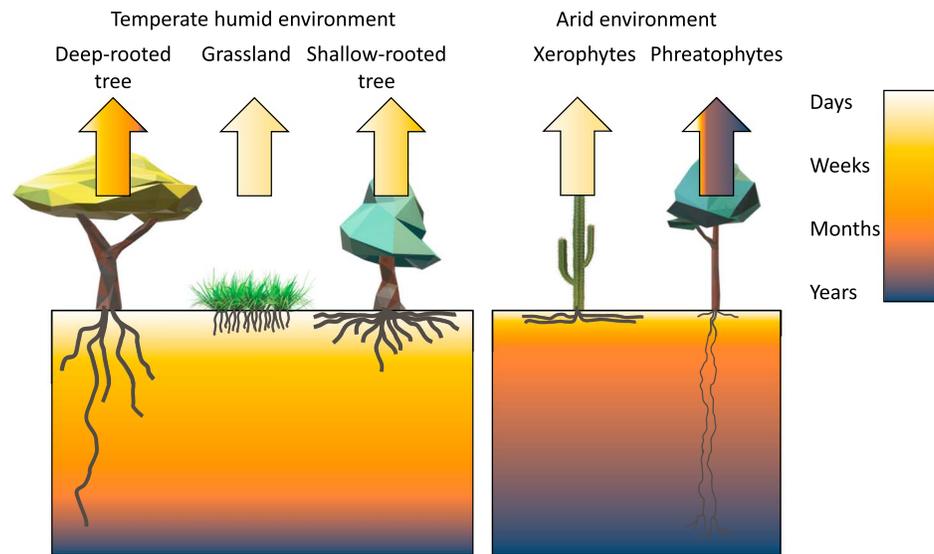


Figure 6. Examples of rooting strategies of different vegetation types in either temperate humid or arid environments. Color code indicates the water age in the soil storage (box) and the root water uptake (arrow).

Understanding infiltration dynamics and rooting patterns supports progress toward 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 and 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 - to 10^1 -cm scale; i.e., Volkmann, Haberer, et al., 2016; Volkmann, Kuhnhammer, et al., 2016, Rothfuss et al., 2015) or short-term (subdaily timescale; e.g., Volkmann, Haberer, et al., 2016; 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 (Bachmann et al., 2015; Scholes & Archer, 1997; West et al., 2012). 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 (Schenk & Jackson, 2002; Stone & Kalisz, 1991). 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 (Hsueh et al., 2016; Ish-Shalom et al., 1992), 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 (Brinkmann et al., 2018; Sprenger, Tetzlaff, Buttle, Laudon, & Soulsby, 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, Tetzlaff, Buttle, Laudon, & Soulsby, 2018). 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 midsummer 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 rainwater into deeper soil layers, or conversely lift older water from deeper soil or even groundwater 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 ecophysiologicals often attribute root architectural patterns to macronutrient distributions in the upper soil layers, competitive effects among neighboring plants (Dubbart & 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 modeling, 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, Breuer, et al., 2018; Orlowski, Winkler, et al., 2018; Penna et al., 2018). Several laboratory- and field-based water extraction methods for isotope analysis have been developed (see review by Sprenger, Herbstritt, & Weiler, 2015). 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., Dubbart et al., 2013; Dubbart et al., 2014; Wang et al., 2012). 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, Kuhnhammer, et al., 2016) 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 and 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).

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 nonlinearity 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 subsurface 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 4 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 topsoil, 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 spatiotemporal 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 left and right in Figure 7). The interactions between storage and release in soils have been observed and described both at small scales, that is, plot to hillslope scale (e.g., Anderson et al., 2009; Weiler & Fluhler, 2004), 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 was observed in lysimeter studies where younger water that bypassed older water were

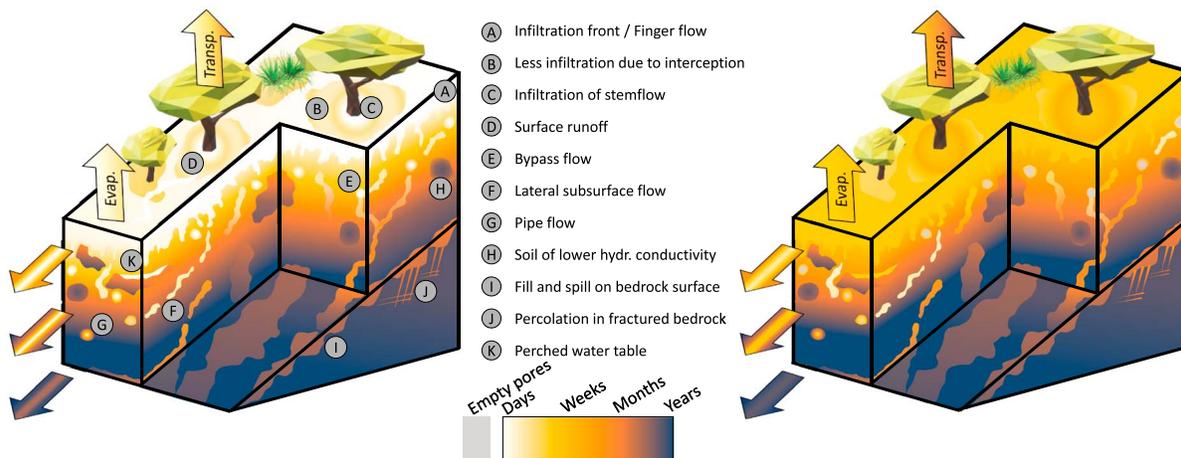


Figure 7. Water ages at the hillslope scale under wet (left) and dry (right) conditions with various processes resulting in high spatial heterogeneity. Colors indicate water age ranging from days (white) to weeks (yellow), months (orange), and years (blue), and arrows represent age distributions in evaporation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

observed in the outflow via stable isotope measurements (Benettin et al., 2019; Evaristo et al., 2019; Stumpp & Maloszewski, 2010). 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 interdependence 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, Leister, et al., 2016).

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 allow for the characterization of the age dynamics of the mobile water within shallow soil profiles (Asano et al., 2002; McDonnell et al., 1991; Muñoz-Villers & McDonnell, 2012; Timbe et al., 2014). Water age estimates can also be inferred from isotope measurements in water from soil cores (Sprenger, Seeger, et al., 2016; Sprenger, Erhardt, et al., 2016). Tracer experiments in large lysimeters (Kim et al., 2016; Queloz, Bertuzzo, et al., 2015; Stumpp et al., 2012) 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, Carraro, et al., 2015; Sprenger, Tetzlaff, Buttle, Laudon, & Soulsby, 2018) 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 (Groh et al., 2018; Quelo, Carraro, et al., 2015; Sprenger, Volkmann, Blume, et al., 2015; Stumpp, Nützmann, et al., 2009). 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 multiobjective 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.

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, Leistert, et al., 2016). 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 semianalytical 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 (Ali et al., 2011; Bishop, 1991; Rinderer et al., 2017; Weiler & McDonnell, 2004). 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 and 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 six 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., Hrachowitz et al., 2015; McMillan et al., 2012) 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 (Rueedi et al., 2005; Zoellmann et al., 2001).

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., Benettin, Bailey, et al., 2015; Benettin, Kirchner, et al., 2015; Birkel & Soulsby, 2016; Hrachowitz et al., 2013; 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; Kuppel et al., 2018; Remondi et al., 2018). Yet the tails of the age distribution of soil water can in certain cases be long (Sprenger, Seeger, et al., 2016), indicating that water can be held for years in the soils depending on the soil type and on the dynamics of evapotranspiration (Brinkmann et al., 2018; Sprenger, Seeger, et al., 2016; Sprenger, Tetzlaff, Buttle, Laudon, & Soulsby, 2018). In arid environments, zero or very small downward fluxes might occur over centuries, as for example, observed by Sandvig and 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 (Benettin, Bailey, et al., 2017; Hrachowitz et al., 2013; 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 square kilometers up to several millions of square kilometers (BGR/UNESCO, 2008), and their permeability spans more than 12 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 reentering the atmospheric cycle through root water uptake (Fan et al., 2017), discharging into lakes or wetlands (Ala-aho et al., 2015; Kluge et al., 2012), 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, and 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 (Beck et al., 2013; Eckhardt, 2005), 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 TTD 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 ¹⁸O and ³H based estimation of TTDs 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 and 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, Bailey, et al. (2015) calculated ²H 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 TTDs separately for all of them using simple analytic formulations (Botter et al., 2011). Comparing wet and dry periods, Benettin, Bailey, et al. (2015) provide clear evidence that stream water ages shift to older values after prolonged recession during drier periods. With a similar modeling approach, Hartmann et al. (2016) calculated TTDs 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., Benettin, Bailey, et al., 2015; Birkel et al., 2011; Birkel et al., 2014), 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 Holoher et al. (2001), who used the ^3H - ^3He 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 ^3H - ^3He data and found increasing water ages in a riparian groundwater along a 500-m stream spanning from 0 to 1 year in the headwaters, to 6 to 7 years midway, 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 (Boano et al., 2014; Cardenas, 2008; Wörman et al., 2007). 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 subdisciplines 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 spatiotemporal 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, Rinaldo, & Botter, 2015).
Catchment	is an area having a common outlet for its surface and subsurface runoff.
Catchment runoff	is the precipitation that flows toward 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, and 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, Rinaldo, & Botter, 2015).
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, and 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 (^2H) and oxygen (^{18}O) occur naturally in water molecules. Their abundance is described by isotope ratios (or isotopic compositions) $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$, often expressed as per mill 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 and 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 a 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.

Author contributions

M. W., C. S., and M. S. conducted the conceptualization; M. W. and C. S. conducted the funding acquisition; M. S. and M. W. conducted the visualization; M. S., S. T. A., P. B., M. D., A. H., M. H., N. O., N. R., C. S., and M. W. conducted the writing of original draft; 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. conducted the writing, review, and editing.

Acknowledgments

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. Goody, P. Königer, M. Loschko, V. Maurer, R. Purtschert, S. Seeger, and H. Wang. M. S. thanks Wassernetzwerk Baden-Württemberg and the Deutsche Forschungsgemeinschaft (DFG)—Project 397306994—for funding. N. R. thanks the Luxembourg National Research Fund (C14/SR/8353440/STORE-AGE) for financial support. A. H. was supported by the Emmy Noether Programme of the Deutsche Forschungsgemeinschaft DFG (HA 8113/1-1). This research manuscript by Matthias Sprenger was supported by the Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg (Az. 33-7533.-25-11/31).

References

- Abbott, B. W., Baranov, V., Mendoza-Lera, C., Nikolakopoulou, M., Harjung, A., Kolbe, T., et al. (2016). Using multi-tracer inference to move beyond single-catchment ecohydrology. *Earth-Science Reviews*, *160*, 19–42. <https://doi.org/10.1016/j.earscirev.2016.06.014>
- Aggarwal, P. (2013). Introduction. In A. Suckow, et al. (Eds.), *Isotope methods for dating old groundwater* (pp. 1–4). Vienna, Austria: International Atomic Energy Agency.
- Aggarwal, P. K., Matsumoto, T., Sturchio, N. C., Chang, H. K., Gastmans, D., Araguas-Araguas, L. J., et al. (2015). Continental degassing of ^4He by surficial discharge of deep groundwater. *Nature Geoscience*, *8*(1), 35–39. <https://doi.org/10.1038/ngeo2302>
- Ala-aho, P., Rossi, P. M., Isokangas, E., & Klöve, B. (2015). Fully integrated surface-subsurface flow modelling of groundwater-lake interaction in an esker aquifer: Model verification with stable isotopes and airborne thermal imaging. *Journal of Hydrology*, *522*, 391–406. <https://doi.org/10.1016/j.jhydrol.2014.12.054>
- Ala-aho, P., Tetzlaff, D., McNamara, J. P., Laudon, H., Kormos, P., & Soulsby, C. (2017). Modeling the isotopic evolution of snowpack and snowmelt: Testing a spatially distributed parsimonious approach. *Water Resources Research*, *53*, 5813–5830. <https://doi.org/10.1002/2017WR020650>
- Ala-aho, P., Tetzlaff, D., McNamara, J., Laudon, H., & Soulsby, C. (2017). Using isotopes to constrain water flux and age estimates in snow-influenced catchments using the STARR (Spatially distributed Tracer-Aided Rainfall-Runoff) model. *Hydrology and Earth System Sciences*, *21*(10), 5089–5110. <https://doi.org/10.5194/hess-21-5089-2017>
- Ali, G. A., L'Heureux, C., Roy, A. G., Turmel, M.-C., & Courchesne, F. (2011). Linking spatial patterns of perched groundwater storage and stormflow generation processes in a headwater forested catchment. *Hydrological Processes*, *25*(25), 3843–3857. <https://doi.org/10.1002/hyp.8238>
- Allen, M. F. (2007). Mycorrhizal fungi: Highways for water and nutrients in arid soils. *Vadose Zone Journal*, *6*(2), 291. <https://doi.org/10.2136/vzj2006.0068>
- Allen, S. T., Brooks, J. R., Keim, R. F., Bond, B. J., & McDonnell, J. J. (2014). The role of pre-event canopy storage in throughfall and stemflow by using isotopic tracers. *Ecohydrology*, *7*(2), 858–868. <https://doi.org/10.1002/eco.1408>
- Allen, S. T., Keim, R. F., Barnard, H. R., McDonnell, J. J., & Renée Brooks, J. (2017). The role of stable isotopes in understanding rainfall interception processes: A review. *Wiley Interdisciplinary Reviews: Water*, *4*(1). <https://doi.org/10.1002/wat2.1187>
- Allen, S. T., Kirchner, J. W., Braun, S., Siegwolf, R. T. W., & Goldsmith, G. R. (2019). Seasonal origins of soil water used by trees. *Hydrology and Earth System Sciences*, *23*(2), 1199–1210. <https://doi.org/10.5194/hess-23-1199-2019>
- Allen, S. T., Kirchner, J. W., & Goldsmith, G. R. (2018). Predicting spatial patterns in precipitation isotope ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) seasonality using sinusoidal isoscapes. *Geophysical Research Letters*, *45*, 4859–4868. <https://doi.org/10.1029/2018GL077458>

- Alley, W. M., Healy, R. W., LaBaugh, J. W., & Reilly, T. E. (2002). Flow and storage in groundwater systems. *Science*, 296(5575), 1985–1990. <https://doi.org/10.1126/science.1067123>
- Ambroggi, R. P. (1977). Underground reservoirs to control the water cycle. *Scientific American*, 236(5), 21–27. <https://doi.org/10.1038/scientificamerican0577-21>
- Ameli, A. A., Gabrielli, C., Morgenstern, U., & McDonnell, J. J. (2018). Groundwater subsidy from headwaters to their parent water watershed: A combined field-modeling approach. *Water Resources Research*, 54, 5110–5125. <https://doi.org/10.1029/2017WR022356>
- Anderson, A. E., Weiler, M., Alila, Y., & Hudson, R. O. (2009). Subsurface flow velocities in a hillslope with lateral preferential flow. *Water Resources Research*, 45, W11407. <https://doi.org/10.1029/2008WR007121>
- Asano, Y., Uchida, T., & Ohte, N. (2002). Residence times and flow paths of water in steep unchanneled catchments, Tanakami, Japan. *Journal of Hydrology*, 261(1–4), 173–192. [https://doi.org/10.1016/S0022-1694\(02\)00005-7](https://doi.org/10.1016/S0022-1694(02)00005-7)
- Asbjornsen, H., Shepherd, G., Helmers, M., & Mora, G. (2008). Seasonal patterns in depth of water uptake under contrasting annual and perennial systems in the Corn Belt Region of the Midwestern U.S. *Plant and Soil*, 308(1–2), 69–92. <https://doi.org/10.1007/s11104-008-9607-3>
- Bachmair, S., & Weiler, M. (2011). New dimensions of hillslope hydrology. In D. F. Levia, et al. (Eds.), *Forest Hydrology and Biogeochemistry*, (Vol. 216, pp. 455–481). Dordrecht, Netherlands: Springer. https://doi.org/10.1007/978-94-007-1363-5_23
- Bachmair, S., Weiler, M., & Nuttmann, G. (2009). Controls of land use and soil structure on water movement: Lessons for pollutant transfer through the unsaturated zone. *Journal of Hydrology*, 369(3–4), 241–252. <https://doi.org/10.1016/j.jhydrol.2009.02.031>
- Bachmann, D., Gockele, A., Ravenek, J. M., Roscher, C., Strecker, T., Weigelt, A., & Buchmann, N. (2015). No evidence of complementary water use along a plant species richness gradient in temperate experimental grasslands. *PLOS ONE*, 10(1), e0116367. <https://doi.org/10.1371/journal.pone.0116367>
- Barbeta, A., Mejia-Chang, M., Ogaya, R., Voltas, J., Dawson, T. E., & Peñuelas, J. (2015). The combined effects of a long-term experimental drought and an extreme drought on the use of plant-water sources in a Mediterranean forest. *Global Change Biology*, 21(3), 1213–1225. <https://doi.org/10.1111/gcb.12785>
- Barbeta, A., & Peñuelas, J. (2017). Relative contribution of groundwater to plant transpiration estimated with stable isotopes. *Scientific Reports*, 7(1), 10580. <https://doi.org/10.1038/s41598-017-09643-x>
- Bauhus, J., & Messier, C. (1999). Soil exploitation strategies of fine roots in different tree species of the southern boreal forest of eastern Canada. *Canadian Journal of Forest Research*, 29(2), 260–273. <https://doi.org/10.1139/x98-206>
- Beck, H. E., van Dijk, A. I. J. M., Miralles, D. G., de Jeu, R. A. M., Sampurno Bruijnzeel, L. A., McVicar, T. R., & Schellekens, J. (2013). Global patterns in base flow index and recession based on streamflow observations from 3394 catchments. *Water Resources Research*, 49, 7843–7863. <https://doi.org/10.1002/2013WR013918>
- Becker, M. W., & Coplen, T. B. (2001). Use of deuterated water as a conservative artificial groundwater tracer. *Hydrogeology Journal*, 9(5), 512–516. <https://doi.org/10.1007/s100400100157>
- Begemann, F., & Libby, W. F. (1957). Continental water balance, ground water inventory and storage times, surface ocean mixing rates and world-wide water circulation patterns from cosmic-ray and bomb tritium. *Geochimica et Cosmochimica Acta*, 12(4), 277–296. [https://doi.org/10.1016/0016-7037\(57\)90040-6](https://doi.org/10.1016/0016-7037(57)90040-6)
- Benettin, P., Bailey, S. W., Campbell, J. L., Green, M. B., Rinaldo, A., Likens, G. E., et al. (2015). Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA. *Water Resources Research*, 51, 9256–9272. <https://doi.org/10.1002/2015WR017552>
- Benettin, P., Bailey, S. W., Rinaldo, A., Likens, G. E., McGuire, K. J., & Botter, G. (2017). Young runoff fractions control streamwater age and solute concentration dynamics. *Hydrological Processes*, 31(16), 2982–2986. <https://doi.org/10.1002/hyp.11243>
- Benettin, P., Kirchner, J. W., Rinaldo, A., & Botter, G. (2015). Modeling chloride transport using travel time distributions at Plynlimon, Wales. *Water Resources Research*, 51, 3259–3276. <https://doi.org/10.1002/2014WR016600>
- Benettin, P., Queloz, P., Bensimon, M., McDonnell, J. J., & Rinaldo, A. (2019). Velocities, residence times, tracer breakthroughs in a vegetated lysimeter: A multitracer experiment. *Water Resources Research*, 55(1), 21–33. <https://doi.org/10.1029/2018WR023894>
- Benettin, P., Rinaldo, A., & Botter, G. (2015). Tracking residence times in hydrological systems: Forward and backward formulations. *Hydrological Processes*, 29(25), 5203–5213. <https://doi.org/10.1002/hyp.10513>
- Benettin, P., Soulsby, C., Birkel, C., Tetzlaff, D., Botter, G., & Rinaldo, A. (2017). Using SAS functions and high-resolution isotope data to unravel travel time distributions in headwater catchments. *Water Resources Research*, 53, 1864–1878. <https://doi.org/10.1002/2016WR020117>
- Benettin, P., van der Velde, Y., van der Zee, S. E. A. T. M., Rinaldo, A., & Botter, G. (2013). Chloride circulation in a lowland catchment and the formulation of transport by travel time distributions. *Water Resources Research*, 49, 4619–4632. <https://doi.org/10.1002/wrcr.20309>
- Berghuijs, W. R., & Kirchner, J. W. (2017). The relationship between contrasting ages of groundwater and streamflow. *Geophysical Research Letters*, 44, 8925–8935. <https://doi.org/10.1002/2017GL074962>
- Berman, E. S. F., Gupta, M., Gabrielli, C., Garland, T., & McDonnell, J. J. (2009). High-frequency field-deployable isotope analyzer for hydrological applications. *Water Resources Research*, 45, W10201. <https://doi.org/10.1029/2009WR008265>
- Berry, Z. C., Evaristo, J., Moore, G., Poca, M., Steppe, K., Verrot, L., et al. (2017). The two water worlds hypothesis: Addressing multiple working hypotheses and proposing a way forward. *Ecohydrology*, 11(3), e1843. <https://doi.org/10.1002/eco.1843>
- Bertrand, G., Masini, J., Goldscheider, N., Meeks, J., Lavastre, V., Celle-Jeanton, H., et al. (2014). Determination of spatiotemporal variability of tree water uptake using stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) in an alluvial system supplied by a high-altitude watershed, Plyn forest, Switzerland. *Ecohydrology*, 7(2), 319–333. <https://doi.org/10.1002/eco.1347>
- Bethke, C. M., & Johnson, T. M. (2008). Groundwater age and groundwater age dating. *Annual Review of Earth and Planetary Sciences*, 36(1), 121–152. <https://doi.org/10.1146/annurev.earth.36.031207.124210>
- Beven, K. (2006). Searching for the Holy Grail of scientific hydrology: $Q_t = (S, R, \Delta t)A$ as closure. *Hydrology and Earth System Sciences*, 10(5), 609–618. <https://doi.org/10.5194/hess-10-609-2006>
- Beven, K., & Germann, P. (1982). Macropores and water flow in soils. *Water Resources Research*, 18(5), 1311–1325. <https://doi.org/10.1029/WR018i005p01311>
- Beven, K., & Germann, P. (2013). Macropores and water flow in soils revisited. *Water Resources Research*, 49, 3071–3092. <https://doi.org/10.1002/wrcr.20156>
- Beyer, M., Koeniger, P., Gaj, M., Hamutoko, J. T., Wanke, H., & Himmelsbach, T. (2016). A deuterium-based labeling technique for the investigation of rooting depths, water uptake dynamics and unsaturated zone water transport in semiarid environments. *Journal of Hydrology*, 533, 627–643. <https://doi.org/10.1016/j.jhydrol.2015.12.037>

- Beyer, M., Morgenstern, U., & Jackson, B. (2014). Review of techniques for dating young groundwater (<100 years) in New Zealand. *Journal of Hydrology (New Zealand)*, 53(2), 93–111.
- BGR/UNESCO (2008). Groundwater resources of the world 1: 25 000 000, https://www.whymap.org/whymap/EN/Home/whymap_node.html.
- Birkel, C., & Soulsby, C. (2015). Advancing tracer-aided rainfall-runoff modelling: A review of progress, problems and unrealised potential. *Hydrological Processes*, 29(25), 5227–5240. <https://doi.org/10.1002/hyp.10594>
- Birkel, C., & Soulsby, C. (2016). Linking tracers, water age and conceptual models to identify dominant runoff processes in a sparsely monitored humid tropical catchment. *Hydrological Processes*, 30(24), 4477–4493. <https://doi.org/10.1002/hyp.10941>
- Birkel, C., Soulsby, C., & Tetzlaff, D. (2014). Developing a consistent process-based conceptualization of catchment functioning using measurements of internal state variables. *Water Resources Research*, 50, 3481–3501. <https://doi.org/10.1002/2013WR014925>
- Birkel, C., Tetzlaff, D., Dunn, S. M., & Soulsby, C. (2011). Using time domain and geographic source tracers to conceptualize streamflow generation processes in lumped rainfall-runoff models. *Water Resources Research*, 47, W02515. <https://doi.org/10.1029/2010WR009547>
- Bishop, K. (1991). Episodic increases in stream acidity, catchment flow pathways and hydrograph separation, University of Cambridge.
- Blöschl, G., & Zehe, E. (2005). Invited commentary—On hydrological predictability. *Hydrological Processes*, 19(19), 3923–3929. <https://doi.org/10.1002/Hyp.6075>
- Boano, F., Harvey, J. W., Marion, A., Packman, A. I., Revelli, R., Ridolfi, L., & Wörman, A. (2014). Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical implications. *Reviews of Geophysics*, 52, 603–679. <https://doi.org/10.1002/2012RG000417>
- Bolin, B., & Rodhe, H. (1973). A note on the concepts of age distribution and transit time in natural reservoirs. *Tellus*, 25(1), 58–62. <https://doi.org/10.1111/j.2153-3490.1973.tb01594.x>
- Botter, G., Bertuzzo, E., & Rinaldo, A. (2010). Transport in the hydrologic response: Travel time distributions, soil moisture dynamics, and the old water paradox. *Water Resources Research*, 46, W03514. <https://doi.org/10.1029/2009wr008371>
- Botter, G., Bertuzzo, E., & Rinaldo, A. (2011). Catchment residence and travel time distributions: The master equation. *Geophysical Research Letters*, 38, L11403. <https://doi.org/10.1029/2011gl047666>
- Bowen, G. J. (2008). Spatial analysis of the intra-annual variation of precipitation isotope ratios and its climatological corollaries. *Journal of Geophysical Research*, 113, D05113. <https://doi.org/10.1029/2007JD009295>
- Bowen, G. J., & Wilkinson, B. (2002). Spatial distribution of $\delta^{18}O$ in meteoric precipitation. *Geology*, 30(4), 315. [https://doi.org/10.1130/0091-7613\(2002\)030<0315:SDOOIM>2.0.CO;2](https://doi.org/10.1130/0091-7613(2002)030<0315:SDOOIM>2.0.CO;2)
- Brandes, E., Wenninger, J., Koeniger, P., Schindler, D., Rennenberg, H., Leibundgut, C., et al. (2007). Assessing environmental and physiological controls over water relations in a Scots pine (*Pinus sylvestris* L.) stand through analyses of stable isotope composition of water and organic matter. *Plant, Cell & Environment*, 30(1), 113–127. <https://doi.org/10.1111/j.1365-3040.2006.01609.x>
- Brantley, S. L., Eissenstat, D. M., Marshall, J. A., Godsey, S. E., Balogh-Brunstad, Z., Karwan, D. L., et al. (2017). Reviews and syntheses: On the roles trees play in building and plumbing the critical zone. *Biogeosciences*, 14(22), 5115–5142. <https://doi.org/10.5194/bg-14-5115-2017>
- Brantley, S. L., Goldhaber, M. B., & Ragnarsdottir, K. V. (2007). Crossing disciplines and scales to understand the critical zone. *Elements*, 3(5), 307–314. <https://doi.org/10.2113/gselements.3.5.307>
- Brinkmann, N., Seeger, S., Weiler, M., Buchmann, N., Eugster, W., & Kahmen, A. (2018). Employing stable isotopes to determine the residence times of soil water and the temporal origin of water taken up by *Fagus sylvatica* and *Picea abies* in a temperate forest. *New Phytologist*, 219(4), 1300–1313. <https://doi.org/10.1111/nph.15255>
- Brooks, J. R., Barnard, H. R., Coulombe, R., & McDonnell, J. J. (2010). Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience*, 3(2), 100–104. <https://doi.org/10.1038/NGEO722>
- Burns, D. A., Plummer, L. N., McDonnell, J. J., Busenberg, E., Casile, G. C., Kendall, C., et al. (2003). The geochemical evolution of riparian ground water in a forested piedmont catchment. *Ground water*, 41(7), 913–925. <https://doi.org/10.1111/j.1745-6584.2003.tb02434.x>
- Caldeira, M. C., Lecomte, X., David, T. S., Pinto, J. G., Bugalho, M. N., & Werner, C. (2015). Synergy of extreme drought and shrub invasion reduce ecosystem functioning and resilience in water-limited climates. *Scientific Reports*, 5(1), 15110. <https://doi.org/10.1038/srep15110>
- Caldwell, M. M., Dawson, T. E., & Richards, J. H. (1998). Hydraulic lift: Consequences of water efflux from the roots of plants. *Oecologia*, 113(2), 151–161. <https://doi.org/10.1007/s004420050363>
- Canadell, J., Jackson, R. B., Ehleringer, J. B., Mooney, H. A., Sala, O. E., & Schulze, E.-D. (1996). Maximum rooting depth of vegetation types at the global scale. *Oecologia*, 108(4), 583–595. <https://doi.org/10.1007/BF00329030>
- Cardenas, M. B. (2008). Surface water-groundwater interface geomorphology leads to scaling of residence times. *Geophysical Research Letters*, 35, L08402. <https://doi.org/10.1029/2008GL033753>
- Carlyle-Moses, D. E., & Gash, J. H. C. (2011). Rainfall interception loss by forest canopies. In D. F. Levia, et al. (Eds.), *Forest Hydrology and Biogeochemistry*, (Vol. 216, pp. 407–424). Dordrecht, Netherlands: Springer. https://doi.org/10.1007/978-94-007-1363-5_20
- Carminati, A., Benard, P., Ahmed, M. A., & Zarebanadkouki, M. (2017). Liquid bridges at the root-soil interface. *Plant and Soil*, 417(1–2), 1–15. <https://doi.org/10.1007/s11104-017-3227-8>
- Carminati, A., Vetterlein, D., Weller, U., Vogel, H.-J., & Oswald, S. E. (2009). When roots lose contact. *Vadose Zone Journal*, 8(3), 805. <https://doi.org/10.2136/vzj2008.0147>
- Cartwright, I., Cendón, D., Currell, M., & Meredith, K. (2017). A review of radioactive isotopes and other residence time tracers in understanding groundwater recharge: Possibilities, challenges, and limitations. *Journal of Hydrology*, 555, 797–811. <https://doi.org/10.1016/j.jhydrol.2017.10.053>
- Cayuela, C., Latron, J., Geris, J., & Llorens, P. (2019). Spatio-temporal variability of the isotopic input signal in a partly forested catchment: Implications for hydrograph separation. *Hydrological Processes*, 33(1), 36–46. <https://doi.org/10.1002/hyp.13309>
- Cayuela, C., Llorens, P., Sánchez-Costa, E., Levia, D. F., & Latron, J. (2018). Effect of biotic and abiotic factors on inter and intra-event variability in stemflow rates in oak and pine stands in a Mediterranean mountain area. *Journal of Hydrology*, 560, 396–406. <https://doi.org/10.1016/j.jhydrol.2018.03.050>
- Cermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology*, 27(2), 181–198. <https://doi.org/10.1093/treephys/27.2.181>
- Čermák, J., Kučera, J., & Nadezhdina, N. (2004). Sap flow measurements with some thermodynamic methods, flow integration within trees and scaling up from sample trees to entire forest stands. *Trees*, 18(5), 529–546. <https://doi.org/10.1007/s00468-004-0339-6>
- Clark, I. D., & Fritz, P. (1997). *Environmental isotopes in hydrogeology*. Boca Raton, USA: CRC press.
- Cook, P. G., & Herczeg, A. L. (Eds) (2000). *Environmental tracers in subsurface hydrology*. Boston, USA: Springer. <https://doi.org/10.1007/978-1-4615-4557-6>

- Cook, P. G., Solomon, D. K., Sanford, W. E., Busenberg, E., Plummer, L. N., & Poreda, R. J. (1996). Inferring shallow groundwater flow in saprolite and fractured rock using environmental tracers. *Water Resources Research*, *32*(6), 1501–1509. <https://doi.org/10.1029/96WR00354>
- Corcho Alvarado, J. A., Purtschert, R., Barbecot, F., Chabault, C., Rueedi, J., Schneider, V., et al. (2007). Constraining the age distribution of highly mixed groundwater using ³⁹Ar: A multiple environmental tracer (³H/³He, ⁸⁵Kr, ³⁹Ar, and ¹⁴C) study in the semiconfined Fontainebleau Sands Aquifer (France). *Water Resources Research*, *43*, W03427. <https://doi.org/10.1029/2006WR005096>
- Cornaton, F., & Perrochet, P. (2006). Groundwater age, life expectancy and transit time distributions in advective-dispersive systems: 1. Generalized reservoir theory. *Advances in Water Resources*, *29*(9), 1267–1291. <https://doi.org/10.1016/j.advwatres.2005.10.009>
- Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, *133*(3465), 1702–1703. <https://doi.org/10.1126/science.133.3465.1702>
- Cuthbert, M. O. (2014). Straight thinking about groundwater recession. *Water Resources Research*, *50*, 2407–2424. <https://doi.org/10.1002/2013WR014060>
- Danckwerts, P. V. (1953). Continuous flow systems: Distribution of residence times. *Chemical Engineering Science*, *2*(1), 1–13. [https://doi.org/10.1016/0009-2509\(53\)80001-1](https://doi.org/10.1016/0009-2509(53)80001-1)
- Danesh-Yazdi, M., Klaus, J., Condon, L. E., & Maxwell, R. M. (2018). Bridging the gap between numerical solutions of travel time distributions and analytical storage selection functions. *Hydrological Processes*, *32*(8), 1063–1076. <https://doi.org/10.1002/hyp.11481>
- Davies, J., Beven, K., Rodhe, A., Nyberg, L., & Bishop, K. (2013). Integrated modeling of flow and residence times at the catchment scale with multiple interacting pathways. *Water Resources Research*, *49*, 4738–4750. <https://doi.org/10.1002/wrcr.20377>
- DeWalle, D. R., Edwards, P. J., Swistock, B. R., Aravena, R., & Drimmie, R. J. (1997). Seasonal isotope hydrology of three Appalachian forest catchments. *Hydrological Processes*, *11*(15), 1895–1906. [https://doi.org/10.1002/\(SICI\)1099-1085\(199712\)11:15<1895::AID-HYP538>3.0.CO;2](https://doi.org/10.1002/(SICI)1099-1085(199712)11:15<1895::AID-HYP538>3.0.CO;2)
- Dick, J., Tetzlaff, D., Bradford, J., & Soulsby, C. (2018). Using repeat electrical resistivity surveys to assess heterogeneity in soil moisture dynamics under contrasting vegetation types. *Journal of Hydrology*, *559*, 684–697. <https://doi.org/10.1016/j.jhydrol.2018.02.062>
- Dietermann, N., & Weiler, M. (2013). Spatial distribution of stable water isotopes in alpine snow cover. *Hydrology and Earth System Sciences*, *17*(7), 2657–2668. <https://doi.org/10.5194/hess-17-2657-2013>
- Dingman, S. L. (2015). *Physical hydrology*, (3rd ed.). Long Grove, USA: Waveland Press.
- Domenico, P. A., & Schwartz, F. W. (1998). *Physical and chemical hydrogeology*, (2nd ed.). Chichester, USA: Wiley.
- Donovan, L. A., & Ehleringer, J. R. (1994). Water stress and use of summer precipitation in a great basin shrub community. *Functional Ecology*, *8*(3), 289–297. <https://doi.org/10.2307/2389821>
- Dooge, J. C. (1973). Linear theory of hydrologic system, Technical Bulletin 1468. Washington, D.C., USA: Agricultural Research Service, USDA.
- Dubbert, M., Caldeira, M. C., Dubbert, D., & Werner, C. (2019). A pool-weighted perspective on the two-water-worlds hypothesis. *New Phytologist*, *222*(3), 1271–1283. <https://doi.org/10.1111/nph.15670>
- Dubbert, M., Cuntz, M., Piayda, A., Maguás, C., & Werner, C. (2013). Partitioning evapotranspiration—Testing the Craig and Gordon model with field measurements of oxygen isotope ratios of evaporative fluxes. *Journal of Hydrology*, *496*, 142–153. <https://doi.org/10.1016/j.jhydrol.2013.05.033>
- Dubbert, M., Piayda, A., Cuntz, M., Correia, A. C., Costa, E., Silva, F., et al. (2014). Stable oxygen isotope and flux partitioning demonstrates understory of an oak savanna contributes up to half of ecosystem carbon and water exchange. *Frontiers in Plant Science*, *5*, A530. <https://doi.org/10.3389/fpls.2014.00530>
- Dubbert, M., & Werner, C. (2019). Water fluxes mediated by vegetation: Emerging isotopic insights at the soil and atmosphere interfaces. *New Phytologist*, *221*(4), 1754–1763. <https://doi.org/10.1111/nph.15547>
- Eberts, S. M., Böhlke, J. K., Kauffman, L. J., & Jurgens, B. C. (2012). Comparison of particle-tracking and lumped-parameter age-distribution models for evaluating vulnerability of production wells to contamination. *Hydrogeology Journal*, *20*(2), 263–282. <https://doi.org/10.1007/s10040-011-0810-6>
- Eckhardt, K. (2005). How to construct recursive digital filters for baseflow separation. *Hydrological Processes*, *19*(2), 507–515. <https://doi.org/10.1002/hyp.5675>
- Ehleringer, J., Phillips, S., Schuster, W. F., & Sandquist, D. (1991). Differential utilization of summer rains by desert plants. *Oecologia*, *88*(3), 430–434. <https://doi.org/10.1007/BF00317589>
- Eller, C. B., Lima, A. L., & Oliveira, R. S. (2013). Foliar uptake of fog water and transport belowground alleviates drought effects in the cloud forest tree species, *Drimys brasiliensis* (Winteraceae). *New Phytologist*, *199*(1), 151–162. <https://doi.org/10.1111/nph.12248>
- Ellsworth, P. Z., & Sternberg, L. S. L. (2015). Seasonal water use by deciduous and evergreen woody species in a scrub community is based on water availability and root distribution. *Ecohydrology*, *8*(4), 538–551. <https://doi.org/10.1002/eco.1523>
- Engdahl, N. B., McCallum, J. L., & Massoudieh, A. (2016). Transient age distributions in subsurface hydrologic systems. *Journal of Hydrology*, *543*, 88–100. <https://doi.org/10.1016/j.jhydrol.2016.04.066>
- Eriksson, E. (1958). The possible use of tritium for estimating groundwater storage. *Tellus*, *10*(4), 472–478. <https://doi.org/10.1111/j.2153-3490.1958.tb02035.x>
- Etcheverry, D., & Perrochet, P. (2000). Direct simulation of groundwater transit-time distributions using the reservoir theory. *Hydrogeology Journal*, *8*(2), 200–208. <https://doi.org/10.1007/s100400050006>
- Evaristo, J., Jasechko, S., & McDonnell, J. J. (2015). Global separation of plant transpiration from groundwater and streamflow. *Nature*, *525*(7567), 91–94. <https://doi.org/10.1038/nature14983>
- Evaristo, J., Kim, M., Haren, J., Pangle, L. A., Harman, C. J., Troch, P. A., & McDonnell, J. J. (2019). Characterizing the fluxes and age distribution of soil water, plant water, and deep percolation in a model tropical ecosystem. *Water Resources Research*, *55*(4), 3307–3327. <https://doi.org/10.1029/2018WR023265>
- Evaristo, J., & McDonnell, J. J. (2017). Prevalence and magnitude of groundwater use by vegetation: A global stable isotope meta-analysis. *Scientific reports*, *7*(1), 44110. <https://doi.org/10.1038/srep44110>
- Fan, Y., Miguez-Macho, G., Jobbágy, E. G., Jackson, R. B., & Otero-Casal, C. (2017). Hydrologic regulation of plant rooting depth. *Proceedings of the National Academy of Sciences of the United States of America*, *114*, 10,572–10,577. <https://doi.org/10.1073/pnas.1712381114>
- Feng, X., Taylor, S., Renshaw, C. E., & Kirchner, J. W. (2002). Isotopic evolution of snowmelt 1. A physically based one-dimensional model. *Water Resources Research*, *38*(10), 1217. <https://doi.org/10.1029/2001WR000814>
- Fenicia, F., Wrede, S., Kavetski, D., Pfister, L., Hoffmann, L., Savenije, H. H. G., & McDonnell, J. J. (2010). Assessing the impact of mixing assumptions on the estimation of streamwater mean residence time. *Hydrological Processes*, *24*(12), 1730–1741. <https://doi.org/10.1002/Hyp.7595>

- Fischer, B. M. C., Stähli, M., & Seibert, J. (2017). Pre-event water contributions to runoff events of different magnitude in pre-alpine headwaters. *Hydrology Research*, 48(1), 28–47. <https://doi.org/10.2166/nh.2016.176>
- Freeze, R. A., & Cherry, J. A. (1979). *Groundwater*. London, UK: Prentice-Hall.
- Freudiger, D., Kohn, I., Seibert, J., Stahl, K., & Weiler, M. (2017). Snow redistribution for the hydrological modeling of alpine catchments. *Wiley Interdisciplinary Reviews: Water*, 4(5), e1232. <https://doi.org/10.1002/wat2.1232>
- Frisbee, M. D., Wilson, J. L., Gomez-Velez, J. D., Phillips, F. M., & Campbell, A. R. (2013). Are we missing the tail (and the tale) of residence time distributions in watersheds? *Geophysical Research Letters*, 40, 4633–4637. <https://doi.org/10.1002/grl.50895>
- Gabrielli, C. P., McDonnell, J. J., & Jarvis, W. T. (2012). The role of bedrock groundwater in rainfall-runoff response at hillslope and catchment scales. *Journal of Hydrology*, 450–451, 117–133. <https://doi.org/10.1016/j.jhydrol.2012.05.023>
- Gao, H., Hrachowitz, M., Schymanski, S. J., Fenicia, F., Sriwongsitanon, N., & Savenije, H. H. G. (2014). Climate controls how ecosystems size the root zone storage capacity at catchment scale. *Geophysical Research Letters*, 41, 7916–7923. <https://doi.org/10.1002/2014GL061668>
- Garvelmann, J., Pohl, S., & Weiler, M. (2015). Spatio-temporal controls of snowmelt and runoff generation during rain-on-snow events in a mid-latitude mountain catchment. *Hydrological Processes*, 29(17), 3649–3664. <https://doi.org/10.1002/hyp.10460>
- Gassen, N., Griebler, C., Werban, U., Trauth, N., & Stumpp, C. (2017). High resolution monitoring above and below the groundwater table uncovers small-scale hydrochemical gradients. *Environmental Science & Technology*, 51(23), 13,806–13,815. <https://doi.org/10.1021/acs.est.7b03087>
- Gerber, C., Vaikmäe, R., Aeschbach, W., Babre, A., Jiang, W., Leuenberger, M., et al. (2017). Using 81Kr and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale. *Geochimica et Cosmochimica Acta*, 205, 187–210. <https://doi.org/10.1016/j.gca.2017.01.033>
- Geris, J., Tetzlaff, D., McDonnell, J., Anderson, J., Paton, G., & Soulsby, C. (2015). Ecohydrological separation in wet, low energy northern environments? A preliminary assessment using different soil water extraction techniques. *Hydrological Processes*, 29(25), 5139–5152. <https://doi.org/10.1002/hyp.10603>
- Gerrits, A. M. J., & Savenije, H. H. G. (2011). Forest floor interception. In D. F. Levina, et al. (Eds.), *Forest Hydrology and Biogeochemistry*, (Vol. 216, pp. 445–454). Dordrecht, Netherlands: Springer. https://doi.org/10.1007/978-94-007-1363-5_22
- Gilmore, T. E., Genereux, D. P., Solomon, D. K., & Solder, J. E. (2016). Groundwater transit time distribution and mean from streambed sampling in an agricultural coastal plain watershed, North Carolina, USA. *Water Resources Research*, 52, 2025–2044. <https://doi.org/10.1002/2015WR017600>
- Ginn, T. R., Haeri, H., Massoudieh, A., & Foglia, L. (2009). Notes on groundwater age in forward and inverse modeling. *Transport in Porous Media*, 79(1), 117–134. <https://doi.org/10.1007/s11242-009-9406-1>
- Gleason, S. M., Butler, D. W., Ziemińska, K., Waryszak, P., & Westoby, M. (2012). Stem xylem conductivity is key to plant water balance across Australian angiosperm species. *Functional Ecology*, 26(2), 343–352. <https://doi.org/10.1111/j.1365-2435.2012.01962.x>
- Gleeson, T., Befus, K. M., Jasechko, S., Luijendijk, E., & Cardenas, M. B. (2016). The global volume and distribution of modern groundwater. *Nature Geoscience*, 9(2), 161–167. <https://doi.org/10.1038/NGEO2590>
- Goldsmith, G. R., Allen, S. T., Braun, S., Engbersen, N., González-Quijano, C. R., Kirchner, J. W., & Siegwolf, R. T. W. (2019). Spatial variation in throughfall, soil, and plant water isotopes in a temperate forest. *Ecohydrology*, e2059. <https://doi.org/10.1002/eco.2059>
- Goldsmith, G. R., Muñoz-Villiers, L. E., Holwerda, F., McDonnell, J. J., Asbjornsen, H., & Dawson, T. E. (2012). Stable isotopes reveal linkages among ecohydrological processes in a seasonally dry tropical montane cloud forest. *Ecohydrology*, 5(6), 779–790. <https://doi.org/10.1002/eco.268>
- Good, S. P., Noone, D., & Bowen, G. (2015). Hydrologic connectivity constrains partitioning of global terrestrial water fluxes. *Science*, 349(6244), 175–177. <https://doi.org/10.1126/science.aaa5931>
- Goode, D. J. (1996). Direct simulation of groundwater age. *Water Resources Research*, 32(2), 289–296. <https://doi.org/10.1029/95WR03401>
- Grabczak, J., Rózański, K., Maloszewski, P., & Zuber, A. (1984). Estimation of the tritium input function with the aid of stable isotopes. *CATENA*, 11(2-3), 105–114. [https://doi.org/10.1016/0341-8162\(84\)90001-8](https://doi.org/10.1016/0341-8162(84)90001-8)
- Grant, G. E., & Dietrich, W. E. (2017). The frontier beneath our feet. *Water Resources Research*, 53, 2605–2609. <https://doi.org/10.1002/2017WR020835>
- Groh, J., Stumpp, C., Lücke, A., Pütz, T., Vanderborght, J., & Vereecken, H. (2018). Inverse estimation of soil hydraulic and transport parameters of layered soils from water stable isotope and lysimeter data. *Vadose Zone Journal*, 17(1), 170168. <https://doi.org/10.2136/vzj2017.09.0168>
- Hale, V. C., & McDonnell, J. J. (2016). Effect of bedrock permeability on stream base flow mean transit time scaling relations: 1. A multiscala catchment intercomparison. *Water Resources Research*, 52, 1358–1374. <https://doi.org/10.1002/2014WR016124>
- Hale, V. C., McDonnell, J. J., Stewart, M. K., Solomon, D. K., Doolittle, J., Ice, G. G., & Pack, R. T. (2016). Effect of bedrock permeability on stream base flow mean transit time scaling relationships: 2. Process study of storage and release. *Water Resources Research*, 52, 1375–1397. <https://doi.org/10.1002/2015WR017660>
- Hallett, P. D., Gordon, D. C., & Bengough, A. G. (2003). Plant influence on rhizosphere hydraulic properties: Direct measurements using a miniaturized infiltrometer. *New Phytologist*, 157(3), 597–603. <https://doi.org/10.1046/j.1469-8137.2003.00690.x>
- Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. *Water Resources Research*, 51, 1–30. <https://doi.org/10.1002/2014WR015707>
- Hartmann, A., Kobler, J., Kralik, M., Dirnböck, T., Humer, F., & Weiler, M. (2016). Model-aided quantification of dissolved carbon and nitrogen release after windthrow disturbance in an Austrian karst system. *Biogeosciences*, 13(1), 159–174. <https://doi.org/10.5194/bg-13-159-2016>
- Heidbüchel, I., Troch, P. A., & Lyon, S. W. (2013). Separating physical and meteorological controls of variable transit times in zero-order catchments. *Water Resources Research*, 49, 7644–7657. <https://doi.org/10.1002/2012WR013149>
- Herbstritt, B., Gralher, B., & Weiler, M. (2018). Real-time observations of stable isotope dynamics during rainfall and throughfall events. *Hydrology and Earth System Sciences Discussions*, 1–16. <https://doi.org/10.5194/hess-2018-301>
- Herrmann, A., Lehrer, M., & Stichler, W. (1981). Isotope input into runoff systems from melting snow covers. *Hydrology Research*, 12(4-5), 309–318. <https://doi.org/10.2166/nh.1981.0025>
- Hervé-Fernández, P., Oyazún, C., Brumbt, C., Huygens, D., Bodé, S., Verhoest, N. E. C., & Boeckx, P. (2016). Assessing the “two water worlds” hypothesis and water sources for native and exotic evergreen species in south-central Chile. *Hydrological Processes*, 30(23), 4227–4241. <https://doi.org/10.1002/hyp.10984>
- Hewlett, J. D., & Hibbert, A. R. (1967). Factors affecting the response of small watersheds to precipitation in humid areas. *Forest hydrology*, 275–290.

- Hinsinger, P., Bengough, A. G., Vetterlein, D., & Young, I. M. (2009). Rhizosphere: Biophysics, biogeochemistry and ecological relevance. *Plant and Soil*, 321(1-2), 117–152. <https://doi.org/10.1007/s11104-008-9885-9>
- Hinsinger, P., Plassard, C., & Jaillard, B. (2006). Rhizosphere: A new frontier for soil biogeochemistry. *Journal of Geochemical Exploration*, 88(1-3), 210–213. <https://doi.org/10.1016/j.gexplo.2005.08.041>
- Hochberg, U., Rockwell, F. E., Holbrook, N. M., & Cochard, H. (2018). Iso/Anisohydry: A plant-environment interaction rather than a simple hydraulic trait. *Trends in Plant Science*, 23(2), 112–120. <https://doi.org/10.1016/j.tplants.2017.11.002>
- Holocher, J., Matta, V., Aeschbach-Hertig, W., Beyerle, U., Hofer, M., Peeters, F., & Kipfer, R. (2001). Noble gas and major element constraints on the water dynamics in an alpine floodplain. *Groundwater*, 39(6), 841–852. <https://doi.org/10.1111/j.1745-6584.2001.tb02472.x>
- Horton, R. E., & Hawkins, R. H. (1965). Flow path of rain from the soil surface to the water table. *Soil Science*, 100(6), 377–383. <https://doi.org/10.1097/00010694-196512000-00001>
- Hrachowitz, M., Benettin, P., van Breukelen, B. M., Fovet, O., Howden, N. J. K., Ruiz, L., et al. (2016). Transit times—The link between hydrology and water quality at the catchment scale. *Wiley Interdisciplinary Reviews: Water*, 3(5), 629–657. <https://doi.org/10.1002/wat2.1155>
- Hrachowitz, M., & Clark, M. P. (2017). HESS opinions: The complementary merits of competing modelling philosophies in hydrology. *Hydrology and Earth System Sciences*, 21(8), 3953–3973. <https://doi.org/10.5194/hess-21-3953-2017>
- Hrachowitz, M., Fovet, O., Ruiz, L., & Savenije, H. (2015). Transit time distributions, legacy contamination and variability in biogeochemical $1/f\alpha$ scaling: How are hydrological response dynamics linked to water quality at the catchment scale? *Hydrological Processes*, 29(25), 5241–5256. <https://doi.org/10.1002/hyp.10546>
- Hrachowitz, M., Savenije, H., Bogaard, T. A., Tetzlaff, D., & Soulsby, C. (2013). What can flux tracking teach us about water age distribution patterns and their temporal dynamics? *Hydrology and Earth System Sciences*, 17(2), 533–564. <https://doi.org/10.5194/hess-17-533-2013>
- Hrachowitz, M., Soulsby, C., Tetzlaff, D., Dawson, J. J. C., Dunn, S. M., & Malcolm, I. A. (2009). Using long-term data sets to understand transit times in contrasting headwater catchments. *Journal of Hydrology*, 367(3-4), 237–248. <https://doi.org/10.1016/j.jhydrol.2009.01.001>
- Hrachowitz, M., Soulsby, C., Tetzlaff, D., & Malcolm, I. A. (2011). Sensitivity of mean transit time estimates to model conditioning and data availability. *Hydrological Processes*, 25(6), 980–990. <https://doi.org/10.1002/Hyp.7922>
- Hsueh, Y.-H., Chambers, J. L., Krauss, K. W., Allen, S. T., & Keim, R. F. (2016). Hydrologic exchanges and baldcypress water use on deltaic hummocks, Louisiana, USA. *Ecohydrology*, 9(8), 1452–1463. <https://doi.org/10.1002/eco.1738>
- Hürkamp, K., Zentner, N., Reckerth, A., Weishaupt, S., Wetzel, K. F., Tschiersch, J., & Stumpp, C. (2019). Spatial and temporal variability of snow isotopic composition on Mt. Zugspitze, Bavarian Alps, Germany. *Journal of Hydrology and Hydromechanics*, 67(1), 49–58. <https://doi.org/10.2478/johh-2018-0019>
- Huscroft, J., Gleeson, T., Hartmann, J., & Börker, J. (2018). Compiling and mapping global permeability of the unconsolidated and consolidated Earth: GLobal HYdrogeology MaPS 2.0 (GLHYMPS 2.0). *Geophysical Research Letters*, 45, 1897–1904. <https://doi.org/10.1002/2017GL075860>
- Ish-Shalom, N., Sternberg, L. D. S. L., Ross, M., O'Brien, J., & Flynn, L. (1992). Water utilization of tropical hardwood hammocks of the Lower Florida Keys. *Oecologia*, 92(1), 108–112. <https://doi.org/10.1007/BF00317270>
- Jackson, R. B., Canadell, J., Ehleringer, J. R., Mooney, H. A., Sala, O. E., & Schulze, E. D. (1996). A global analysis of root distributions for terrestrial biomes. *Oecologia*, 108(3), 389–411. <https://doi.org/10.1007/BF00333714>
- James, S., Meinzer, F., Goldstein, G., Woodruff, D., Jones, T., Restom, T., et al. (2003). Axial and radial water transport and internal water storage in tropical forest canopy trees. *Oecologia*, 134(1), 37–45. <https://doi.org/10.1007/s00442-002-1080-8>
- Jasechko, S. (2019). Global isotope hydrogeology—Review. *Reviews of Geophysics*. <https://doi.org/10.1029/2018RG000627>
- Jasechko, S., Kirchner, J. W., Welker, J. M., & McDonnell, J. J. (2016). Substantial proportion of global streamflow less than three months old. *Nature Geoscience*, 9(2), 126–129. <https://doi.org/10.1038/ngeo2636>
- Jasechko, S., Perrone, D., Befus, K. M., Bayani Cardenas, M., Ferguson, G., Gleeson, T., et al. (2017). Global aquifers dominated by fossil groundwaters but wells vulnerable to modern contamination. *Nature Geoscience*, 10(6), 425–429. <https://doi.org/10.1038/ngeo2943>
- Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E., & Marshall, L. A. (2009). Hydrologic connectivity between landscapes and streams: Transferring reach-and plot-scale understanding to the catchment scale. *Water Resources Research*, 45, W04428. <https://doi.org/10.1029/2008WR007225>
- Katsuyama, M., Tani, M., & Nishimoto, S. (2010). Connection between streamwater mean residence time and bedrock groundwater recharge/discharge dynamics in weathered granite catchments. *Hydrological Processes*, 24(16), 2287–2299. <https://doi.org/10.1002/hyp.7741>
- Kavetski, D., Kuczera, G., & Franks, S. W. (2006). Bayesian analysis of input uncertainty in hydrological modeling: 1. Theory. *Water Resources Research*, 42, W03407. <https://doi.org/10.1029/2005WR004368>
- Kazda, M., & Schmid, I. (2009). Clustered distribution of tree roots and soil water exploitation. In U. Lüttge, et al. (Eds.), *Progress in Botany*, (pp. 223–239). Berlin, Germany: Springer. https://doi.org/10.1007/978-3-540-68421-3_10
- Keim, R. F., Skaugset, A. E., & Weiler, M. (2005). Temporal persistence of spatial patterns in throughfall. *Journal of Hydrology*, 314(1-4), 263–274. <https://doi.org/10.1016/j.jhydrol.2005.03.021>
- Keim, R. F., Skaugset, A. E., & Weiler, M. (2006). Storage of water on vegetation under simulated rainfall of varying intensity. *Advances in Water Resources*, 29(7), 974–986. <https://doi.org/10.1016/j.advwatres.2005.07.017>
- Kim, M., Pangle, L. A., Cardoso, C., Lora, M., Volkmann, T. H. M., Wang, Y., et al. (2016). Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability. *Water Resources Research*, 52, 7105–7129. <https://doi.org/10.1002/2016WR018620>
- Kipfer, R., Aeschbach-Hertig, W., Peeters, F., & Stute, M. (2002). Noble gases in lakes and ground waters. *Reviews in Mineralogy and Geochemistry*, 47(1), 615–700. <https://doi.org/10.2138/rmg.2002.47.14>
- Kirchner, J. W. (2003). A double paradox in catchment hydrology and geochemistry. *Hydrological Processes*, 17(4), 871–874. <https://doi.org/10.1002/Hyp.5108>
- Kirchner, J. W. (2006). Getting the right answers for the right reasons: Linking measurements, analyses, and models to advance the science of hydrology. *Water Resources Research*, 42, W03S04. <https://doi.org/10.1029/2005WR004362>
- Kirchner, J. W. (2016a). Aggregation in environmental systems - Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. *Hydrology and Earth System Sciences*, 20(1), 279–297. <https://doi.org/10.5194/hess-20-279-2016>
- Kirchner, J. W. (2016b). Aggregation in environmental systems—Part 2: Catchment mean transit times and young water fractions under hydrologic nonstationarity. *Hydrology and Earth System Sciences*, 20(1), 299–328. <https://doi.org/10.5194/hess-20-299-2016>

- Kirchner, J. W. (2019). Quantifying new water fractions and transit time distributions using ensemble hydrograph separation: theory and benchmark tests. *Hydrology and Earth System Sciences*, 23(1), 303–349. <https://doi.org/10.5194/hess-23-303-2019>
- Kirchner, J. W., Feng, X. H., & Neal, C. (2000). Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, 403(6769), 524–527. <https://doi.org/10.1038/35000537>
- Kirchner, J. W., Feng, X. H., & Neal, C. (2001). Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. *Journal of Hydrology*, 254(1–4), 82–101. [https://doi.org/10.1016/S0022-1694\(01\)00487-5](https://doi.org/10.1016/S0022-1694(01)00487-5)
- Klaus, J., Chun, K. P., McGuire, K. J., & McDonnell, J. J. (2015). Temporal dynamics of catchment transit times from stable isotope data. *Water Resources Research*, 51, 4208–4223. <https://doi.org/10.1002/2014WR016247>
- Klaus, J., & McDonnell, J. J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. *Journal of Hydrology*, 505, 47–64. <https://doi.org/10.1016/j.jhydrol.2013.09.006>
- Klaus, J., Zehe, E., Elsner, M., Külls, C., & McDonnell, J. J. (2013). Macropore flow of old water revisited: Experimental insights from a tile-drained hillslope. *Hydrology and Earth System Sciences*, 17(1), 103–118. <https://doi.org/10.5194/hess-17-103-2013>
- Kleidon, A., & Heimann, M. (1998). A method of determining rooting depth from a terrestrial biosphere model and its impacts on the global water and carbon cycle. *Global Change Biology*, 4(3), 275–286. <https://doi.org/10.1046/j.1365-2486.1998.00152.x>
- Kluge, T., von Rohden, C., Sonntag, P., Lorenz, S., Wieser, M., Aeschbach-Hertig, W., & Ilmberger, J. (2012). Localising and quantifying groundwater inflow into lakes using high-precision ²²²Rn profiles. *Journal of Hydrology*, 450–451, 70–81. <https://doi.org/10.1016/j.jhydrol.2012.05.026>
- Knighton, J., Saia, S. M., Morris, C. K., Archibald, J. A., & Walter, M. T. (2017). Ecohydrologic considerations for modeling of stable water isotopes in a small intermittent watershed. *Hydrological Processes*, 31(13), 2438–2452. <https://doi.org/10.1002/hyp.11194>
- Koeniger, P., Gaj, M., Beyer, M., & Himmelsbach, T. (2016). Review on soil water isotope based groundwater recharge estimations. *Hydrological Processes*, 30(16), 2817–2834. <https://doi.org/10.1002/hyp.10775>
- Koeniger, P., Leibundgut, C., Link, T., & Marshall, J. D. (2010). Stable isotopes applied as water tracers in column and field studies. *Organic Geochemistry*, 41(1), 31–40. <https://doi.org/10.1016/j.orggeochem.2009.07.006>
- Korzun, V. I., Sokolov, A. A., Budyko, M. I., Voskresensky, K. P., Kalinin, G. P., Konoplyantsev, A. A., et al. (1978). *World water balance and water resources of the earth*. Studies and Reports in Hydrology (UNESCO). UNESCO Press.
- Kreft, A., & Zuber, A. (1978). On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. *Chemical Engineering Science*, 33(11), 1471–1480. [https://doi.org/10.1016/0009-2509\(78\)85196-3](https://doi.org/10.1016/0009-2509(78)85196-3)
- Kuppel, S., Tetzlaff, D., Maneta, M. P., & Soulsby, C. (2018). EcH2O-iso 1.0: Water isotopes and age tracking in a process-based, distributed ecohydrological model. *Geoscientific Model Development*, 11(7), 3045–3069. <https://doi.org/10.5194/gmd-11-3045-2018>
- Läderach, A., & Sodemann, H. (2016). A revised picture of the atmospheric moisture residence time. *Geophysical Research Letters*, 43, 924–933. <https://doi.org/10.1002/2015GL067449>
- Landsberg, J., Waring, R., & Ryan, M. (2017). Water relations in tree physiology: Where to from here? *Tree Physiology*, 37(1), 18–32. <https://doi.org/10.1093/treephys/tpw102>
- Larcher, W. (2003). *Physiological plant ecology*. Berlin, Germany: Springer. <https://doi.org/10.1007/978-3-662-05214-3>
- Legout, C., Molenat, J., Aquilina, L., Gascuel-Oudou, C., Faucheu, M., Fauvel, Y., & Bariac, T. (2007). Solute transfer in the unsaturated zone-groundwater continuum of a headwater catchment. *Journal of Hydrology*, 332(3–4), 427–441. <https://doi.org/10.1016/j.jhydrol.2006.07.017>
- Leibundgut, C., Maloszewski, P., & Külls, C. (2009). *Tracers in hydrology*. Chichester, UK: John Wiley & Sons, Ltd. <https://doi.org/10.1002/9780470747148>
- Lewis, S., & Nir, A. (1978). On tracer theory in geophysical systems in the steady and non-steady state Part II. Non-steady state-theoretical introduction. *Tellus*, 30(3), 260–271. <https://doi.org/10.1111/j.2153-3490.1978.tb00841.x>
- Libby, W. F. (1953). The potential usefulness of natural tritium. *Proceedings of the National Academy of Sciences*, 39(4), 245–247. <https://doi.org/10.1073/pnas.39.4.245>
- Limm, E. B., Simonin, K. A., Bothman, A. G., & Dawson, T. E. (2009). Foliar water uptake: A common water acquisition strategy for plants of the redwood forest. *Oecologia*, 161(3), 449–459. <https://doi.org/10.1007/s00442-009-1400-3>
- Lu, Z.-T., Schlosser, P., Smethie, W. M. Jr., Sturchio, N. C., Fischer, T. P., Kennedy, B. M., et al. (2014). Tracer applications of noble gas radionuclides in the geosciences. *Earth-Science Reviews*, 138, 196–214. <https://doi.org/10.1016/j.earscirev.2013.09.002>
- Maher, K. (2010). The dependence of chemical weathering rates on fluid residence time. *Earth and Planetary Science Letters*, 294(1–2), 101–110. <https://doi.org/10.1016/j.epsl.2010.03.010>
- Maloszewski, P., Rauert, W., Stichler, W., & Herrmann, A. (1983). Application of flow models in an alpine catchment area using tritium and deuterium data. *Journal of Hydrology*, 66(1–4), 319–330. [https://doi.org/10.1016/0022-1694\(83\)90193-2](https://doi.org/10.1016/0022-1694(83)90193-2)
- Maloszewski, P., Stichler, W., Zuber, A., & Rank, D. (2002). Identifying the flow systems in a karstic-fissured-porous aquifer, the Schneealpe, Austria, by modelling of environmental ¹⁸O and ³H isotopes. *Journal of Hydrology*, 256(1–2), 48–59. [https://doi.org/10.1016/S0022-1694\(01\)00526-1](https://doi.org/10.1016/S0022-1694(01)00526-1)
- Maloszewski, P., & Zuber, A. (1982). Determining the turnover time of groundwater systems with the aid of environmental tracers. *Journal of Hydrology*, 57(3–4), 207–231. [https://doi.org/10.1016/0022-1694\(82\)90147-0](https://doi.org/10.1016/0022-1694(82)90147-0)
- Massoudieh, A., Sharifi, S., & Solomon, D. K. (2012). Bayesian evaluation of groundwater age distribution using radioactive tracers and anthropogenic chemicals. *Water Resources Research*, 48, W09529. <https://doi.org/10.1029/2012WR011815>
- Massoudieh, A., Visser, A., Sharifi, S., & Broers, H. P. (2014). A Bayesian modeling approach for estimation of a shape-free groundwater age distribution using multiple tracers. *Applied Geochemistry*, 50, 252–264. <https://doi.org/10.1016/j.apgeochem.2013.10.004>
- Matsumoto, T., Chen, Z., Wei, W., Yang, G.-M., Hu, S.-M., & Zhang, X. (2018). Application of combined ⁸¹Kr and ⁴He chronometers to the dating of old groundwater in a tectonically active region of the North China Plain. *Earth and Planetary Science Letters*, 493, 208–217. <https://doi.org/10.1016/j.epsl.2018.04.042>
- Maxwell, R. M., Condon, L. E., Kollet, S. J., Maher, K., Haggerty, R., & Forrester, M. M. (2016). The imprint of climate and geology on the residence times of groundwater. *Geophysical Research Letters*, 43, 701–708. <https://doi.org/10.1002/2015GL066916>
- McCallum, J. L., Cook, P. G., & Simmons, C. T. (2015). Limitations of the use of environmental tracers to infer groundwater age. *Ground Water*, 53(S1), 56–70. <https://doi.org/10.1111/gwat.12237>
- McCallum, J. L., Engdahl, N. B., Ginn, T. R., & Cook, P. G. (2014). Nonparametric estimation of groundwater residence time distributions: What can environmental tracer data tell us about groundwater residence time? *Water Resources Research*, 50, 2022–2038. <https://doi.org/10.1002/2013WR014974>
- McDonnell, J. J. (2017). Beyond the water balance. *Nature Geoscience*, 10(6), 396. <https://doi.org/10.1038/ngeo2964>

- McDonnell, J. J., & Beven, K. (2014). Debates—The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph. *Water Resources Research*, *50*, 5342–5350. <https://doi.org/10.1002/2013WR015141>
- McDonnell, J. J., McGuire, K., Aggarwal, P., Beven, K. J., Biondi, D., Destouni, G., et al. (2010). How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis. *Hydrological Processes*, *24*(12), 1745–1754. <https://doi.org/10.1002/Hyp.7796>
- McDonnell, J. J., Stewart, M. K., & Owens, I. F. (1991). Effect of catchment-scale subsurface mixing on stream isotopic response. *Water Resources Research*, *27*(12), 3065–3073. <https://doi.org/10.1029/91WR02025>
- McGuire, K. J., & McDonnell, J. J. (2006). A review and evaluation of catchment transit time modeling. *Journal of Hydrology*, *330*(3-4), 543–563. <https://doi.org/10.1016/j.jhydrol.2006.04.020>
- McGuire, K. J., McDonnell, J. J., Weiler, M., Kendall, C., McGlynn, B. L., Welker, J. M., & Seibert, J. (2005). The role of topography on catchment-scale water residence time. *Water Resources Research*, *41*, W05002. <https://doi.org/10.1029/2004WR003657>
- McMillan, H., Tetzlaff, D., Clark, M., & Soulsby, C. (2012). Do time-variable tracers aid the evaluation of hydrological model structure? A multimodel approach. *Water Resources Research*, *48*, W05501. <https://doi.org/10.1029/2011WR011688>
- Meinzer, F. C., Brooks, J. R., Domec, J. C., Gartner, B. L., Warren, J. M., Woodruff, D. R., et al. (2006). Dynamics of water transport and storage in conifers studied with deuterium and heat tracing techniques. *Plant, Cell & Environment*, *29*(1), 105–114. <https://doi.org/10.1111/j.1365-3040.2005.01404.x>
- Molina, A. J., Llorens, P., Garcia-Estringana, P., de las Heras, M. M., Cayuela, C., Gallart, F., & Latron, J. (2019). Contributions of throughfall, forest and soil characteristics to near-surface soil water-content variability at the plot scale in a mountainous Mediterranean area. *Science of the Total Environment*, *647*, 1421–1432. <https://doi.org/10.1016/j.scitotenv.2018.08.020>
- Molz, F. J. (1981). Models of water transport in the soil-plant system: A review. *Water Resources Research*, *17*(5), 1245–1260. <https://doi.org/10.1029/WR017i005p01245>
- Munksgaard, N. C., Wurster, C. M., Bass, A., & Bird, M. I. (2012). Extreme short-term stable isotope variability revealed by continuous rainwater analysis. *Hydrological Processes*, *26*(23), 3630–3634. <https://doi.org/10.1002/hyp.9505>
- Muñoz-Villers, L. E., & McDonnell, J. J. (2012). Runoff generation in a steep, tropical montane cloud forest catchment on permeable volcanic substrate. *Water Resources Research*, *48*, W09528. <https://doi.org/10.1029/2011WR011316>
- National Research Council (2001). *Basic research opportunities in Earth science*. Washington, D.C.: National Academies Press.
- Neumann, R. B., & Cardon, Z. G. (2012). The magnitude of hydraulic redistribution by plant roots: a review and synthesis of empirical and modeling studies. *New Phytologist*, *194*(2), 337–352. <https://doi.org/10.1111/j.1469-8137.2012.04088.x>
- Newman, B. D., Osenbrück, K., Aeschbach-Hertig, W., Solomon, D. K., Cook, P., Rózański, K., & Kipfer, R. (2010). Dating of 'young' groundwaters using environmental tracers: Advantages, applications, and research needs. *Isotopes in Environmental and Health Studies*, *46*(3), 259–278. <https://doi.org/10.1080/10256016.2010.514339>
- Niemi, A. J. (1977). Residence time distributions of variable flow processes. *The International Journal of Applied Radiation and Isotopes*, *28*(10-11), 855–860. [https://doi.org/10.1016/0020-708X\(77\)90026-6](https://doi.org/10.1016/0020-708X(77)90026-6)
- Nir, A., & Lewis, S. (1975). On tracer theory in geophysical systems in the steady and non-steady state Part I. *Tellus*, *27*(4), 372–383. <https://doi.org/10.1111/j.2153-3490.1975.tb01688.x>
- Oki, T., Entekhabi, D., & Harrold, T. I. (2004). The global water cycle. In R. S. J. Sparks, & C. J. Hawkesworth (Eds.), *The state of the planet: Frontiers and challenges in geophysics*, IUGG, (Vol. v. 19, pp. 225–237). Washington, DC: American Geophysical Union.
- Oki, T., & Kanae, S. (2006). Global hydrological cycles and world water resources. *Science*, *313*(5790), 1068–1072. <https://doi.org/10.1126/science.1128845>
- Or, D., Lehmann, P., Shahraeeni, E., & Shokri, N. (2013). Advances in soil evaporation physics—A review. *Vadose Zone Journal*, *12*(4). <https://doi.org/10.2136/vzj2012.0163>
- Orlowski, N., Breuer, L., Angeli, N., Boeckx, P., Brumbt, C., Cook, C. S., et al. (2018). Inter-laboratory comparison of cryogenic water extraction systems for stable isotope analysis of soil water. *Hydrology and Earth System Sciences*, *22*(7), 3619–3637. <https://doi.org/10.5194/hess-22-3619-2018>
- Orlowski, N., Pratt, D. L., & McDonnell, J. J. (2016). Intercomparison of soil pore water extraction methods for stable isotope analysis. *Hydrological Processes*, *30*(19), 3434–3449. <https://doi.org/10.1002/hyp.10870>
- Orlowski, N., Winkler, A., McDonnell, J. J., & Breuer, L. (2018). A simple greenhouse experiment to explore the effect of cryogenic water extraction for tracing plant source water. *Ecohydrology*, *11*(5), e1967. <https://doi.org/10.1002/eco.1967>
- Oshun, J., Dietrich, W. E., Dawson, T. E., & Fung, I. (2016). Dynamic, structured heterogeneity of water isotopes inside hillslopes. *Water Resources Research*, *52*, 164–189. <https://doi.org/10.1002/2015WR017485>
- Pangle, L. A., Kim, M., Cardoso, C., Lora, M., Meira Neto, A. A., Volkmann, T. H. M., et al. (2017). The mechanistic basis for storage-dependent age distributions of water discharged from an experimental hillslope. *Water Resources Research*, *53*, 2733–2754. <https://doi.org/10.1002/2016WR019901>
- Penna, D., Hopp, L., Scandellari, F., Allen, S. T., Benettin, P., Beyer, M., et al. (2018). Ideas and perspectives: Tracing ecosystem water fluxes using hydrogen and oxygen stable isotopes—Challenges and opportunities from an interdisciplinary perspective. *Biogeosciences*, *15*(21), 6399–6415. <https://doi.org/10.5194/bg-15-6399-2018>
- Petermann, E., Gibson, J. J., Knöller, K., Pannier, T., Weiß, H., & Schubert, M. (2018). Determination of groundwater discharge rates and water residence time of groundwater-fed lakes by stable isotopes of water (18 O, 2 H) and radon (222 Rn) mass balances. *Hydrological Processes*, *32*(6), 805–816. <https://doi.org/10.1002/hyp.11456>
- Piayda, A., Dubbert, M., Siegwolf, R., Cuntz, M., & Werner, C. (2017). Quantification of dynamic soil-vegetation feedbacks following an isotopically labelled precipitation pulse. *Biogeosciences*, *14*(9), 2293–2306. <https://doi.org/10.5194/bg-14-2293-2017>
- Pierret, A., Moran, C. J., & Pankhurst, C. E. (1999). Differentiation of soil properties related to the spatial association of wheat roots and soil macropores. *Plant and Soil*, *211*(1), 51–58. <https://doi.org/10.1023/A:1004490800536>
- Pinder, G. F., & Celia, M. A. (2006). *Subsurface hydrology*. Hoboken, USA: Wiley. <https://doi.org/10.1002/0470044209>
- Plummer, L. N. (2005). Dating of Young Groundwater. In P. K. Aggarwal, et al. (Eds.), *Isotopes in the water cycle: Past, present and future of a developing science*, (pp. 193–218). Dordrecht, Netherlands: Springer. https://doi.org/10.1007/1-4020-3023-1_14
- Plummer, L. N., Busenberg, E., Böhlke, J. K., Nelms, D. L., Michel, R. L., & Schlosser, P. (2001). Groundwater residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: a multi-tracer approach. *Chemical Geology*, *179*(1-4), 93–111. [https://doi.org/10.1016/S0009-2541\(01\)00317-5](https://doi.org/10.1016/S0009-2541(01)00317-5)
- Porporato, A., & Calabrese, S. (2015). On the probabilistic structure of water age. *Water Resources Research*, *51*, 3588–3600. <https://doi.org/10.1002/2015WR017027>

- Prieto, I., Armas, C., & Pugnaire, F. I. (2012). Water release through plant roots: New insights into its consequences at the plant and ecosystem level. *New Phytologist*, *193*(4), 830–841. <https://doi.org/10.1111/j.1469-8137.2011.04039.x>
- Queloz, P., Bertuzzo, E., Carraro, L., Botter, G., Miglietta, F., Rao, P. S. C., & Rinaldo, A. (2015). Transport of fluorobenzoate tracers in a vegetated hydrologic control volume: 1. Experimental results. *Water Resources Research*, *51*, 2773–2792. <https://doi.org/10.1002/2014WR016433>
- Queloz, P., Carraro, L., Benettin, P., Botter, G., Rinaldo, A., & Bertuzzo, E. (2015). Transport of fluorobenzoate tracers in a vegetated hydrologic control volume: 2. Theoretical inferences and modeling. *Water Resources Research*, *51*, 2793–2806. <https://doi.org/10.1002/2014WR016508>
- Rascher, K. G., Große-Stoltenberg, A., Máguas, C., & Werner, C. (2011). Understorey invasion by *Acacia longifolia* alters the water balance and carbon gain of a Mediterranean Pine Forest. *Ecosystems*, *14*(6), 904–919. <https://doi.org/10.1007/s10021-011-9453-7>
- Remondi, F., Kirchner, J. W., Burlando, P., & Faticchi, S. (2018). Water flux tracking with a distributed hydrological model to quantify controls on the spatio-temporal variability of transit time distributions. *Water Resources Research*, *54*, 3081–3099. <https://doi.org/10.1002/2017WR021689>
- Rempe, D. M., & Dietrich, W. E. (2018). Direct observations of rock moisture, a hidden component of the hydrologic cycle. *Proceedings of the National Academy of Sciences of the United States of America*, *115*(11), 2664–2669. <https://doi.org/10.1073/pnas.1800141115>
- Rinaldo, A., Benettin, P., Harman, C., Hrachowitz, M., McGuire, K., van der Velde, Y., et al. (2015). Storage selection functions: A coherent framework for quantifying how catchments store and release water and solutes. *Water Resources Research*, *51*, 4840–4847. <https://doi.org/10.1002/2015WR017273>
- Rinderer, M., McGlynn, B. L., & van Meerveld, H. J. (2017). Groundwater similarity across a watershed derived from time-warped and flow-corrected time series. *Water Resources Research*, *53*, 3921–3940. <https://doi.org/10.1002/2016WR019856>
- Ritterbusch, F., Ebser, S., Welte, J., Reichel, T., Kersting, A., Purtschert, R., et al. (2014). Groundwater dating with Atom Trap Trace Analysis of ³⁹Ar. *Geophysical Research Letters*, *41*, 6758–6764. <https://doi.org/10.1002/2014GL061120>
- Robinson, D., Hodge, A., & Fitter, A. (2003). Constraints on the form and function of root systems. In H. de Kroon, & E. J. W. Visser (Eds.), *Root Ecology*, (pp. 1–31). Berlin, Germany: Springer. https://doi.org/10.1007/978-3-662-09784-7_1
- Rodell, M., Beaudoing, H. K., L'Ecuyer, T. S., Olson, W. S., Famiglietti, J. S., Houser, P. R., et al. (2015). The observed state of the water cycle in the early twenty-first century. *Journal of Climate*, *28*(21), 8289–8318. <https://doi.org/10.1175/JCLI-D-14-00555.1>
- Rodhe, A., Nyberg, L., & Bishop, K. (1996). Transit times for water in a small till catchment from a steep shift in the oxygen 18 content of the water input. *Water Resources Research*, *32*(12), 3497–3511. <https://doi.org/10.1029/95WR01806>
- Rodríguez, N. B., McGuire, K. J., & Klaus, J. (2018). Time-varying storage-water age relationships in a catchment with a Mediterranean climate. *Water Resources Research*, *54*, 3988–4008. <https://doi.org/10.1029/2017WR021964>
- Rodríguez-Iturbe, I., Porporato, A., Ridolfi, L., Isham, V., & Cox, D. R. (1999). Probabilistic modelling of water balance at a point: The role of climate, soil and vegetation. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *455*(1990), 3789–3805. <https://doi.org/10.1098/rspa.1999.0477>
- Rothfuss, Y., & Javaux, M. (2017). Reviews and syntheses: Isotopic approaches to quantify root water uptake: A review and comparison of methods. *Biogeosciences*, *14*(8), 2199–2224. <https://doi.org/10.5194/bg-14-2199-2017>
- Rothfuss, Y., Merz, S., Vanderborght, J., Hermes, N., Weuthen, A., Pohlmeier, A., et al. (2015). Long-term and high-frequency non-destructive monitoring of water stable isotope profiles in an evaporating soil column. *Hydrology and Earth System Sciences*, *19*(10), 4067–4080. <https://doi.org/10.5194/hess-19-4067-2015>
- Rothfuss, Y., Vereecken, H., & Brüggemann, N. (2013). Monitoring water stable isotopic composition in soils using gas-permeable tubing and infrared laser absorption spectroscopy. *Water Resources Research*, *49*, 3747–3755. <https://doi.org/10.1002/wrcr.20311>
- Rouxel, M., Molénat, J., Ruiz, L., Legout, C., Faucheux, M., & Gascuel-Odoux, C. (2011). Seasonal and spatial variation in groundwater quality along the hillslope of an agricultural research catchment (Western France). *Hydrological Processes*, *25*(6), 831–841. <https://doi.org/10.1002/hyp.7862>
- Rozanski, K. (1985). Deuterium and oxygen-18 in European groundwaters—Links to atmospheric circulation in the past. *Chemical Geology: Isotope Geoscience section*, *52*(3–4), 349–363. [https://doi.org/10.1016/0168-9622\(85\)90045-4](https://doi.org/10.1016/0168-9622(85)90045-4)
- Rudolph-Mohr, N., Vontobel, P., & Oswald, S. E. (2014). A multi-imaging approach to study the root-soil interface. *Annals of botany*, *114*(8), 1779–1787. <https://doi.org/10.1093/aob/mcu200>
- Rueedi, J., Brennwald, M. S., Purtschert, R., Beyerle, U., Hofer, M., & Kipfer, R. (2005). Estimating amount and spatial distribution of groundwater recharge in the Iullemeden basin (Niger) based on ³H, ³He and CFC-11 measurements. *Hydrological Processes*, *19*(17), 3285–3298. <https://doi.org/10.1002/hyp.5970>
- Rühle, F. A., Zentner, N., & Stumpp, C. (2015). Changes in water table level influence solute transport in uniform porous media. *Hydrological Processes*, *29*(6), 875–888. <https://doi.org/10.1002/hyp.10200>
- Sade, N., Gebremedhin, A., & Moshelion, M. (2012). Risk-taking plants: Anisohydric behavior as a stress-resistance trait. *Plant Signaling & Behavior*, *7*(7), 767–770. <https://doi.org/10.4161/psb.20505>
- Salehin, M., Packman, A. I., & Paradis, M. (2004). Hyporheic exchange with heterogeneous streambeds: Laboratory experiments and modeling. *Water Resources Research*, *40*, W11504. <https://doi.org/10.1029/2003WR002567>
- Sandvig, R. M., & Phillips, F. M. (2006). Ecohydrological controls on soil moisture fluxes in arid to semiarid vadose zones. *Water Resources Research*, *42*, W08422. <https://doi.org/10.1029/2005WR004644>
- Sardans, J., & Peñuelas, J. (2014). Hydraulic redistribution by plants and nutrient stoichiometry: Shifts under global change. *Ecohydrology*, *7*(1), 1–20. <https://doi.org/10.1002/eco.1459>
- Savenije, H. H. G., & Hrachowitz, M. (2017). HESS opinions: “Catchments as meta-organisms—A new blueprint for hydrological modeling”. *Hydrology and Earth System Sciences*, *21*(2), 1107–1116. <https://doi.org/10.5194/hess-21-1107-2017>
- Scaini, A., Hissler, C., Fenicia, F., Juilleret, J., Iffy, J. F., Pfister, L., & Beven, K. (2017). Hillslope response to sprinkling and natural rainfall using velocity and celerity estimates in a slate-bedrock catchment. *Journal of Hydrology*, *558*, 366–379. <https://doi.org/10.1016/j.jhydrol.2017.12.011>
- Schenk, H. J., & Jackson, R. B. (2002). Rooting depths, lateral root spreads and below-ground/above-ground allometries of plants in water-limited ecosystems. *Journal of Ecology*, *90*(3), 480–494. <https://doi.org/10.1046/j.1365-2745.2002.00682.x>
- Schenk, H. J., & Jackson, R. B. (2005). Mapping the global distribution of deep roots in relation to climate and soil characteristics. *Geoderma*, *126*(1–2), 129–140. <https://doi.org/10.1016/j.geoderma.2004.11.018>
- Scholes, R. J., & Archer, S. R. (1997). Tree-grass interactions in savannas. *Annual Review of Ecology and Systematics*, *28*(1), 517–544. <https://doi.org/10.1146/annurev.ecolsys.28.1.517>
- Seeger, S., & Weiler, M. (2014). Lumped convolution integral models revisited: On the meaningfulness of inter catchment comparisons. *Hydrology and Earth System Sciences*, *18*(12), 4751–4771. <https://doi.org/10.5194/hess-18-4751-2014>

- Sheets, R. A., Bair, E. S., & Rowe, G. L. (1998). Use of $3\text{H}/3\text{He}$ Ages to evaluate and improve groundwater flow models in a complex buried-valley aquifer. *Water Resources Research*, *34*(5), 1077–1089. <https://doi.org/10.1029/98WR00007>
- Šimůnek, J. (2005). Models of water flow and solute transport in the unsaturated zone. In M. Anderson (Ed.), *Encyclopedia of Hydrological Sciences* (Chap. 78). Lancaster, UK: John Wiley & Sons, Ltd. <https://doi.org/10.1002/0470848944.hsa080>
- Smith, A. A., Tetzlaff, D., & Soulsby, C. (2018). On the use of StorAge Selection functions to assess time-variant travel times in lakes. *Water Resources Research*, *54*, 5163–5185. <https://doi.org/10.1029/2017WR021242>
- Solomon, D. K., Gilmore, T. E., Solder, J. E., Kimball, B., & Genereux, D. P. (2015). Evaluating an unconfined aquifer by analysis of age-dating tracers in stream water. *Water Resources Research*, *51*, 8883–8899. <https://doi.org/10.1002/2015WR017602>
- Song, L., Zhu, J., Li, M., & Yu, Z. (2014). Water utilization of *Pinus sylvestris* var. *mongolica* in a sparse wood grassland in the semiarid sandy region of Northeast China. *Trees*, *28*(4), 971–982. <https://doi.org/10.1007/s00468-014-1010-5>
- Soulsby, C., Birkel, C., Geris, J., Dick, J., Tunaley, C., & Tetzlaff, D. (2015). Stream water age distributions controlled by storage dynamics and nonlinear hydrologic connectivity: Modeling with high-resolution isotope data. *Water Resources Research*, *51*, 7759–7776. <https://doi.org/10.1002/2015WR017888>
- Soulsby, C., Tetzlaff, D., & Hrachowitz, M. (2010). Are transit times useful process-based tools for flow prediction and classification in ungauged basins in montane regions? *Hydrological Processes*, *24*(12), 1685–1696. <https://doi.org/10.1002/Hyp.7578>
- Speed, M., Tetzlaff, D., Soulsby, C., Hrachowitz, M., & Waldron, S. (2010). Isotopic and geochemical tracers reveal similarities in transit times in contrasting mesoscale catchments. *Hydrological Processes*, *24*(9), 1211–1224. <https://doi.org/10.1002/Hyp.7593>
- Sprenger, M., Erhardt, H., Riedel, M., & Weiler, M. (2016). Historical tracking of nitrate in contrasting vineyards using water isotopes and nitrate depth profiles. *Agriculture, Ecosystems & Environment*, *222*, 185–192. <https://doi.org/10.1016/j.agee.2016.02.014>
- Sprenger, M., Herbstritt, B., & Weiler, M. (2015). Established methods and new opportunities for pore water stable isotope analysis. *Hydrological Processes*, *29*(25), 5174–5192. <https://doi.org/10.1002/hyp.10643>
- Sprenger, M., Leistert, H., Gimbel, K., & Weiler, M. (2016). Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. *Reviews of Geophysics*, *54*, 674–704. <https://doi.org/10.1002/2015RG000515>
- Sprenger, M., Llorens, P., Cayuela, C., Gallart, F., & Latron, J. (2019). Mechanisms of consistently disconnected soil water pools over (pore) space and time. *Hydrology and Earth System Sciences Discussions*, 1–18. <https://doi.org/10.5194/hess-2019-143>
- Sprenger, M., Seeger, S., Blume, T., & Weiler, M. (2016). Travel times in the vadose zone: Variability in space and time. *Water Resources Research*, *52*, 5727–5754. <https://doi.org/10.1002/2015WR018077>
- Sprenger, M., Tetzlaff, D., Buttle, J., Laudon, H., Leistert, H., Mitchell, C. P. J., et al. (2018). Measuring and modelling stable isotopes of mobile and bulk soil water. *Vadose Zone Journal*, *17*(1). <https://doi.org/10.2136/VZJ2017.08.0149>
- Sprenger, M., Tetzlaff, D., Buttle, J., Laudon, H., & Soulsby, C. (2018). Water ages in the critical zone of long-term experimental sites in northern latitudes. *Hydrology and Earth System Sciences*, *22*(7), 3965–3981. <https://doi.org/10.5194/hess-22-3965-2018>
- Sprenger, M., Tetzlaff, D., & Soulsby, C. (2017). Soil water stable isotopes reveal evaporation dynamics at the soil-plant-atmosphere interface of the critical zone. *Hydrology and Earth System Sciences*, *21*(7), 3839–3858. <https://doi.org/10.5194/hess-21-3839-2017>
- Sprenger, M., Tetzlaff, D., Tunaley, C., Dick, J., & Soulsby, C. (2017). Evaporation fractionation in a peatland drainage network affects stream water isotope composition. *Water Resources Research*, *53*, 851–866. <https://doi.org/10.1002/2016WR019258>
- Sprenger, M., Volkmann, T. H. M., Blume, T., & Weiler, M. (2015). Estimating flow and transport parameters in the unsaturated zone with pore water stable isotopes. *Hydrology and Earth System Sciences*, *19*(6), 2617–2635. <https://doi.org/10.5194/hess-19-2617-2015>
- Staudinger, M., Stoelzle, M., Cochand, F., Seibert, J., Weiler, M., & Hunkeler, D. (2019). Your work is my boundary condition! Challenges and approaches for a closer collaboration between hydrologists and hydrogeologists. *Journal of Hydrology*, *571*, 235–243. <https://doi.org/10.1016/j.jhydrol.2019.01.058>
- Stewart, J. B., Moran, C. J., & Wood, J. T. (1999). Macropore sheath: Quantification of plant root and soil macropore association. *Plant and Soil*, *211*(1), 59–67. <https://doi.org/10.1023/A:1004405422847>
- Stewart, M. K., Morgenstern, U., & McDonnell, J. J. (2010). Truncation of stream residence time: how the use of stable isotopes has skewed our concept of streamwater age and origin. *Hydrological Processes*, *24*(12), 1646–1659. <https://doi.org/10.1002/hyp.7576>
- Stichler, W., & Schotterer, U. (2000). From accumulation to discharge: Modification of stable isotopes during glacial and post-glacial processes. *Hydrological Processes*, *14*(8), 1423–1438. [https://doi.org/10.1002/1099-1085\(20000615\)14:8<1423::AID-HYP991>3.0.CO;2-X](https://doi.org/10.1002/1099-1085(20000615)14:8<1423::AID-HYP991>3.0.CO;2-X)
- Stockinger, M. P., Bogena, H. R., Lücke, A., Diekkrüger, B., Cornelissen, T., & Vereecken, H. (2016). Tracer sampling frequency influences estimates of young water fraction and streamwater transit time distribution. *Journal of Hydrology*, *541*, 952–964. <https://doi.org/10.1016/j.jhydrol.2016.08.007>
- Stockinger, M. P., Bogena, H. R., Lücke, A., Diekkrüger, B., Weiler, M., & Vereecken, H. (2014). Seasonal soil moisture patterns: Controlling transit time distributions in a forested headwater catchment. *Water Resources Research*, *50*, 5270–5289. <https://doi.org/10.1002/2013WR014815>
- Stockinger, M. P., Lücke, A., McDonnell, J. J., Diekkrüger, B., Vereecken, H., & Bogena, H. R. (2015). Interception effects on stable isotope driven streamwater transit time estimates. *Geophysical Research Letters*, *42*, 5299–5308. <https://doi.org/10.1002/2015GL064622>
- Stoelzle, M., Stahl, K., & Weiler, M. (2013). Are streamflow recession characteristics really characteristic? *Hydrology and Earth System Sciences*, *17*(2), 817–828. <https://doi.org/10.5194/hess-17-817-2013>
- Stolp, B. J., Solomon, D. K., Suckow, A., Vitvar, T., Rank, D., Aggarwal, P. K., & Han, L. F. (2010). Age dating base flow at springs and gaining streams using helium-3 and tritium: Fischa-Dagnitz system, southern Vienna Basin, Austria. *Water Resources Research*, *46*, W07503. <https://doi.org/10.1029/2009WR008006>
- Stone, E. L., & Kalisz, P. J. (1991). On the maximum extent of tree roots. *Forest Ecology and Management*, *46*(1–2), 59–102. [https://doi.org/10.1016/0378-1127\(91\)90245-Q](https://doi.org/10.1016/0378-1127(91)90245-Q)
- Stumpp, C., & Maloszewski, P. (2010). Quantification of preferential flow and flow heterogeneities in an unsaturated soil planted with different crops using the environmental isotope $\delta^{18}\text{O}$. *Journal of Hydrology*, *394*(3–4), 407–415. <https://doi.org/10.1016/j.jhydrol.2010.09.014>
- Stumpp, C., Maloszewski, P., Stichler, W., & Fank, J. (2009). Environmental isotope ($\delta^{18}\text{O}$) and hydrological data to assess water flow in unsaturated soils planted with different crops: Case study lysimeter station “Wagna” (Austria). *Journal of Hydrology*, *369*(1–2), 198–208. <https://doi.org/10.1016/j.jhydrol.2009.02.047>
- Stumpp, C., Maloszewski, P., Stichler, W., & Maciejewski, S. (2007). Quantification of the heterogeneity of the unsaturated zone based on environmental deuterium observed in lysimeter experiments. *Hydrological Sciences Journal*, *52*(4), 748–762. <https://doi.org/10.1623/hysj.52.4.748>
- Stumpp, C., Nützmann, G., Maciejewski, S., & Maloszewski, P. (2009). A comparative modeling study of a dual tracer experiment in a large lysimeter under atmospheric conditions. *Journal of Hydrology*, *375*(3–4), 566–577. <https://doi.org/10.1016/j.jhydrol.2009.07.010>

- Stumpp, C., Stichler, W., Kandolf, M., & Šimůnek, J. (2012). Effects of land cover and fertilization method on water flow and solute transport in five lysimeters: A long-term study using stable water isotopes. *Vadose Zone Journal*, 11(1). <https://doi.org/10.2136/vzj2011.0075>
- Stumpp, C., Stichler, W., & Maloszewski, P. (2009). Application of the environmental isotope $\delta^{18}\text{O}$ to study water flow in unsaturated soils planted with different crops: Case study of a weighable lysimeter from the research field in Neuherberg, Germany. *Journal of Hydrology*, 368(1-4), 68–78. <https://doi.org/10.1016/j.jhydrol.2009.01.027>
- Sturm, N., Reber, S., Kessler, A., & Tenhunen, J. D. (1996). Soil moisture variation and plant water stress at the Hartheim Scots pine plantation. *Theoretical and Applied Climatology*, 53(1-3), 123–133. <https://doi.org/10.1007/BF00866417>
- Suckow, A. (2014). The age of groundwater—Definitions, models and why we do not need this term. *Applied Geochemistry*, 50, 222–230. <https://doi.org/10.1016/j.apgeochem.2014.04.016>
- Suckow, A., Aggarwal, P. K., & Araguás Araguás, L. (Eds) (2013). *Isotope methods for dating old groundwater*. Vienna, Austria: International Atomic Energy Agency.
- Taniguchi, M., Burnett, W. C., Cable, J. E., & Turner, J. V. (2002). Investigation of submarine groundwater discharge. *Hydrological Processes*, 16(11), 2115–2129. <https://doi.org/10.1002/hyp.1145>
- Tardieu, F., & Simonneau, T. (1998). Variability among species of stomatal control under fluctuating soil water status and evaporative demand: Modelling isohydric and anisohydric behaviours. *Journal of experimental botany*, 49(Special), 419–432. https://doi.org/10.1093/jxb/49.Special_Issue.419
- Taylor, S., Feng, X., Kirchner, J. W., Osterhuber, R., Klaue, B., & Renshaw, C. E. (2001). Isotopic evolution of a seasonal snowpack and its melt. *Water Resources Research*, 37(3), 759–769. <https://doi.org/10.1029/2000WR900341>
- Taylor, S., Feng, X., Renshaw, C. E., & Kirchner, J. W. (2002). Isotopic evolution of snowmelt 2. Verification and parameterization of a one-dimensional model using laboratory experiments. *Water Resources Research*, 38(10), 1218. <https://doi.org/10.1029/2001WR000815>
- Tetzlaff, D., Birkel, C., Dick, J., Geris, J., & Soulsby, C. (2014). Storage dynamics in hydrogeological units control hillslope connectivity, runoff generation and the evolution of catchment transit time distributions. *Water Resources Research*, 50, 969–985. <https://doi.org/10.1002/2013WR014147>
- Thomas, E. M., Lin, H., Duffy, C. J., Sullivan, P. L., Holmes, G. H., Brantley, S. L., & Jin, L. (2013). Spatiotemporal patterns of water stable isotope compositions at the Shale Hills Critical Zone Observatory: Linkages to subsurface hydrologic processes. *Vadose Zone Journal*, 12(4). <https://doi.org/10.2136/vzj2013.01.0029>
- Thomas, S. C., & Winner, W. E. (2002). Photosynthetic differences between saplings and adult trees: An integration of field results by meta-analysis. *Tree Physiology*, 22(2-3), 117–127. <https://doi.org/10.1093/treephys/22.2-3.117>
- Timbe, E., Windhorst, D., Crespo, P., Frede, H.-G., Feyen, J., & Breuer, L. (2014). Understanding uncertainties when inferring mean transit times of water trough tracer-based lumped-parameter models in Andean tropical montane cloud forest catchments. *Hydrology and Earth System Sciences*, 18(4), 1503–1523. <https://doi.org/10.5194/hess-18-1503-2014>
- Troch, P. A., Carrillo, G. A., Heidebüchel, I., Rajagopal, S., Switanek, M., Volkman, T. H. M., & Yaeger, M. (2009). Dealing with landscape heterogeneity in watershed hydrology: A review of recent progress toward new hydrological theory. *Geography Compass*, 3(1), 375–392. <https://doi.org/10.1111/j.1749-8198.2008.00186.x>
- Trolborg, L., Jensen, K. H., Engesgaard, P., Refsgaard, J. C., & Hinsby, K. (2008). Using environmental tracers in modeling flow in a complex shallow aquifer system. *Journal of Hydrologic Engineering*, 13(11), 1037–1048. [https://doi.org/10.1061/\(ASCE\)1084-0699\(2008\)13:11\(1037\)](https://doi.org/10.1061/(ASCE)1084-0699(2008)13:11(1037))
- Turnadge, C., & Smerdon, B. D. (2014). A review of methods for modelling environmental tracers in groundwater: Advantages of tracer concentration simulation. *Journal of Hydrology*, 519, 3674–3689. <https://doi.org/10.1016/j.jhydrol.2014.10.056>
- Tyree, M. T., & Zimmermann, M. H. (2002). *Xylem structure and the ascent of sap*, Springer Series in Wood Science. Berlin, Germany: Springer.
- Uchida, T., McDonnell, J. J., & Asano, Y. (2006). Functional intercomparison of hillslopes and small catchments by examining water source, flowpath and mean residence time. *Journal of Hydrology*, 327(3-4), 627–642. <https://doi.org/10.1016/j.jhydrol.2006.02.037>
- van der Ent, R. J., & Tuinenburg, O. A. (2017). The residence time of water in the atmosphere revisited. *Hydrology and Earth System Sciences*, 21(2), 779–790. <https://doi.org/10.5194/hess-21-779-2017>
- van Geldern, R., Baier, A., Subert, H. L., Kowol, S., Balk, L., & Barth, J. A. C. (2014). Pleistocene paleo-groundwater as a pristine fresh water resource in southern Germany—Evidence from stable and radiogenic isotopes. *Science of The Total Environment*, 496, 107–115. <https://doi.org/10.1016/j.scitotenv.2014.07.011>
- Vargas, A. I., Schaffer, B., Yuhong, L., & Sternberg, L. D. S. L. (2017). Testing plant use of mobile vs immobile soil water sources using stable isotope experiments. *New Phytologist*, 215(2), 582–594. <https://doi.org/10.1111/nph.14616>
- Varni, M., & Carrera, J. (1998). Simulation of groundwater age distributions. *Water Resources Research*, 34(12), 3271–3281. <https://doi.org/10.1029/98WR02536>
- van der Velde, Y., de Rooij, G. H., Rozemeijer, J. C., van Geer, F. C., & Broers, H. P. (2010). Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics. *Water Resources Research*, 46, W11534. <https://doi.org/10.1029/2010wr009105>
- van der Velde, Y., Heidebüchel, I., Lyon, S. W., Nyberg, L., Rodhe, A., Bishop, K., & Troch, P. A. (2015). Consequences of mixing assumptions for time-variable travel time distributions. *Hydrological Processes*, 29(16), 3460–3474. <https://doi.org/10.1002/hyp.10372>
- van der Velde, Y., Torfs, P. J. J. F., van der Zee, S. E. A. T. M., & Uijlenhoet, R. (2012). Quantifying catchment-scale mixing and its effect on time-varying travel time distributions. *Water Resources Research*, 48, W06536. <https://doi.org/10.1029/2011WR011310>
- van Huijgevoort, M. H. J., Tetzlaff, D., Sutanudjaja, E. H., & Soulsby, C. (2016). Using high resolution tracer data to constrain water storage, flux and age estimates in a spatially distributed rainfall-runoff model. *Hydrological Processes*, 30(25), 4761–4778. <https://doi.org/10.1002/hyp.10902>
- Visser, A., Broers, H. P., Purtschert, R., Sültenfuß, J., & de Jonge, M. (2013). Groundwater age distributions at a public drinking water supply well field derived from multiple age tracers (85Kr, 3H/3He, and 39Ar). *Water Resources Research*, 49, 7778–7796. <https://doi.org/10.1002/2013WR014012>
- Visser, A., Heerdink, R., Broers, H. P., & Bierkens, M. F. P. (2009). Travel time distributions derived from particle tracking in models containing weak sinks. *Ground water*, 47(2), 237–245. <https://doi.org/10.1111/j.1745-6584.2008.00542.x>
- Visser, A., Thaw, M., Deinhard, A., Bibby, R., Safeeq, M., Conklin, M., et al. (2019). Cosmogenic isotopes unravel the hydrochronology and water storage dynamics of the Southern Sierra Critical Zone. *Water Resources Research*, 55, 1429–1450. <https://doi.org/10.1029/2018WR023665>

- Volkman, T. H. M., Haberer, K., Gessler, A., & Weiler, M. (2016). High-resolution isotope measurements resolve rapid ecohydrological dynamics at the soil-plant interface. *New Phytologist*, *210*(3), 839–849. <https://doi.org/10.1111/nph.13868>
- Volkman, T. H. M., Kuhnhammer, K., Herbstritt, B., Gessler, A., & Weiler, M. (2016). A method for in situ monitoring of the isotope composition of tree xylem water using laser spectroscopy. *Plant, Cell & Environment*, *39*(9), 2055–2063. <https://doi.org/10.1111/pce.12725>
- Volkman, T. H. M., & Weiler, M. (2014). Continual in-situ monitoring of pore water stable isotopes in the subsurface. *Hydrology and Earth System Sciences*, *18*(5), 1819–1833. <https://doi.org/10.5194/hess-18-1819-2014>
- von Buttlar, H. (1959). Ground-water studies in New Mexico using tritium as a tracer: II. *Journal of Geophysical Research*, *64*(8), 1031–1038. <https://doi.org/10.1029/JZ064i008p01031>
- von Freyberg, J., Allen, S. T., Seeger, S., Weiler, M., & Kirchner, J. W. (2018). Sensitivity of young water fractions to hydro-climatic forcing and landscape properties across 22 Swiss catchments. *Hydrology and Earth System Sciences*, *22*(7), 3841–3861. <https://doi.org/10.5194/hess-22-3841-2018>
- von Freyberg, J., Studer, B., & Kirchner, J. W. (2017). A lab in the field: High-frequency analysis of water quality and stable isotopes in stream water and precipitation. *Hydrology and Earth System Sciences*, *21*(3), 1721–1739. <https://doi.org/10.5194/hess-21-1721-2017>
- Vrugt, J. A., ter Braak, C. J. F., Clark, M. P., Hyman, J. M., & Robinson, B. A. (2008). Treatment of input uncertainty in hydrologic modeling: Doing hydrology backward with Markov chain Monte Carlo simulation. *Water Resources Research*, *44*, W00B09. <https://doi.org/10.1029/2007WR006720>
- Wachniew, P., Zurek, A. J., Stumpp, C., Gemtzi, A., Gargini, A., Filippini, M., et al. (2016). Toward operational methods for the assessment of intrinsic groundwater vulnerability: A review. *Critical Reviews in Environmental Science and Technology*, *46*(9), 827–884. <https://doi.org/10.1080/10643389.2016.1160816>
- Wang, L., Caylor, K. K., Villegas, J. C., Barron-Gafford, G. A., Breshears, D. D., & Huxman, T. E. (2010). Partitioning evapotranspiration across gradients of woody plant cover: Assessment of a stable isotope technique. *Geophysical Research Letters*, *37*, L09401. <https://doi.org/10.1029/2010GL043228>
- Wang, L., van Meerveld, H., & Seibert, J. (2018). Effect of observation errors on the timing of the most informative isotope samples for event-based model calibration. *Hydrology*, *5*(1), 4. <https://doi.org/10.3390/hydrology5010004>
- Wang, P., Song, X., Han, D., Zhang, Y., & Zhang, B. (2012). Determination of evaporation, transpiration and deep percolation of summer corn and winter wheat after irrigation. *Agricultural Water Management*, *105*, 32–37. <https://doi.org/10.1016/j.agwat.2011.12.024>
- Weiler, M., & Fluhler, H. (2004). Inferring flow types from dye patterns in macroporous soils. *Geoderma*, *120*(1–2), 137–153. <https://doi.org/10.1016/j.geoderma.2003.08.014>
- Weiler, M., & McDonnell, J. (2004). Virtual experiments: A new approach for improving process conceptualization in hillslope hydrology. *Journal of Hydrology*, *285*(1–4), 3–18. [https://doi.org/10.1016/S0022-1694\(03\)00271-3](https://doi.org/10.1016/S0022-1694(03)00271-3)
- Weiler, M., McGlynn, B. L., McGuire, K. J., & McDonnell, J. J. (2003). How does rainfall become runoff?: A combined tracer and runoff transfer function approach. *Water Resources Research*, *39*(11), 1315. <https://doi.org/10.1029/2003WR002331>
- Weiler, M., & Naef, F. (2003). An experimental tracer study of the role of macropores in infiltration in grassland soils. *Hydrological Processes*, *17*(2), 477–493. <https://doi.org/10.1002/Hyp.1136>
- Werner, C., Correia, O., & Beyschlag, W. (2002). Characteristic patterns of chronic and dynamic photoinhibition of different functional groups in a Mediterranean ecosystem. *Functional Plant Biology*, *29*(8), 999–1011. <https://doi.org/10.1071/PP01143>
- Werner, C., & Dubbert, M. (2016). Resolving rapid dynamics of soil-plant-atmosphere interactions. *New Phytologist*, *210*(3), 767–769. <https://doi.org/10.1111/nph.13936>
- West, A. G., Dawson, T. E., February, E. C., Midgley, G. F., Bond, W. J., & Aston, T. L. (2012). Diverse functional responses to drought in a Mediterranean-type shrubland in South Africa. *New Phytologist*, *195*(2), 396–407. <https://doi.org/10.1111/j.1469-8137.2012.04170.x>
- Wilusz, D. C., Harman, C. J., & Ball, W. P. (2017). Sensitivity of catchment transit times to rainfall variability under present and future climates. *Water Resources Research*, *53*, 10,231–10,256. <https://doi.org/10.1002/2017WR020894>
- WMO (2009). Manual on low-flow estimation and prediction, operational hydrology report No. 50. Geneva, Switzerland: World Meteorological Organization.
- Wörman, A., Packman, A. I., Marklund, L., Harvey, J. W., & Stone, S. H. (2007). Fractal topography and subsurface water flows from fluvial bedforms to the continental shield. *Geophysical Research Letters*, *34*, L07402. <https://doi.org/10.1029/2007GL029426>
- Wullschlegel, S. D., Meinzer, F. C., & Vertessy, R. A. (1998). A review of whole-plant water use studies in tree. *Tree Physiology*, *18*(8–9), 499–512. <https://doi.org/10.1093/treephys/18.8-9.499>
- Yang, J., Chen, H., Nie, Y., Zhang, W., & Wang, K. (2016). Spatial variability of shallow soil moisture and its stable isotope values on a karst hillslope. *Geoderma*, *264*, 61–70. <https://doi.org/10.1016/j.geoderma.2015.10.003>
- Yang, J., Heidbüchel, I., Musolff, A., Reinstorf, F., & Fleckenstein, J. H. (2018). Exploring the dynamics of transit times and subsurface mixing in a small agricultural catchment. *Water Resources Research*, *54*, 2317–2335. <https://doi.org/10.1002/2017WR021896>
- Yang, Y., Donohue, R. J., & McVicar, T. R. (2016). Global estimation of effective plant rooting depth: Implications for hydrological modeling. *Water Resources Research*, *52*, 8260–8276. <https://doi.org/10.1002/2016WR019392>
- Yecheili, Y., Yokochi, R., Zilberbrand, M., Lu, Z.-T., Purtschert, R., Sueltenfuss, J., et al. (2019). Recent seawater intrusion into deep aquifer determined by the radioactive noble-gas isotopes ^{81}Kr and ^{39}Ar . *Earth and Planetary Science Letters*, *507*, 21–29. <https://doi.org/10.1016/j.epsl.2018.11.028>
- Zapata-Rios, X., McIntosh, J., Rademacher, L., Troch, P. A., Brooks, P. D., Rasmussen, C., & Chorover, J. (2015). Climatic and landscape controls on water transit times and silicate mineral weathering in the critical zone. *Water Resources Research*, *51*, 6036–6051. <https://doi.org/10.1002/2015WR017018>
- Zarebanadkouki, M., Ahmed, M. A., & Carminati, A. (2016). Hydraulic conductivity of the root-soil interface of lupin in sandy soil after drying and rewetting. *Plant and Soil*, *398*(1–2), 267–280. <https://doi.org/10.1007/s11104-015-2668-1>
- Zehe, E., & Jackisch, C. (2016). A Lagrangian model for soil water dynamics during rainfall-driven conditions. *Hydrology and Earth System Sciences*, *20*(9), 3511–3526. <https://doi.org/10.5194/hess-20-3511-2016>
- Zehe, E., & Sivapalan, M. (2009). Threshold behaviour in hydrological systems as (human) geo-ecosystems: Manifestations, controls, implications. *Hydrology and Earth System Sciences*, *13*(7), 1273–1297. <https://doi.org/10.5194/hess-13-1273-2009>
- Zhang, Y., Niu, J., Zhu, W., Du, X., & Li, J. (2015). Effects of plant roots on soil preferential pathways and soil matrix in forest ecosystems. *Journal of Forestry Research*, *26*(2), 397–404. <https://doi.org/10.1007/s11676-015-0023-2>
- Zhang, Z. Q., Si, B. C., Li, Z., Evaristo, J., & McDonnell, J. J. (2017). Tritium analysis shows apple trees may be transpiring water several decades old. *Hydrological Processes*, *31*(5), 1196–1201. <https://doi.org/10.1002/hyp.11108>
- Zimmermann, M. H., & Brown, C. L. (1971). *Trees: Structure and function*. Heidelberg, Germany: Springer. <https://doi.org/10.1007/978-3-642-88528-0>

- Zipper, S. C., Dallemagne, T., Gleeson, T., Boerman, T. C., & Hartmann, A. (2018). Groundwater pumping impacts on real stream networks: Testing the performance of simple management tools. *Water Resources Research*, *54*, 5471–5486. <https://doi.org/10.1029/2018WR022707>
- Zoellmann, K., Kinzelbach, W., & Fulda, C. (2001). Environmental tracer transport (3H and SF6) in the saturated and unsaturated zones and its use in nitrate pollution management. *Journal of Hydrology*, *240*(3-4), 187–205. [https://doi.org/10.1016/S0022-1694\(00\)00326-7](https://doi.org/10.1016/S0022-1694(00)00326-7)