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Key Points:

- We present how soil water stable isotopes provide valuable insight into water flow processes
- We review the influential factors at the soil-vegetation-atmosphere interface altering soil water isotopes
- We discuss current issues and challenges for soil water isotope studies

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Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes

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Abstract Water stable isotopes (¹⁸O and ²H) are widely used as ideal tracers to track water through the soil and to separate evaporation from transpiration. Due to the technical developments in the last two decades, soil water stable isotope data have become easier to collect. Thus, the application of isotope methods in soils is growing rapidly. Studies that make use of soil water stable isotopes often have a multidisciplinary character since an interplay of processes that take place in the vadose zone has to be considered. In this review, we provide an overview of the hydrological processes that alter the soil water stable isotopic composition and present studies utilizing pore water stable isotopes. The processes that are discussed include the water input as precipitation or throughfall, the output as evaporation, transpiration, or recharge, and specific flow and transport processes. Based on the review and supported by additional data and modeling results, we pose a different view on the recently proposed two water world hypothesis. As an alternative to two distinct pools of soil water, where one pool is enriched in heavy isotopes and used by the vegetation and the other pool does not undergo isotopic fractionation and becomes recharge, the water gets successively mixed with newly introduced rainwater during the percolation process. This way, water initially isotopically enriched in the topsoil loses the fractionation signal with increasing infiltration depth, leading to unfractionated isotopic signals in the groundwater.

1. Introduction

Soils have long been acknowledged to play a crucial role in the hydrologic cycle, with their functional properties controlling infiltration [Horton, 1933], percolation of water through the pore space [Lutz and Leamer, 1940] and the accompanied leaching of solutes [Fairburn, 1929], storage capacity [Hursh and Fletcher, 1942], soil evaporation [Penman, 1948; Stanhill, 1955], and transpiration [Penman, 1951]. Within the soil, the partitioning of the rainfall into a vapor flux back into the atmosphere by evaporation or transpiration on the one hand and recharge water on the other hand takes place [Brooks et al., 2015]. Consequently, the vadose zone, as the unsaturated soil and sediments between soil surface and groundwater table [Hopmans and van Genuchten, 2005], is a key factor for understanding and modeling hydrological processes from the plot scale to the global scale.

Because of the role of the vadose zone as a mediator between other compartments in the hydrologic cycle, a better understanding of the water and solute transport in the vadose zone is needed to challenge our perception of the hydrological processes and their implementation in hydrological models at different scales. For example, it has been shown that the representation of the vadose zone processes has a significant influence on the estimations of how long water takes to reach the catchment outlet or pass to the groundwater (travel times) [e.g., Hrachowitz et al., 2013; McMillan et al., 2012]. Hence, the vadose zone plays not only a central role in understanding the soil-vegetation-atmosphere exchange but also the integrated processes at the catchment scale. We will therefore focus our review on studies that were conducted in the vadose zone and deal with the atmospheric drivers, interactions with the vegetation, and subsurface flow paths. We provide an overview of the fast growing highly interdisciplinary research that makes use of soil water stable isotopes as a tracer. We first give a short introduction into water stable isotopes in soil hydrology to ensure an understanding of the basic concepts to address a multidisciplinary readership (section 2). Afterward, we present the important processes including atmospheric influences (section 3), impacts of the vegetation (section 4), and processes mainly taking place within the soil (section 5). The purpose of this categorization is to ease the readability, while the described processes obviously interact across the hydrologic compartments. We further present and discuss a different view on the two water world hypothesis (section 6) and present an outlook for future applications and development of water stable isotope methods to study soil hydrology

(section 7). At the end, we provide a concluding summary (section 8). A glossary provides brief explanations of selected technical terms.

2. Introduction to Water Stable Isotopes in Soil Hydrology

The method of choice to track water flow paths in the vadose zone is the variation of stable isotopes of water ($^1\text{H}/^2\text{H}$ and $^{16}\text{O}/^{18}\text{O}$) in the subsurface. They are seen as ideal (natural) tracers, since they are part of the water molecule itself [Kendall and McDonnell, 1998]. The concentrations of the heavy water stable isotopes are given in the δ notation (isotope delta), which represents the relative difference in the ratio of heavy to light isotopes (e.g., $^2\text{H}/^1\text{H}$ for deuterium and $^{18}\text{O}/^{16}\text{O}$ for oxygen-18) of a water sample to a standard water, the Vienna Standard Mean Ocean Water (VSMOW) [Craig, 1961; Gonfiantini et al., 1995]. While the isotope delta is a dimensionless quantity, the values are given in ‰ due to the low variation in natural abundance of water stable isotopes [Coplen, 2011]. Water stable isotopes have allowed new views on the hydrological response at the catchment (reviewed by McGuire and McDonnell [2007] and Vitvar et al. [2005]), hillslope [e.g., McGuire and McDonnell, 2010; Garvelmann et al., 2012; Mueller et al., 2014], and the soil profile scale [e.g., Maloszewski et al., 2006; Stumpp et al., 2009a; Sprenger et al., 2016a]. The latter two scales are of specific interest for our review, bringing together 50 years of soil water isotope studies. There have been reviews published focusing on the different methods to sample the soil water stable isotopes [Sprenger et al., 2015a], on the measurement and modeling of soil water vapor [Soderberg et al., 2012], on isotope based groundwater recharge estimates [Koeniger et al., 2016], on the application of isotope techniques to study soil salinization [Cui et al., 2011], or on the partitioning of evapotranspiration using water stable isotopes among other methods [Kool et al., 2014]. However, we present here an integrated view of the processes at the soil-vegetation-atmosphere interface, which appears to be highly relevant for the environmental science community due to the fast growing availability of water stable isotope data and its application in a multidisciplinary context.

The first studies that realized the potential of water isotopes in soils to detect subsurface processes focused on the radioactive tritium (^3H) concentration after the peak of the nuclear bomb test in the 1950s and 1960s [Munnich, 1963] or in tracer experiments with tritiated (artificially ^3H enriched) water [Zimmermann et al., 1966; Blume et al., 1967; Kline and Jordan, 1968]. However, the potential of the natural seasonal variation of the stable isotopes in the rainfall water was also acknowledged during that time [Brinkmann et al., 1963]. Since then, the isotopic composition of the soil waters has been used in various studies dealing with a wide range of processes that occur in the critical zone between the groundwater and the atmosphere. These processes and the accompanied alteration of the soil water stable isotopic composition are presented in the Figure 1. While water fluxes between hydrological compartments like precipitation input, infiltration into the soil, percolation through the soil, and root water uptake do not change the isotopic composition by fractionation processes (indicated by "O" in Figure 1), phase changes (e.g., liquid to vapor) result in enrichment and depletion of heavy isotopes (indicated by "+" and "-" in Figure 1). The conceptual visualization in Figure 1 provides an overview of the general hydrological processes that occur within the context of the vadose zone, while the following sections will describe and discuss the effects in detail.

3. Atmospheric Influences

3.1. Input of Precipitation, Throughfall, Stemflow, and Snowmelt

The isotopic composition of the precipitation is crucial to understand the variation of the pore water isotope signal over the soil depth and time. The isotopic composition of the global precipitation is described by the following relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ [Rozanski et al., 1993]:

$$\delta^2\text{H} = 8.2 \delta^{18}\text{O} + 11.27 \quad (1)$$

This regression line in a $\delta^{18}\text{O}$ - $\delta^2\text{H}$ (dual-isotope) plot, as shown in Figure 2, describes equilibrium fractionation and is defined as the global meteoric water line (GMWL) [Craig, 1961]. This relationship between ^{18}O and ^2H results from Rayleigh processes (equilibrium fractionation) governed by the temperature and pressure conditions during the phase changes between liquid water and water vapor [Dansgaard, 1964]. In accordance with the GMWL, one can also derive a local meteoric water line (LMWL, shown in Figure 2) describing the stable isotopic composition in rainfall water on a regionally limited scale [Dansgaard, 1964]. This way, LMWLs take into account the spatiotemporal variation of the water isotopic composition of precipitation.

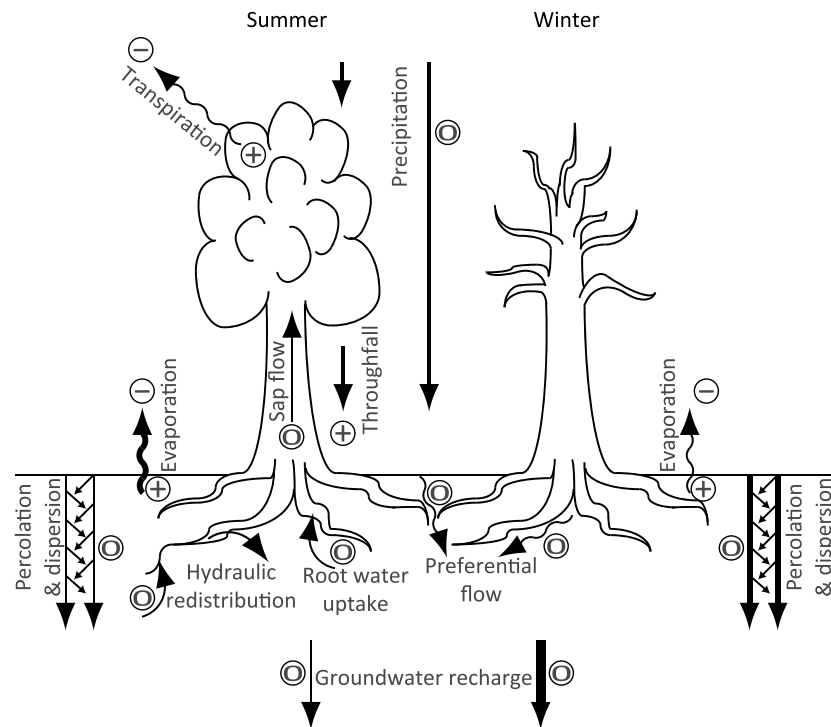


Figure 1. Conceptualization of the processes affecting the pore water stable isotope composition in the vadose zone during summer and winter in a temperate climate. The plus sign indicates an isotopic fractionation process leading of enrichment in heavy isotopes, the minus represents depletion in heavy isotopes, and the zero is a sign of nonfractionating processes. The text indicates the labels of the closest up to two arrows. Detailed information about spatiotemporal variations of each process are given in the sections 3 to 6.

The spatial variability of the isotopic composition of the rainfall was found to be related to the temperature and humidity during the vapor generation, cloud generation, and rainout, mixing of air masses, in-cloud processes [Gat, 1996], and rain out and reevaporation during the advective transport leading to altitude effects [e.g., Ambach et al., 1968; Gonfiantini et al., 2001; Windhorst et al., 2013], latitude effects [Dutton et al., 2005], and continental effects [Ingraham and Taylor, 1991; Welker, 2000; Liu et al., 2010]. Guidelines on precipitation sampling for isotopic analysis are provided by International Atomic Energy Agency [2014] and precipitation isotope data is available from the Global Network of Isotopes in Precipitation published by the International Atomic Energy Agency under <http://www.iaea.org/water>. The Online Isotopes in Precipitation Calculator (OIPC, available at http://wateriso.utah.edu/waterisotopes/pages/information/oipc_info.html) provides global mean annual and monthly ^2H and ^{18}O precipitation data based on algorithms given in Bowen et al. [2005].

For pore water stable isotope studies, the temporal variation of the isotopic composition of precipitation (as shown in Figure 3) is crucial. In tropical regions, the isotopic composition correlates with the precipitation amount (“amount effect”) [Araguás-Araguás et al., 2000]. Outside the tropics, the observed seasonality of the rainfall isotopic signal is driven by seasonal variations (i) of the temperature at the origin of the water vapor, (ii) of the evaporation intensity on the land surface (recycling), and (iii) of the temperature during the precipitation [Araguás-Araguás et al., 2000]. In temperate regions, these effects lead to heavy isotopes being depleted during winter and in isotopically enriched precipitation during summer. Figure 3a shows the annual variation of the isotopic composition of precipitation for a study site in the Attert catchment in Luxembourg (see Sprenger et al. [2016b] for details regarding the site). Figure 2 visualizes the monthly weighted averages of the isotopic signal of the same precipitation composition in a dual-isotope plot. Arrows in Figure 2 depict the influencing factors how rain water becomes more enriched or depleted in heavy isotopes. The isotopic signal can vary within rain events, due to changes in rainfall intensities and rainout effects [McDonnell et al., 1990], leading often to an increasing depletion in heavy isotopes over the time of an event [Pionke and DeWalle, 1992]. At the end of an event, rainwater is often slightly enriched in heavy isotopes again, leading to a “V-shaped” event pattern [Kendall and McDonnell, 1993; Pangle et al., 2013; Allen et al., 2014].

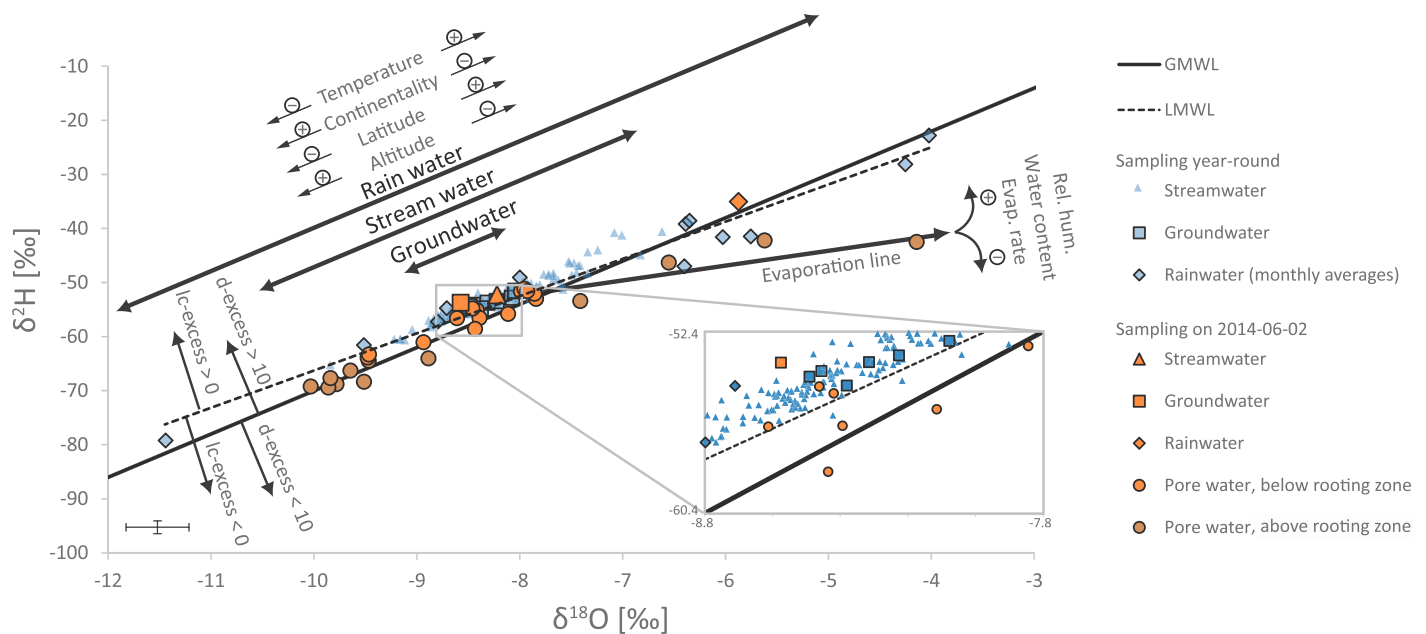


Figure 2. Dual-isotope plot for water samples of rainfall, soil pores (the same as in Figure 3; LMWL: $\delta^2\text{H} = 6.79 \times \delta^{18}\text{O} + 1.74$), streamflow and groundwater in the Weierbach catchment in Luxemburg. Processes affecting the different compartments are shown with indication of fractionating effects as in Figure 1. The standard error of the pore water analysis (0.31‰ for $\delta^{18}\text{O}$ and 1.16‰ for $\delta^2\text{H}$) is shown in the error bars in the lower left.

The isotope composition in precipitation can be further altered before infiltration into the soil due to interception in the vegetation canopy and litter often resulting in an isotopically enriched throughfall [Liu et al., 2006; Muñoz-Villers and McDonnell, 2012]. This isotopic enrichment of throughfall is higher for smaller rain events [DeWalle and Swistock, 1994; Allen et al., 2015]. However, for medium intensity rain events (5–10 mm), Zhang et al. [2010b] reported throughfall that was depleted in heavy isotopes, due to dilution effects on the saturated water vapor interface in the wet canopy. This dilution toward lighter isotopes was found to happen at high humidity when intense exchange with the atmosphere takes place [Zhang et al., 2010b]. For high-intensity rainfalls, the difference between the isotopic composition of the open precipitation and throughfall diminishes [DeWalle and Swistock, 1994; Zhang et al., 2010b]. Furthermore, the deviation between the isotopic composition of open rainfall and throughfall was found to be higher under the center of the crown than in the crown periphery for beech and spruce [Brodersen et al., 2000], while others did not see such a significant relation between distance to trees and throughfall isotopic composition for Douglas fir [Allen et al., 2015]. No effect of throughfall was observed during leaf-off conditions [Kendall and McDonnell, 1993]. However, the high spatial variability of the throughfall and its isotopic composition can potentially be explained by mixing with the pre-event canopy storage [Allen et al., 2014]. Besides throughfall, also stem-flow can show a signal of enrichment of heavy isotopes, which is primary due to mixing with pre-event water and only partly due to evaporation [Ikawa et al., 2011; Allen et al., 2014]. In addition, can influence the soil waters isotopic composition, since it is usually isotopic enriched compared to the precipitation at the location (see review by Scholl et al. [2011]). For snowfall, the spatial variability of the throughfall driven by the canopy density further affects the isotopic composition of the snowpack [Koeniger et al., 2008], which can result in variable input into the soil during snowmelt. Also, fractionation processes within the snowpack by exchange between the solid and liquid phase, resulting in enrichment in ^2H in the melt water compared to the original snow, can lead to an altered input signal of the snow melt water [Zhou et al., 2008; Lee et al., 2010].

In conclusion, the driving processes governing the spatiotemporal patterns of the throughfall isotopic composition are not yet fully understood [Allen et al., 2015]. However, new opportunities to sample the short-term variability of the rainfall isotopic signal using continuous measurements of the water stable isotopes with laser spectrometer [Berman et al., 2009; Herbstritt et al., 2012; Pangle et al., 2014] may allow us to gain more

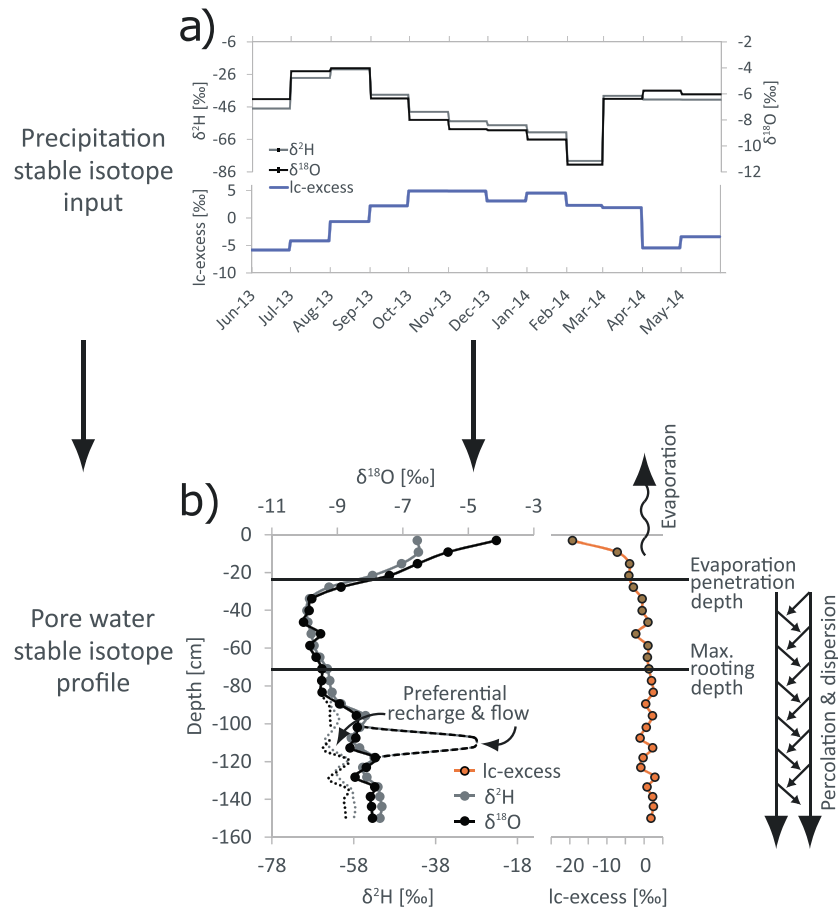


Figure 3. Monthly weighted isotopic signal ($\delta^2\text{H}$, $\delta^{18}\text{O}$, and lc-excess) of (a) precipitation between June 2013 and June 2014 in the Weierbach catchment in Luxembourg and (b) an exemplary profile of the isotopic signal in the pore water at the beginning of June 2014 (end of the time series in Figure 3a) in this watershed. The axes of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are relatively scaled according to the LMWL ($\delta^2\text{H} = 6.79 \times \delta^{18}\text{O} + 1.74$) and the lc-excess is calculated according to equation (3). Dotted and dashed lines present hypothetical changes of the isotope profile due to preferential recharge and preferential flow, respectively. Brown circles indicate soil samples of the rooting zone (same as in Figure 2). Standard error of the liquid water analysis is 0.2‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$ and for the pore water analysis they are 0.31‰ for $\delta^{18}\text{O}$ and 1.16‰ for $\delta^2\text{H}$. For detailed info on the rainfall stable isotope signal see section 3.1, on evaporation fractionation in soils see section 3.2, on percolation and dispersion see section 5.2, on preferential flow see section 5.3, and on preferential recharge see section 5.4.

insights into these temporal and spatially dynamic processes. So far, the influence of the spatiotemporal variation of the infiltrating water on the spatiotemporal variation of soil water stable isotopes has not yet been tested and is therefore usually ignored.

3.2. Soil Evaporation

Precipitation water entering the soil may become partly evaporated, and the water remaining in the soil will thus get enriched in heavy isotopes by evaporation fractionation. Since oxygen has a higher atomic weight than hydrogen, the $^1\text{H}_2\text{ }^{18}\text{O}$ (molecular weight = 20.015 g mol⁻¹, Horita *et al.* [2008]) is less likely to change from the liquid phase to the gaseous phase than the $^1\text{H}_2\text{H}^{16}\text{O}$ (molecular weight = 19.017 g mol⁻¹ [Horita *et al.*, 2008]) (for nonequilibrium conditions) [Craig *et al.*, 1963]. Consequently, the relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for water experiencing kinetic fractionation due to evaporation will deviate from the GMWL or LMWL. The deviation of the relation between ^2H and ^{18}O of a water sample compared to the average isotopic composition of the global precipitation was defined by Dansgaard [1964] as the deuterium excess (short d-excess) based on transforming equation (1):

$$\text{d-excess} = \delta^2\text{H} - 8 \times \delta^{18}\text{O} \tag{2}$$

As such, d-excess values of water influenced by evaporation will be $< 10\text{‰}$ and water remaining in the soil pores will therefore plot below the GMWL on a dual-isotope plot.

Landwehr and Coplen [2006] proposed a more general concept, named line-conditioned excess (short lc-excess) defined as:

$$\text{lc-excess} = \delta^2\text{H} - a \times \delta^{18}\text{O} - b \quad (3)$$

where a and b represent the slope and intercept of the LMWL. Thus, water that is experiencing fractionation by evaporation has a negative lc-excess and plots below the LMWL in a dual-isotope plot [*Landwehr and Coplen*, 2014].

In Figure 3b, soil profiles are visualized that show the $\delta^{18}\text{O}$, $\delta^2\text{H}$, and the resulting lc-excess for a study site in the Attert catchment, Luxembourg, on 2 June 2014 (see *Sprenger et al.* [2016b] for details about pore water stable isotope sampling). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ axes are scaled according to the LMWL, and thus, the divergence between $\delta^{18}\text{O}$ (grey) and $\delta^2\text{H}$ (black) indicates evaporation fractionation, as also shown in the lc-excess depth profile (orange). The same pore water stable isotope data are also plotted in dual-isotope plot in Figure 2 to visualize the general concepts related to soil evaporation as presented in this section.

Subsequent kinetic fractionation of water increases the deviation from the GMWL in a dual-isotope plot leading to an evaporation line with a slope < 8 . The slope becomes smaller for a lower relative humidity [*Dincer et al.*, 1974; *Gibson et al.*, 2008], lower soil water content [*Allison et al.*, 1983; *Barnes and Allison*, 1988], or lower evaporation rate [*Allison et al.*, 1983] (Figure 2). As a consequence, the differences in d-excess of the soil water in the top 0.1 m to the subsoil was shown to be higher during summer and spring compared to fall and winter [*Barbeta et al.*, 2015] and higher for low altitudes compared to high altitudes [*Cui et al.*, 2009]. The local evaporation lines of soil water show usually slopes between 2 and 6.5 with slopes > 5 for midlatitudes and lower slopes for arid climates [*Gibson et al.*, 2008]. After a rain event, when evaporation initiates, isotopic enrichment due to kinetic fractionation (more negative lc-excess value) takes place. The kinetic fractionation was found to be highest for the litter layer directly after a rain event [*Liu et al.*, 2015]. Evaporation profiles with fractionated pore waters at the topsoil develop within a few days of dryness, as observed in an arid climate [*Gaj et al.*, 2016], cool temperate climate [*Twining et al.*, 2006], and in a laboratory experiment [*Rothfuss et al.*, 2015].

The evaporation front, defined as the maximum depth of the pore water kinetic fractionation signal [*Barnes and Allison*, 1988], moves downward into the soil over a dry period [*Münnich et al.*, 1980; *Gaj et al.*, 2016], and its maximum penetration depth depends on the duration of the dry period, the water content in the soil, the incoming solar radiation, and the porosity and tortuosity of the soil [*Zimmermann et al.*, 1967a]. Due to mixing with the atmospheric water vapor, the top of the soil can be isotopically depleted, while below, the soil water is fractionated due to soil evaporation [*Gangi et al.*, 2015]. Conditions in arid climates can lead to a steady state of exponentially decreasing fractionation over depth [*Dincer et al.*, 1974; *Allison et al.*, 1983].

Figure 4 shows the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of soil water reported in 25 studies, of which 22 studies were considered in a meta-analysis by *Evaristo et al.* [2015], who compared the isotopic signal of transpired water, soil water, groundwater, and streamwater for different climates classified into temperate forests, temperate grasslands, Mediterranean, arid, and tropics. In addition to these 22 studies, we added three recently published studies [*Song et al.*, 2014; *Cui et al.*, 2015; *Sprenger et al.*, 2016b]. The pore water stable isotope data of the 25 studies show the pattern that evaporation fractionation is generally limited to the upper 0.3 m of the soil. The reviewed studies used either cryogenic vacuum extraction [*West et al.*, 2006; *Koeniger et al.*, 2011; *Orlowski et al.*, 2013], azeotropic distillation [*Revesz and Woods*, 1990], or direct equilibration [*Wassenaar et al.*, 2008] to determine the pore water isotopic composition. While these methods are known for sampling both mobile and less mobile soil water, it is not yet fully understood in which way the methods differ from each other with regard to the sampled pore space (as reviewed by *Sprenger et al.* [2015a]). Several pore water isotope studies showed that the kinetic fractionation is usually limited to the upper -0.2 to -0.3 m in temperate regions [e.g., *Komor and Emerson*, 1994; *Gazis and Feng*, 2004; *Zhang et al.*, 2011; *Sutanto et al.*, 2012], increases to 0.5 m in Mediterranean climates [*Simonin et al.*, 2014; *Oshun et al.*, 2016], and can reach down to -3 m in arid climates [*Allison and Hughes*, 1983; *Singleton et al.*, 2004]. Figure 5 supports these findings, where we present the lc-excess over the depth. Since the studies did not give lc-excess values, we derived them from the published soil water ^2H and ^{18}O data and the LMWL from the individual study sites according to equation (3). The

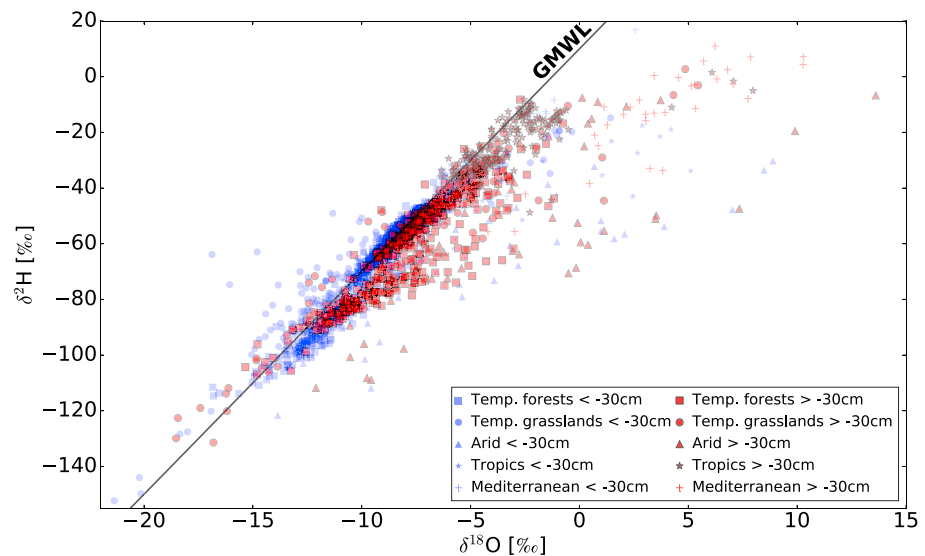


Figure 4. Dual-isotope plot revealing that the evaporation fractionation, as an altered ^2H - ^{18}O relation of the soil water compared to the relation in the precipitation water (GMWL), is globally limited to the upper 30 cm of the soil for most soil water isotope studies [Snyder, 2000; Williams and Ehleringer, 2000; Ohte et al., 2003; Kurz-Besson et al., 2006; Holland et al., 2006; Eggemeyer et al., 2008; Sun et al., 2008; Brooks et al., 2010; Wang et al., 2010b; Rong et al., 2011; Zhou et al., 2011; Jia et al., 2012; Goldsmith et al., 2012; Bertrand et al., 2012; Zhu et al., 2012; Zhou et al., 2013; Wei et al., 2013; Schwendenmann, 2016; Berry et al., 2014; Swaffer et al., 2014; Song et al., 2014; Cui et al., 2015; Sprenger et al., 2016b].

compilation of the Ic-excess data clearly shows that the evaporation fractionation can reach significant depths in arid and Mediterranean climates. In temperate and tropical climates, the kinetic fractionation in the topsoil is relatively little. High-frequency measurements in an evaporating soil column under laboratory conditions confirmed that the pore water at -0.4 and -0.6 m soil depth did not experience any evaporation fractionation within more than 280 days of intense evaporation, while the pore water in the top -0.2 m got fractionated along an evaporation line of a slope between 3 and 5 [Rothfuss et al., 2015].

Ultimately, the investigation of the evaporation and the accompanied fractionation in the topsoil depends on the method of choice for the pore water stable isotope sampling. Studies using zero tension, suction lysimeters, or wick samplers, which only investigate water in the large pore sizes, reported only little to no fractionation in the top soil [e.g., Landon et al., 2000; Asano et al., 2002; Timbe et al., 2014; Muñoz-Villers and McDonnell, 2012; Kim and Jung, 2014; Geris et al., 2015; Comas-Bru and McDermott, 2015], while other studies using centrifugation [Kudo et al., 2013], cryogenic vacuum extraction [e.g., Brooks et al., 2010; Goldsmith et al., 2012], or the direct equilibration [e.g., Garvelmann et al., 2012; Bertrand et al., 2012] found a fractionation in the upper soil layer. However, recent publications showed that especially the latter two methods are not necessarily comparable [Orlowski et al., 2016b]. Further, the carrier gas can influence the ^2H to ^{18}O ratio when applying the direct equilibration method [Gralher et al., 2016], which can lead to overestimations of evaporation fractionation. In situ measurements of the soil water isotopic composition [Volkman and Weiler, 2014; Rothfuss et al., 2013] will allow to study the evaporation fractionation in high temporal and spatial resolution, as shown in a laboratory experiment by Rothfuss et al. [2015].

The simulation of the evaporation fractionation processes in the soil is included into conceptual approaches based on the Craig-Gordon model [Craig and Gordon, 1965] and into soil physical models [e.g., Mathieu and Bariac, 1996; Braud et al., 2005], as recently reviewed by Soderberg et al. [2012]. The vadose zone evaporation fractionation on the catchment scale is difficult to assess and it is seldom considered in catchment models [e.g., Birkel et al., 2011; Soulsby et al., 2015]. However, a better understanding of the temporal dynamics of the evaporation intensity and the partitioning into evaporation and discharge could be gained by taking vadose zone isotopic fractionation into account. As shown by Good et al. [2015], estimating of the mass balance of stable isotopes fluxes of evaporation and discharge on the catchment scale can challenge the perception of subsurface processes (as further discussed in section 6).

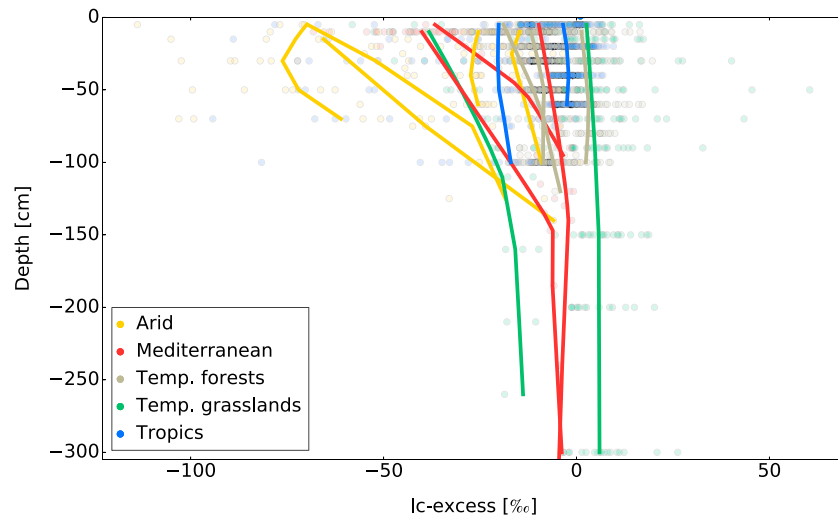


Figure 5. $\delta^2\text{H}$ -excess as defined in equation (3) over the soil depth as reported in the literature. Points represent the original data and the lines show a local regression for the individual studies (Python statsmodel.lowess). Data for the tropics by Schwendenmann [2016] and Goldsmith *et al.* [2012]; for the Mediterranean by Ohte *et al.* [2003], Kurz-Besson *et al.* [2006], and Swaffer *et al.* [2014]; for arid regions by Snyder [2000], Zhou *et al.* [2011, 2013], Wei *et al.* [2013], and Cui *et al.* [2015]; for the temperate forests by Brooks *et al.* [2010], Wang *et al.* [2010b], Rong *et al.* [2011], and Bertrand *et al.* [2012]; and for the temperate grasslands by Holland *et al.* [2006], Eggemeyer *et al.* [2008], and Song *et al.* [2014].

It was shown that a vegetation cover generally diminishes kinetic fractionation processes in the soil water [Zimmermann *et al.*, 1967a; Burger and Seiler, 1992; Dubbert *et al.*, 2013] and that the evaporation fractionation of soil water increases with distance from the vegetation canopy margin [McCole and Stern, 2007]. Also, a high humidity in forest stands can reduce the isotopic fractionation effect [Zhang *et al.*, 2011]. Topography also influences the evaporation fractionation with lower $\delta^2\text{H}$ -excess found on hillslopes compared to the valley bottoms during summer [Simonin *et al.*, 2014]. The kinetic fractionation due to evaporation follows a seasonal pattern [Ferretti *et al.*, 2003] and correlates positively with potential evapotranspiration and negatively with annual precipitation [Hsieh *et al.*, 1998] due to the interplay between kinetic fractionation of soil water by soil evaporation and input from nonfractionated precipitation.

4. Vegetation Influences

4.1. Transpiration/Root Water Uptake

Although root water uptake by plants does not fractionate pore waters, in general [Zimmermann *et al.*, 1967b; Allison *et al.*, 1984; Bariac *et al.*, 1990; Wershaw *et al.*, 1966], some halophytes [Lin and Sternberg, 1993] and woody xerophytes [Ellsworth and Williams, 2007] change the $^1\text{H}/^2\text{H}$ ratio of soil water. The better a plant is adapted to salt-rich environments, the higher is the isotopic difference between xylem and soil water [Ellsworth and Williams, 2007; Lin and Sternberg, 1993], which may reach as much as 13‰ for $\delta^2\text{H}$ [Lin and Sternberg, 1993]. The evaporation of water through the stomata in leaves generally fractionates the water in the leaves depending on the relative humidity of the air [Bariac *et al.*, 1990]. Thus, the evapotranspiration (ET) can be partitioned via the differences between the isotopic signal in the atmospheric water, the transpired pore/twig/xylem water and the soil evaporation water applying mixing models [Zhang *et al.*, 2010a; Wang *et al.*, 2012a]. Such partitioning studies showed that transpiration makes up almost all the water in a tropical forest [Moreira *et al.*, 1997] and more than 65% of the ET in an alpine oak shrubland ecosystem [Xu *et al.*, 2008]. Other studies looked at diurnal cycles [Lai *et al.*, 2006], the daily variation [Wenninger *et al.*, 2010], or at variations over the year [Robertson and Gazis, 2006]. It was shown that the annual variation of the partitioning between transpiration (T) and evaporation (E) is mainly driven by the vegetation leading to evaporation-evapotranspiration ratios (E/ET) between zero during growing season and >90% in the dormant season [Ferretti *et al.*, 2003]. Laser spectrometry using chamber-based approaches allows continuous isotope measurements of, e.g., leaf transpiration [Wang *et al.*, 2012b; Dubbert *et al.*, 2014a], enabling a partitioning between herbaceous transpiration and soil evaporation over

the growing season. Such studies revealed the importance of the understory transpiration and its interplay with soil evaporation during wet and dry periods in semiarid ecosystems [Dubbart *et al.*, 2014b]. In order to achieve a higher temporal resolution of the E/ET ratio, Sutanto *et al.* [2012] tested a soil physical model (HYDRUS-1D) on the laboratory scale and found that the model slightly overestimated the total ET compared to an isotope mass balance approach, while the partitioning was acceptably represented with the model. Generally, the E/ET ratio is lower for a denser woody cover [Wang *et al.*, 2010a], more rain, and lower air temperature [Hsieh *et al.*, 1998]. Since the isotope mass balance analyses are based on the differences between the fractionating signal due to evaporation and nonfractionating signal of transpiration, the best potential of such partitioning studies are in midlatitudes, where evaporation leads to a pronounced fractionation signal [Gibson *et al.*, 2008].

Besides the partitioning of ET, pore water stable isotope analyses are also applied to study the root water uptake depth or distribution by comparing the isotopic composition of the xylem water with the isotopic composition of the rainfall, pore water, and groundwater. However, it is a precondition that the sampling frequencies in space (e.g., soil depth) [White and Smith, 2015] and time are sufficient to cover the potential source of root water uptake. Since different combinations of potential water sources for the vegetation can reproduce the xylem water signal, the nonuniqueness needs to be taken into account by presenting distributions of feasible solutions of root water uptake pattern rather than single values, as done in the IsoSource model [Phillips and Gregg, 2003]. Constraining the possible root water uptake in simple linear mixing models with prior knowledge within a Bayesian framework allows considering multiple sources of uncertainty (e.g., MixSIR by Moore and Semmens [2008] and SIAR by Parnell *et al.* [2010]). However, including biophysical conditions in a process-based mixing model (RAPID by Ogle *et al.* [2004]) showed lower prediction uncertainty and a more realistic representation of the root water uptake pattern in a comparison to a simple linear mixing model [Ogle *et al.*, 2014].

Root water uptake patterns were studied using pore water stable isotopes under various climatic conditions and vegetations, as, for example, for crops in a warm temperate monsoon climate [Wang *et al.*, 2010b], for grasses and shrubs in a humid savanna [Le Roux *et al.*, 1995], for subalpine shrubland [Liu *et al.*, 2011], and for trees in the tropical [Meinzer *et al.*, 1999] or temperate region [Bertrand *et al.*, 2012; Meißner *et al.*, 2012]. It has been shown in comparisons among the stable isotope composition of groundwater, soil water, and xylem water that the plant water use is either limited to the soil water or includes also groundwater depending on the topographical position [Rossatto *et al.*, 2012; Penna *et al.*, 2013], tree size [Dawson, 1996], the vegetation rooting system [White *et al.*, 1985; Ehleringer *et al.*, 1991; Ehleringer and Dawson, 1992; Meinzer *et al.*, 1999; Rossatto *et al.*, 2014], soil water content [Mensforth *et al.*, 1994; Bertrand *et al.*, 2012], or irrigation in urban areas [Bijoor *et al.*, 2012]. For example, Boutton *et al.* [1999] revealed with water stable isotopes that a conversion from grassland to woodland in a subtropical savanna will lead to lower recharge fluxes to the groundwater due to the continued access to subsoil water of tree roots during dry periods. The xylem water of trees that use mainly soil water has a seasonal isotopic variation in accordance to the isotopic composition of the precipitation during the growing season [Leng *et al.*, 2013; Song *et al.*, 2014; Treydte *et al.*, 2014]. Several studies showed with a dual-isotope approach that the xylem water covers similar regions in a dual-isotope plot as the top soil [e.g., Goldsmith *et al.*, 2012; Bertrand *et al.*, 2012; Schwendenmann *et al.*, 2015]. Nevertheless, during dry periods, the vegetation might even utilize gypsum crystallization water instead of less bound soil water as shown by Palacio *et al.* [2014]. However, due to mixing with the water stored in the xylem and lowered transport, the isotopic signal of the xylem water was reported to be attenuated compared to the soil water stable isotopes during the dormant season [Brandes *et al.*, 2007]. The xylem water of trees using groundwater was found to vary little over time in its isotopic composition and was similar to the groundwater isotopic signal [David *et al.*, 2013]. Some water stable isotope studies found a correlation between maximum root density (in the topsoil) and water uptake depth for grasses and shrubs [Le Roux *et al.*, 1995; Liu *et al.*, 2011]. However, several studies showed by comparing the water stable isotopic composition of xylem waters with soil waters that the root water uptake is governed by the root distribution during wet periods, while the soil water availability is the main driver during dry periods [Rose *et al.*, 2003; McCole and Stern, 2007; Asbjornsen *et al.*, 2008; Song *et al.*, 2014; Dai *et al.*, 2015; Ellsworth and Sternberg, 2015]. Such a modification of the uptake pattern during water scarcity was also shown for woody plants by injection experiments with ^2H enriched water [Kulmatiski and Beard, 2013; Volkman *et al.*, 2016a]. Injection of water enriched in ^{18}O in the topsoil and water enriched in ^2H in the subsoil during the growing season accompanied by a

sampling of the xylem water 2 days later was shown to allow a delineation of the water uptake pattern in space under grassland communities [Bachmann *et al.*, 2015]. Alternatively, the injection can be limited to the cheaper available water enriched in ^2H , if the deuterated water is injected at several sites at varying depths, which enables also an investigation of active root water uptake depth [Kulmatiski *et al.*, 2010; Beyer *et al.*, 2016]. The injection of isotopically enriched water and the calculation of the tracer recovery of a repeated sampling can further provide information about the mass of soil water being evaporated over time [Beyer *et al.*, 2015]. How long it takes for the water to arrive at the leaves of the vegetation (travel time of the transpiration) can as well be traced by injection of water enriched in heavy isotopes into the sapwood [Meinzer *et al.*, 2006] or into the soil [Kulmatiski *et al.*, 2010; Volkmann *et al.*, 2016a, 2016b].

4.2. Hydraulic Redistribution

The root water uptake can be sustained via hydraulic redistribution of water in the vadose zone during dry periods, due to a passive transport of soil water along a hydraulic gradient through the rooting system [Richards and Caldwell, 1987]. Dawson [1993] showed with the help of stable pore water isotopes that the source depths and amount of hydraulic redistribution of a tree also increase the resistance of the understory to drought stress. However, isotopic measurements alone are not sufficient to estimate volumes of hydraulic redistribution [Emerman and Dawson, 1996]. Therefore, matric potential measurements are usually applied to show that hydraulic redistribution can move considerable amounts of water. For example, Mediterranean oak species were found to redistribute between 17% and 81% of the daily transpired water [Kurz-Besson *et al.*, 2006]. A single sugar maple tree is able to redistribute 102 ± 54 L per day [Emerman and Dawson, 1996], while species adapted to dry savannah conditions can redistribute 247 L per day [Bayala *et al.*, 2008].

Generally, isotope source mixing models are a good way to quantify the share of hydraulic redistributed water of the root water uptake [Hao *et al.*, 2013]. Jackson *et al.* [1999] found under dense vegetation that the soil water isotope signal at -0.5 m depth was shifted toward the signal of deep soil. This shift was explained by hydraulic lift, since such a shift in the isotopic signal was not observed under bare soil [Jackson *et al.*, 1999]. In contrast, Kurz-Besson *et al.* [2006] found relatively light waters (depleted in ^{18}O and ^2H compared to the precipitation input) in -0.4 to -1 m soil depth and also related that to hydraulic redistribution. They explained this finding by redistributed water leaving the roots to be kinetically fractionated, because lighter water vapor would diffuse faster than heavier. Thus, the water closer to the roots that was taken up again by the roots was enriched in heavy isotopes compared to the remaining soil water [Kurz-Besson *et al.*, 2006]. Hydraulic redistribution also takes place horizontally as shown in sprinkling experiments with deuterated (enriched in ^2H) water by Brooks *et al.* [2002, 2006] and Kulmatiski *et al.* [2010]. They found the isotopically enriched sprinkling water several meters away from the watering source in soil samples, the tree xylem [Brooks *et al.*, 2002, 2006], and grass samples [Kulmatiski *et al.*, 2010]. In conclusion, the pore water stable isotopic composition can be influenced via redistribution by roots, but model analysis showed that this influence is small on the isotopic composition of the recharge [Walter, 2010].

5. Processes in the Soil

5.1. Percolation and Groundwater Recharge

Percolation processes through the vadose zone can be traced using the seasonally variable isotopic composition of the rainwater (e.g., lysimeter study by Stumpp *et al.* [2012]) or by sprinkling experiments with artificial isotopically enriched water (e.g., lysimeter study by Mali *et al.* [2007]). If the seasonal variation is used, different states of the soil hydrological system (wet/dry) over seasonal variable boundary conditions can be observed. Similarly, sprinkling experiments can be repeated under different conditions and hydrological states. This way, isotopically marked water and its fate in the soil can be traced in various experimental setups.

The seasonal isotopic composition of the infiltrated rainwater is attenuated in the soil by dispersion, which is the spreading of a tracer during the water flow and transport and depends on the pore size distribution and therefore, the soil texture. When the water flow and transport is simulated with the advection-dispersion model, the dispersivity parameter is required to describe the hydrodynamic dispersion. Vanderborght and Vereecken [2007] reviewed studies that estimated the dispersivity in soils, and they found that fine textured soils often have a higher dispersivity than coarse textured soils, an information that can also be derived using

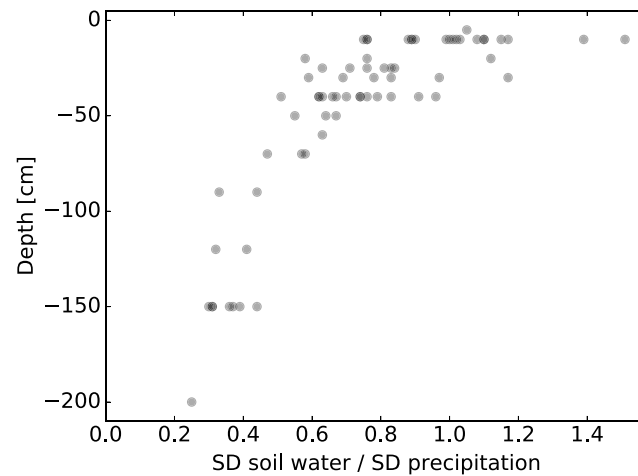


Figure 6. Relation between the standard deviation of the isotopic signal (SD) of the pore water at different depths and the respective precipitation input. Circles represent reviewed studies, where pore water stable isotope sampling was done by suction lysimeters [Asano *et al.*, 2002; Muñoz-Villers and McDonnell, 2012], wick samplers [Timbe *et al.*, 2014], centrifugation [Kudo *et al.*, 2013], cryogenic extraction [Wang *et al.*, 2010b], direct water vapor equilibration [Bertrand *et al.*, 2012], or at lysimeter outflows (C. Stumpp, personal communication, 2015).

soil water stable isotopes [Adomako *et al.*, 2010; Sprenger *et al.*, 2015b, 2016b; Huang *et al.*, 2015]. Despite the site specific complex interplay of environmental conditions, a dampening of the precipitation signal in the soil profile expressed as the relation between the standard deviation (SD) of the pore water stable isotopes observed over a time period at a specific soil depth and the SD of the precipitation signal is found for several studies (Figure 6). The seven reviewed studies shown in Figure 6 cover different environments, but the sampling number is too small to derive patterns related to, e.g., climate or soil texture. The variability decreases exponentially with depth— independent from the applied pore water isotope sampling strategies that ranged from sampling of freely draining soil water like the lysimeter outflow (C. Stumpp, personal communication, 2015) or wick samplers [Timbe *et al.*, 2014] to sampling relatively mobile water in suction lysimeter [Asano *et al.*, 2002; Muñoz-Villers and McDonnell, 2012] or by centrifugation [Kudo *et al.*, 2013], or sampling the bulk soil water including tightly bound water using direct water vapor equilibration [Bertrand *et al.*, 2012] or cryogenic extraction [Wang *et al.*, 2010b]. Thus, considering that the different applied pore water stable isotope analysis methods sample different pore sizes and either flux or resident concentrations as discussed in a method comparison by Sprenger *et al.* [2015a], the dampening of the precipitation signal indicates that mixing of soil water occurs for both the mobile (freely draining) and less mobile (held against gravity) pore waters. However, the intensity of mixing was found to be smaller for mobile pore waters sampled with wick samplers (giving flux concentrations) compared to pore waters extracted by suction lysimeters (giving neither flux nor resident concentration) or by azeotropic distillation (giving resident concentrations) [Landon *et al.*, 1999]. However, the interaction between soil water in small and big pores is not yet understood (see section 6.1). While the pore water isotopic composition in the top 0.1 m varies usually as much or even more (due to evaporative enrichment see section 3.2) than the isotopic signal of the precipitation, the pore water isotope dynamic is highly damped within the upper 0.5 m (Figure 6). This intense dampening of the rainfall signal in the upper 0.5 m of the soil is related to canopy and litter interception, root water uptake, and preferential uptake during the vegetation season in addition to dispersion [Stewart and McDonnell, 1991; Gehrels *et al.*, 1998; Brodersen *et al.*, 2000; Tang and Feng, 2001; Gazis and Feng, 2004; O'Driscoll *et al.*, 2005; Comas-Bru and McDermott, 2015]. A “critical depth,” defined as the depth at which annual variations in the isotopic composition do not exceed the analytical precision, can be derived [Clark and Fritz, 1997]. The analytical precision for pore water stable isotope analysis is usually reported to be between 0.2 to 0.5‰ for $\delta^{18}\text{O}$ and 0.7 to 2‰ for $\delta^2\text{H}$, as reviewed in Sprenger *et al.* [2015b]. Such a homogenization of the isotopic signal in the subsurface depends on the vegetation pattern, rain intensities, and soil characteristics with less dampening in sandy and/or freely draining soils [Wenner *et al.*, 1991; Geris *et al.*, 2015]. Besides the one-dimensional attenuation of the precipitation signal in a soil profile, a two-dimensional component on the hillslope scale leads to lower isotopic variations and longer residence times downslope toward a stream [McDonnell *et al.*, 1991; Asano *et al.*, 2002; Kabeya *et al.*, 2007; Rossatto *et al.*, 2012; Garvelmann *et al.*, 2012; Mueller *et al.*, 2014; Tetzlaff *et al.*, 2014]. In conclusion, the seasonal variation of the isotopic signal in the precipitation input is often highly damped before the soil water reaches the saturated zone (Figures 3, 2, and 6). Thus, the vadose zone holds an intermediate position between the high variation in precipitation and low variation in the groundwater or stream base flow [McGuire *et al.*, 2002; O'Driscoll *et al.*, 2005; Song *et al.*, 2009]. Because of this important role of the vadose zone in rainfall-runoff generation, the pore water stable

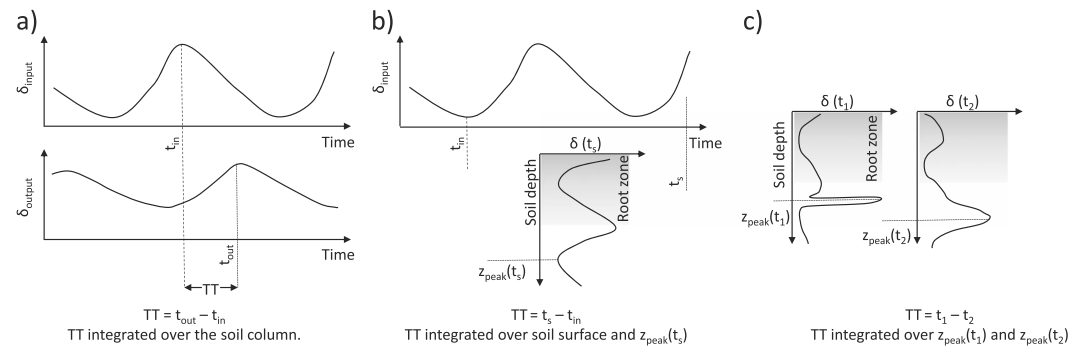


Figure 7. Peak shift methods to estimate transit times: (a) The lag time between a peak in the isotopic signal of the input time series (δ_{input}) and the signal in the output (e.g., outflow of a lysimeter or soil water sampled with wick samplers or suction cup lysimeter) (δ_{output}) is used. (b) A distinct signal in the input time series (δ_{input}) is related to a peak in the isotopic signal of the soil water $\delta(t_s)$ sampled at time t_s at depth z_{peak} . (c) A distinct isotopic signal is introduced at time t_1 at soil depth $z_{peak}(t_1)$ and found at depth $z_{peak}(t_2)$ at time t_2 .

isotope composition can serve to benchmark conceptual catchment models or improve the identifiability of their calibrated parameters [Birkel et al., 2014; Sprenger et al., 2016b]. With regard to stream water hydrograph separation techniques, where the soil water often represents one end-member besides input water and groundwater in a three component mixing model [Klaus and McDonnell, 2013], the spatial variability of the isotopic composition of the pore water appears to cause uncertainties in event water estimates [Kendall and Gu, 1992]. Herein, the isotopic variation in the groundwater is usually low [e.g., Fujimoto et al., 2014; Orlowski et al., 2015] but reflects some kind of a mixture of summer (e.g., enriched in ^{18}O and ^2H) and winter rainfall (e.g., depleted in ^{18}O and ^2H) in temperate regions [Burger and Seiler, 1992]. This mixture depends on the seasonal variability of precipitation (Figures 2 and 3a) and evapotranspiration, resulting in an isotopic composition of deep soil pores in the vadose zone or saturated pores in the groundwater that is either similar to the weighted average isotopic composition of the precipitation [Darling and Bath, 1988; Gehrels et al., 1998; Thomas et al., 2013; Cheng et al., 2014; Oshun et al., 2016] or depleted in ^{18}O and ^2H compared to the precipitation [Simpson et al., 1970; Sauzay, 1974; Wenner et al., 1991; Hsieh et al., 1998; O'Driscoll et al., 2005; Yeh et al., 2011; Bertrand et al., 2012]. The isotopically depleted signal results from seasonal root water uptake and evaporation losses during the growing season and elevated evaporation rates, when the (isotopically enriched) summer precipitation is more likely to leave the soil via evapotranspiration. This preferential loss of rainfall input back into the atmosphere would shift the pore water stable isotope composition toward isotopically depleted values due to preferential recharge of winter rainfalls (indicated with the dotted line in Figure 3b). Under arid conditions, where evaporation rates are high, the groundwater can be enriched in heavy isotopes compared to the precipitation input (plotting below the LMWL) [e.g., Sami, 1992; Murad and Krishnamurthy, 2008; Murad and Mirghni, 2012].

The already illustrated combination of relatively slow water movement in the soil matrix and fast preferential flows leads to a bimodal recharge flux, where the groundwater hydraulic response is either slow resulting in a damped isotope signal or rapid leading to an isotopic reaction in the groundwater [Mathieu and Bariac, 1996]. Such pronounced recharge seasonality is found globally in areas with high recharge in the winter of temperate and arid regions or during the wet season in the tropics [Jasechko et al., 2014]. The groundwater signal is usually not altered in Ic-excess, indicating that the recharge water is not affected by soil evaporation, although the pore water in the topsoil shows fractionation (Figures 4 and 5). This issue will be discussed in more detail in section 6.

5.2. Vadose Zone Travel Time Modeling

The travel time is defined as the time a water particle takes to pass through a hydrological system [McDonnell et al., 2010]. As such, travel time estimations are applied on scales ranging from catchments [e.g., Rodhe et al., 1996; McGuire and McDonnell, 2006] to hillslopes [McGuire et al., 2007] and soil profiles [e.g., Stewart and McDonnell, 1991; Lindström and Rodhe, 1992]. One way to estimate how fast the water moves through the soil profile is the peak displacement or shift method, as recently reviewed by Koeniger et al. [2016]. This method

makes use of an isotopically distinguished input either by seasonal peaks in the isotopic signal of precipitation or by injection of isotopically enriched water [Zimmermann *et al.*, 1966; Blume *et al.*, 1967]. Usually, the peak shift method is limited to estimate the advective transport, since the dispersion is not considered. However, mean travel times can be estimated taking the dispersivity into consideration [Leibundgut *et al.*, 2009, p. 132] as applied in a study by Stumpp *et al.* [2012] using ^{18}O data in lysimeter outflows. Figure 7 shows conceptually how the advective transit time can be derived. One can (i) use the delayed response to the input signal in pore water stable isotope time series for a certain soil depth (e.g., sampled with suction lysimeter or wick samplers) or in the outflow of lysimeter [Stumpp *et al.*, 2012] (Figure 7a), (ii) or relate an isotopic peak at a certain soil depth in a pore water isotope depth profile taken at a certain time to a corresponding input signal [Saxena and Dressie, 1984; Bengtsson *et al.*, 1987; Barnes and Allison, 1988; Adomako *et al.*, 2010] (Figure 7b), or (iii) use the displacement of an artificially injected isotopic labeled water is studied [Saxena and Dressie, 1984; Beyer *et al.*, 2015] (Figure 7c). The three different peak shift/displacement methods differ with respect to their required data and experimental effort. While collecting time series of soil water isotopes, as required for approach shown in Figure 7a, is time consuming and labor intensive, the method shown in Figure 7b requires, beside information on the isotopic input signal, only the collection of one pore water isotope depth profile. However, the method shown in Figure 7b is limited to environments, where the water flow and transport is dominated by advection-dispersion to enable referring the peaks in the input signal to the peaks in the isotope depth profile. Otherwise, the peak in the profile could be caused by preferential flow or hydraulic redistribution (see sections 4.2 and 5.3, respectively). For the method in Figure 7c, no prior information on the isotopic input is required, since the artificially introduced isotopic tracer will provide a distinct signal to the natural background which can be traced in the soil over time or by a pore water isotope depth profile. Besides the estimation of advective travel times, the peak shift/ displacement methods also provide information of the recharge amounts, if the water content is known and assuming that the water passed the rooting zone [Saxena and Dressie, 1984; Koeniger *et al.*, 2016].

The above mentioned studies give a snapshot of the travel times, and the results of such estimates depend on the sampling time [Koeniger *et al.*, 2010], since the percolation rate is not constant. Instead, an average percolation rate integrating information over various seasons can be derived using transit time models. We compiled travel time studies in the vadose zone and list their characteristics in Table 1. The vadose zone travel time studies are based on different soil water sampling methods, which has a direct influence on the data used for model calibration, since different methods sample different pore sizes [Sprenger *et al.*, 2015a]. In almost all of the reviewed travel times studies, the soil water sampling was limited to the mobile water: Studies using the outflow of lysimeter [e.g., Lindström and Rodhe, 1992; Mali and Urbanc, 2006; Maloszewski *et al.*, 2006; Stumpp *et al.*, 2009a, 2009b] or water sampled by wick samplers [e.g., Timbe *et al.*, 2014] and zero-tension lysimeter [e.g., Asano *et al.*, 2002] infer the travel times on freely draining waters. Less mobile was included in the travel times estimations, if a suction is applied at the lysimeter [e.g., Leopoldo *et al.*, 1984; Stewart and McDonnell, 1991; Kabeya *et al.*, 2007, 2011; McGuire and McDonnell, 2010; Muñoz-Villers and McDonnell, 2012; Kim and Jung, 2014; Tetzlaff *et al.*, 2014; Hu *et al.*, 2015]. While sampling of freely draining water will give information of the flux concentrations, suction cup lysimeter influence the flow field, which impedes a reference to flow concentration in that case. Recently, Sprenger *et al.* [2016b] used resident concentrations of the pore water isotopic composition for travel time simulations.

Since the soil water sampling is time consuming, vadose zone transit time studies are often limited to a few soil depths and number of profiles. Replicate sampling, to account for the heterogeneity of the soil, is usually missing (Table 1). Only a handful studies base their answer to the research questions on replicated soil water samples [Leopoldo *et al.*, 1984; Asano *et al.*, 2002; Timbe *et al.*, 2014; Sprenger *et al.*, 2016b]. Given that the soil texture is crucial for water flow and transport in the subsurface, it is surprising that more than one third of the reviewed studies do not provide any soil textural information in their manuscripts (Table 1). Our review further highlights that the studies within the temperate climate represent about two thirds of all the vadose zone transit time studies. In conclusion, the assessment of transit times is often limited to a few studied soils and the heterogeneity within soil types and between different climates is not sufficiently captured yet.

The MTT estimated from lysimeter, wick samplers, or suction cup lysimeter isotope data are mostly based on lumped convolution models that assume steady state conditions, which may not hold in nature [Botter *et al.*, 2010; Sprenger *et al.*, 2016b]. Maloszewski *et al.* [2006] showed in a study on unvegetated lysimeters filled with

Table 1. Overview of the Studies Estimating the Transit Times in the Vadose Zone^a

| Study | R | N | RQ | Model | Method | Frequency | Depths (cm) | MTT (weeks) | Texture | Soil Type | Climate | Study Location |
|---|---|---|--|----------------------------|------------------------|---|-----------------------------------|---|---------------------------|---|-----------------|--|
| <i>Timbe et al.</i> [2014] | 3 | 6 | Land use (forest versus pasture) and comparison between models | LM; EM; EPM; LPM; GM; TPLR | Wick samplers | Weekly | 10, 25, 40 | 2.3–6.3 for pasture; 3.7–9.2 for forest | NA | Histosols associated with stagnasols, cambisols, and regosols | Tropics | San Francisco, Ecuador |
| <i>Asano et al.</i> [2002] | 2 | 4 | Depth and upslope contributing area | EM and EPM | Zero-tension lysimeter | 2–3 weeks interval | 10, 40 | 0–1.6 for 10 cm; 1.4–3.8 for 40 cm | NA | Cambisols and regosols | Temperate | Fudoji, Japan; Rachidani, Japan |
| <i>McGuire and McDonnell</i> [2010] | 0 | 3 | Slope positions | DM | Suction lysimeter | Daily to weekly | 30, 70, 90 | 1.4–2.9 for 30 cm; 2.7–3.4 for 70 cm; 2.9–3.6 for 90 cm | Clay loam | Typic Dystrocrepts | Mediterranean | H. J. Andrews Experimental Forest, USA |
| <i>Muñoz-Villers and McDonnell</i> [2012] | 0 | 3 | Depth and upslope contributing area | EM and DM | Suction lysimeter | Partly daily to every 25 days and partly weekly | 30, 60, 90, 120 | 3–6 at 30 cm; 9–23 at 60 cm; 13–42 at 90 cm; 20–26 at 120 cm | Loam to silt clay loam | Umbric Andosols | Tropics | Cofre de Perote, Mexico |
| <i>Stewart and McDonnell</i> [1991] | 0 | 6 | Depth and upslope contributing area | EM and DM | Suction lysimeter | Weekly | 20, 40, 80 | 2 at 20 cm; 6 at 40 cm; 9 at 80 cm | NA | Yellow brown earth, Gley, Podzols, and Grey Podzols | Humid temperate | Maimai M8, New Zealand |
| <i>Kim and Jung</i> [2014] | 0 | 6 | Depth and upslope contributing area | EM and DM | Suction lysimeter | Fortnightly | 10, 30 | 4–8 at 10 cm; 5.7–6.4 at 30 cm; 7.4 at 60 cm | Sandy loam and loamy sand | Leptosol | Temperate | Sulmachun, South Korea |
| <i>Kabaya et al.</i> [2007] | 0 | 3 | Depth | EPM and DM | Suction lysimeter | Monthly | 10, 20, 30, 50, 100 | 4–19 at 10 cm; 4–11 at 20 cm; 3–16 at 30 cm; 6–17 at 50 cm; 10–20 at 100 cm | NA | NA | Temperate | Kiryu, Japan |
| <i>Kabaya et al.</i> [2011] | 0 | 4 | Depth and upslope contributing area | DM | Suction lysimeter | Monthly to fortnightly | 10, 20, 30, 50, 75, 100, 200, 250 | 10–17 at 10 cm; 14–20 at 50 cm; 21–61 at 100 cm; 43–72 at 200 cm | NA | Cambisol | Temperate | Tsukuba, Japan |
| <i>Kudo et al.</i> [2013] | 0 | 2 | Forest versus grassland | DM | Centrifugation | Monthly | 0–10, 10–20, 20–30, 30–40 | 2–9 at 10 cm; 15–28 at 20 cm; 10–15 at 30 cm; 12–14 at 40 cm; 3–10 at 20 cm; 9–57 at 60 cm; 12–60 at 100 cm | NA | NA | Temperate | Mount Aso, Japan |
| <i>Hu et al.</i> [2015] | 0 | 4 | Depth and upslope contributing area | EM and DM | Suction lysimeter | Weekly | 20, 40, 60, 80, 100 | 10 at 30 cm; 29 at 60 cm; 28 at 80 cm | Clay to clay loam | NA | Subtropical | Huanjiang, China |
| <i>Lee et al.</i> [2007] | 0 | 1 | Depth | EM and EPM | Suction lysimeter | Fortnightly | 30, 60, 80 | 10 at 30 cm; 29 at 60 cm; 28 at 80 cm | Silty clay to clay loam | NA | Temperate | Jeju Island, South Korea |
| <i>Tetzlaff et al.</i> [2014] | 0 | 3 | Soil type | GM | Suction lysimeter | Weekly | 10, 30, 50 | 258 at 30 cm in riparian peat soil; 87 at 30 cm in peaty gley; 22 at 30 cm in podzol | NA | Podzols and peaty gleys | Temperate | Brunland Burn, UK |
| | 0 | 5 | | | Lysimeter | | 150 | 30–39 at 200 cm | Silt loam | Dystric Cambisol | Temperate | |

Table 1. (continued)

| Study | R | N | RQ | Model | Method | Frequency | Depths (cm) | MTT (weeks) | Texture | Soil Type | Climate | Study Location |
|-----------------------------------|---------|----|--|---------------------------------|------------------------|------------------------|--|--|---|---|-------------------|---|
| <i>Stumpp et al.</i> [2012] | 0 | 1 | Land use (Crop and fertilizer) Variability in time | Peak shift, DM, TNM modified DM | Lysimeter | Event basis and weekly | 200 | 26–59 at 200 cm; variable over time | Sand | Cambisol | Temperate | Gumpenstein, Austria Neuherberg, Germany |
| <i>Stumpp et al.</i> [2009a] | 0 | 2 | Crop and comparison between models | DM and TNM | Lysimeter | Weekly | 150 | 31 and 28 for Maize and Intercrop based on H1D and 32 and 31 based on DM, respectively | Loamy sand | Dystric Cambisol | Temperate | Wagna, Austria |
| <i>Leopoldo et al.</i> [1984] | 2 | 4 | Soil texture | RM | Suction lysimeter | Weekly | 15, 25, 50, 80, 120 | 0.9 and 0.7 at 15 cm depth and 1.6 and 1.2 at 25 cm depth for clay and sandy-clay soil, respectively | Clay and sandy-clay | NA | Tropics | Model Basin, Brazil |
| <i>Lindström and Rodhe</i> [1992] | 0 | 3 | Testing mixing assumptions | Mixing-Piston flow model | Lysimeter | Twice a month | 15, 40, 80 | 4 at 15 cm; 9 at 40 cm; 17 at 80 cm | NA | NA | Humid continental | Stubbetorp, Sweden |
| <i>McGuire et al.</i> [2002] | 0 | 2 | Soil texture | EPM and DM | Suction lysimeter | Fortnightly | 100 | 7 or loamy-skeletal and 9.5 for silt loam | Loamy-skeletal and silt loams | Utisols/inceptisols and Typic Hapludult | Humid continental | Leading Ridge and Mahantango, USA |
| <i>DeWalle et al.</i> [1997] | 0 | 1 | Comparison to rainfall and streamflow data | EM | Suction lysimeter | Fortnightly | 30 | 10.4 at 30 cm | stony, sandy loams | NA | Temperate | Benner Run, US |
| <i>Mali and Urbanc</i> [2006] | 0 | 1 | Depth | EPM and DM | Zero-tension lysimeter | Monthly | 82, 108, 152, 204, 241, 295, 340, 393, 439 | 11 at 82 cm; 15–19 at 152 to 241 cm; 30–39 at 295 to 439 cm | Coarse gravel | NA | Temperate | Selniska Dobrava, Slovenia |
| <i>Maloszewski et al.</i> [2006] | 0 | 5 | Soil texture | DM and TNM | Lysimeter | Weekly | 200 | 8–31 at 200 cm depending on grain sizes | Quartz sands, quartz gravel, tertiary sands | NA | Temperate | Neuherberg, Germany |
| <i>Sprenger et al.</i> [2016b] | 7 to 16 | 35 | Soil type | TNM | Direct equilibration | Twice | 10, 30, 50, 100, 150, 200 | 1.8–6.4 at 10 cm; 10–21 at 50 cm; 31–178 at 200 cm | Sandy, silty loam, clay | Arenosols, cambisols, stagnosols | Temperate | Attert, Luxembourg |

^aThe number of replicates (R), the total number of soil profiles (N), the research question (RQ), applied transit time model (LM = linear model; EM = exponential flow model; EPM = exponential piston flow model; DM = dispersion model; LPM = Linear-piston flow model; GM = gamma model; TPLR = two parallel linear reservoirs; TNM = transient numerical model; RM = regression model;) pore water sampling and analysis method, sampling frequency, studied depths, resulted range of mean transit times (MTT), soil texture and soil types of the studied soils, climate, and name of the study sites.

coarse material that the dispersion model was able to describe the isotopic transport under variable flow conditions as well as a numerical model based on the Richards equation and the advection-dispersion equation. *Stumpp et al.* [2009c] modified the input function of the lumped dispersion model by taking the evapotranspiration losses (weighable vegetated lysimeter) into account.

It was shown that the MTT estimations in the soil depend on the applied travel time model [*Timbe et al.*, 2014] and also the sampling frequency has an influence on the estimates of MTT [*Timbe et al.*, 2015]. An alternative dynamic model approach is a combination of mixing and piston flow assumptions, which were shown to be able to simulate the temporal variable travel times through a lysimeter [*Lindström and Rodhe*, 1992] or the stable isotope dynamics of mobile water in 0.6 m soil depth [*Comas-Bru and McDermott*, 2015]. Given the hydroecological feedbacks presented in the previous sections, which influence the water flow and solute transport, lumped convolution approaches that do not consider transient water flow and evapotranspiration losses within the soil profile seem to oversimplify the processes. In contrast, numerical simulations showed promising opportunities to account for time variable travel times at the hillslope scale [*Rinaldo et al.*, 2011; *Ali et al.*, 2014], while parameterization of such models is problematic [e.g., *Beven*, 2006]. *Windhorst et al.* [2014] found that a physical hillslope model can simulate—despite a bias of about -17% for $\delta^2\text{H}$ —the temporal dynamics of the pore water isotopic signal. They argue that it is unlikely that the bias is caused by evaporation fractionation of the soil water, which was not accounted for. Instead, isotopically enriched fog drip, also not considered in the model, might alter the input signal [*Windhorst et al.*, 2014]. *Windhorst et al.* [2014] used solely isotope data for calibrating the hydraulic conductivity and porosity and limited the simulation to the advective transport. *Sprenger et al.* [2015b] included for soil profiles in addition to pore water isotope data also soil moisture data to estimate water flow and transport parameters (dispersivity). Such a combination of hydrometric data (i.e., soil moisture time series) with pore water stable isotope data was shown to provide valuable information for calibrating soil physical models to derive time variable travel time estimations [*Sprenger et al.*, 2016a, 2016b]. This way, resident concentrations of the water stable isotopic composition, which can be either sampled destructive or in situ [*Rothfuss et al.*, 2013; *Volkman and Weiler*, 2014; *Gaj et al.*, 2016], are applicable for time variable travel time calculations.

Such knowledge about the vadose zone travel times can serve to benchmark or calibrate catchment models as shown by *Birkel et al.* [2014]. Especially, the long tails of travel time distributions on the catchment scale could potentially be better understood by comparably long travel times in the unsaturated zone [*Seiler et al.*, 2002; *Sprenger et al.*, 2016b].

5.3. Preferential Flow

Preferential flow, as bypass flow or lateral subsurface flow from the upslope, can be identified by a high variability of the isotopic signal in a certain soil depth over space [*Zhang et al.*, 2011; *Eisele*, 2013; *Thomas et al.*, 2013; *Peralta-Tapia et al.*, 2015] or time [*Brodersen et al.*, 2000; *Song et al.*, 2009]. Also, an absence of the seasonal variation of the precipitation signal in pore water stable isotope profiles can indicate preferential flow [*Gehrels et al.*, 1998; *Orlowski et al.*, 2015], while a pronounced cyclic variation of the isotopic composition reflects vertical displacement of old water by new water [*Eichler*, 1966; *Sprenger et al.*, 2016a]. However, a distinct isotopic signal in the soil indicates vertical or lateral preferential flow path ways (conceptually visualized in Figure 2b). For example, pronounced peaks of a depleted $\delta^{18}\text{O}$ signal in isotope depth profiles were found during snow melt at -1.2 to -1.3 m soil depth by *Kelln et al.* [2007] and at -2 to -2.5 m by *Peralta-Tapia et al.* [2015]. Many pore water isotope studies found a combination of slow flow in the soil matrix and a rapid flow in macropores [*Mathieu and Bariac*, 1996; *Seiler et al.*, 2002; *Cheng et al.*, 2014]. Which of the coexisting process dominates depends, besides the soil structure and texture, on the size of the precipitation event and the soil moisture [*Gazis and Feng*, 2004]. The isotopic composition of water in preferential flow paths was shown to be similar to the event water for soil with a well-developed system of biopores [*Leaney et al.*, 1993]. However, more often macropore flow shows a different isotopic signal than the precipitation input [*DeWalle et al.*, 1988; *McDonnell*, 1990; *Wenner et al.*, 1991; *Anderson et al.*, 1997; *Kelln et al.*, 2007], indicating that an interaction (mixing) between the water in the soil matrix and macropore flow takes place. This interaction can be induced by backing up of water in macropores and infiltrating into the matrix from where it seeps into lateral pipes [*McDonnell*, 1990] or when moisture thresholds in the soil matrix are exceeded and displacement of old water initiates macropore flow [*Anderson et al.*, 1997; *Klaus et al.*, 2013]. Pore water stable isotope sampling prior and after sprinkling experiments with isotopically enriched water showed preferential flow patterns

for loess soils [Eisele, 2013] and tertiary sands [Seiler *et al.*, 2002]. Since no preferential flow was observed in sprinkling experiments with deuterated water at a site with fluvial deposits on sand and coarse gravel [Koeniger *et al.*, 2010], the pore size distribution governs the infiltration pattern. If the input signal in sprinkling experiments is not distinct from the background isotopic composition of the soil water, preferential flow cannot be recognized [Klaus *et al.*, 2013]. A mismatch between observed isotope depth profiles and simulated profiles using numerical soil models based on the Richards equation can also help to examine preferential flow processes, when the simulations cannot reflect the observations [Stumpp and Hendry, 2012; Mueller *et al.*, 2014]. The relevance of preferential flow can be quantified accounting for preferential and matrix flow separately. Stumpp *et al.* [2007] proposed a conceptual model, where the slow flow through the matrix was represented with a dispersion model and the fast flow in macropores was simulated by a piston flow model. This approach showed that the fast component in the outflow amounted to 7–30% in bare soil lysimeters filled with fluvial gravel [Stumpp *et al.*, 2007] and 7–10% for vegetated lysimeters filled with an undisturbed sandy soil (Humic Cambisol) [Stumpp and Maloszewski, 2010]. A similar dual-continuum approach for a hillslope could reproduce both the gradual changes of the observed $\delta^{18}\text{O}$ values in the soil matrix sampled by suction lysimeter and the quick changes of $\delta^{18}\text{O}$ in the hillslope drainage [Vogel *et al.*, 2010]. While irrigation experiments with isotopically enriched waters generally allow for direct recognition of bypass flow in the field for short time scales; also, the natural variation and anomalies of the isotopic composition of the soil water over time and/or in space may provide valuable insights into preferential flow pathways.

6. Recent Challenge in Pore Water Stable Isotope Hydrology

6.1. Two Water World Hypothesis

Differences between the isotopic signal in groundwater and stream water on the one side and soil and vegetation on the other side (“ecohydrological separation”) has recently motivated studies to propose the two water world hypothesis, defined as “vegetation and streams returning different pools of water to the hydrosphere” [McDonnell, 2014], which can affect the global partitioning of hydrologic fluxes [Good *et al.*, 2015]. In fact, Brooks *et al.* [2010] and Goldsmith *et al.* [2012] found xylem water to be of similar fractionated isotopic composition as soil water of the topsoil analyzed with cryogenic extraction. At the same time, the groundwater and stream water consisted of unfractionated water similar to the soil water sampled via suction cup lysimeters (60 kPa) [Brooks *et al.*, 2010; Goldsmith *et al.*, 2012]. As shown in a meta-analysis by Evaristo *et al.* [2015], this pattern of an evaporation fractionation signal in the xylem and soil water and no evaporation fractionation in stream water and groundwater is present in various studies conducted in different climates around the world. However, Evaristo *et al.* [2015] did not consider that the deviation of soil samples from the GMWL diminishes with increasing depth as shown in Figure 4 using data from the same studies as presented in Evaristo *et al.* [2015]. Therefore, we believe it is not paradoxical that the mobile water (draining water, e.g., sampled with lysimeter, suction cup lysimeter, or wick samplers), the stream water, or water recharging to the groundwater lays on the LMWL in a dual-isotope plot, while the immobile water (held against the gravity, e.g., sampled with cryogenic extraction or direct equilibration) shows an evaporative fractionation signal.

Why groundwater or streamwater does not show an evaporation fractionation signal has been studied for decades. Possible explanations include that the evaporation fractionation signal in the topsoil is equalized by the preferential recharge of in heavy isotopes depleted water during the vegetation dormancy [e.g., Brinkmann *et al.*, 1963] or that the groundwater recharge is limited to high-intensity rainfall events or snow melt bypassing the topsoil through preferential flow paths without altering its isotopic composition by evaporation [e.g., Komor and Emerson, 1994; Mathieu and Bariac, 1996; Schlaepfer *et al.*, 2014]. The other way around, Gat and Airey [2006] suggested that an evaporation fractionation signal could only be introduced into the groundwater when the antecedent soil water of negative lc -excess is flushed with newly introduced rainwater. However, such an isotopic enrichment of the groundwater compared to the precipitation water was not observed in a global groundwater data set [Evaristo *et al.*, 2015].

6.2. Subsequent Fading of Fractionation Effects

Based on the literature review and considering the fact that the evaporation fractionation signal diminishes within the first 0.5 m soil for temperate climates, we propose that subsequent mixing of the evaporated soil water with nonfractionated precipitation water could explain the differences in the isotopic signal of water

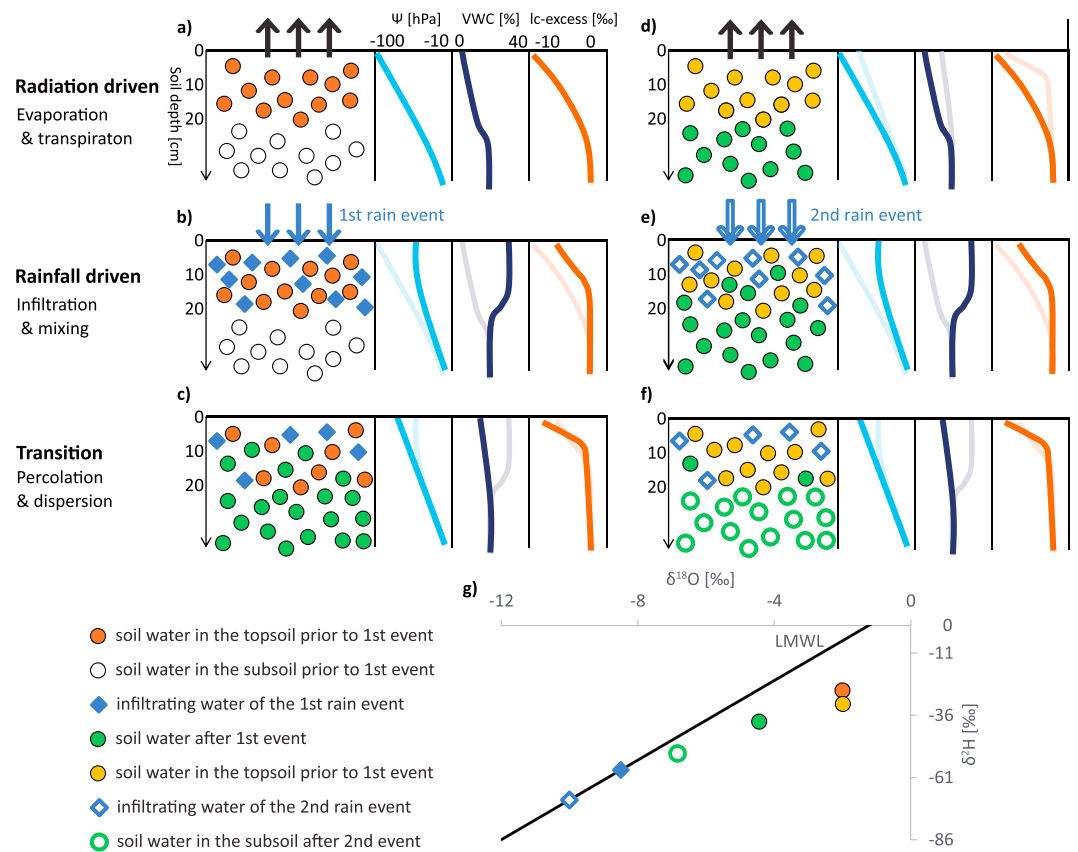


Figure 8. Conceptualization of the hydrological processes influencing the matric potential (ψ), volumetric water content (VWC), and isotopic composition (lc-excess) in the upper 0.5 m of the soil during a (a and d) dry period, a (b and e) rain event, and (c and f) the time in between. Graphs Figures 8a to 8f are in chronological order, and the prior state of ψ , VWC, and lc-excess is shown in semitransparent colors, respectively. (g) The dual-isotope plot shows the isotopic composition of fractionated soil water (orange circle), fictitious rainwater (blue diamonds), and the resulting subsequent mixture soil water (green circles).

in the top soil and in the xylem of plants on the one hand and groundwater and streamwater on the other hand. Figure 8 visualizes the concept of a subsequent mixing of pore waters resulting in a fading of the evaporation fractionation signal. The pore water in the topsoil becomes isotopic fractionated during a dry period (Figure 8a). The infiltrating water of a precipitation event mixes with the pre-event water (Figure 8b), and the increased pressure head initiates percolation of the mixed water (Figure 8c). Due to this successive mixing of the “old” pore waters with newly introduced rain water over time and with increasing soil depth (Figures 8d–8f), the isotopic signal of the pore water converges toward the LMWL (Figure 8g). Generally, the topsoil with its enriched isotopic composition is very small in volume (very low soil moisture content) compared to the total water volume in the vadose zone [Darling and Bath, 1988] and with increasing depth, the infiltrating water mixes with higher volume of water already present in the pores [Wenner et al., 1991]. This water will not be affected by evaporation fractionation anymore as soon as it percolates below the maximum evaporation penetration depth. However, the maximum evaporation penetration depth will depend on the soil texture and the climatic conditions as discussed earlier, since it is deeper in arid and Mediterranean climates than in temperate climates (Figure 5). Thus, the recharge water will eventually due to subsequent mixing have an isotopic signal that does not show considerable fractionation effects anymore or at least the effects are smaller than the measurement error for isotope analysis.

We underline the conceptual framework with numerical simulations of a soil hydrological model. The simulations were performed for a sandy soil under a temperate climate for the time period of 3.5 years (January 2011 to June 2014) on a daily basis. To reduce the effect of the initial conditions, the 3.5 years of available atmospheric forcing were put in front of the simulation run. Water flow and isotope transport in the model

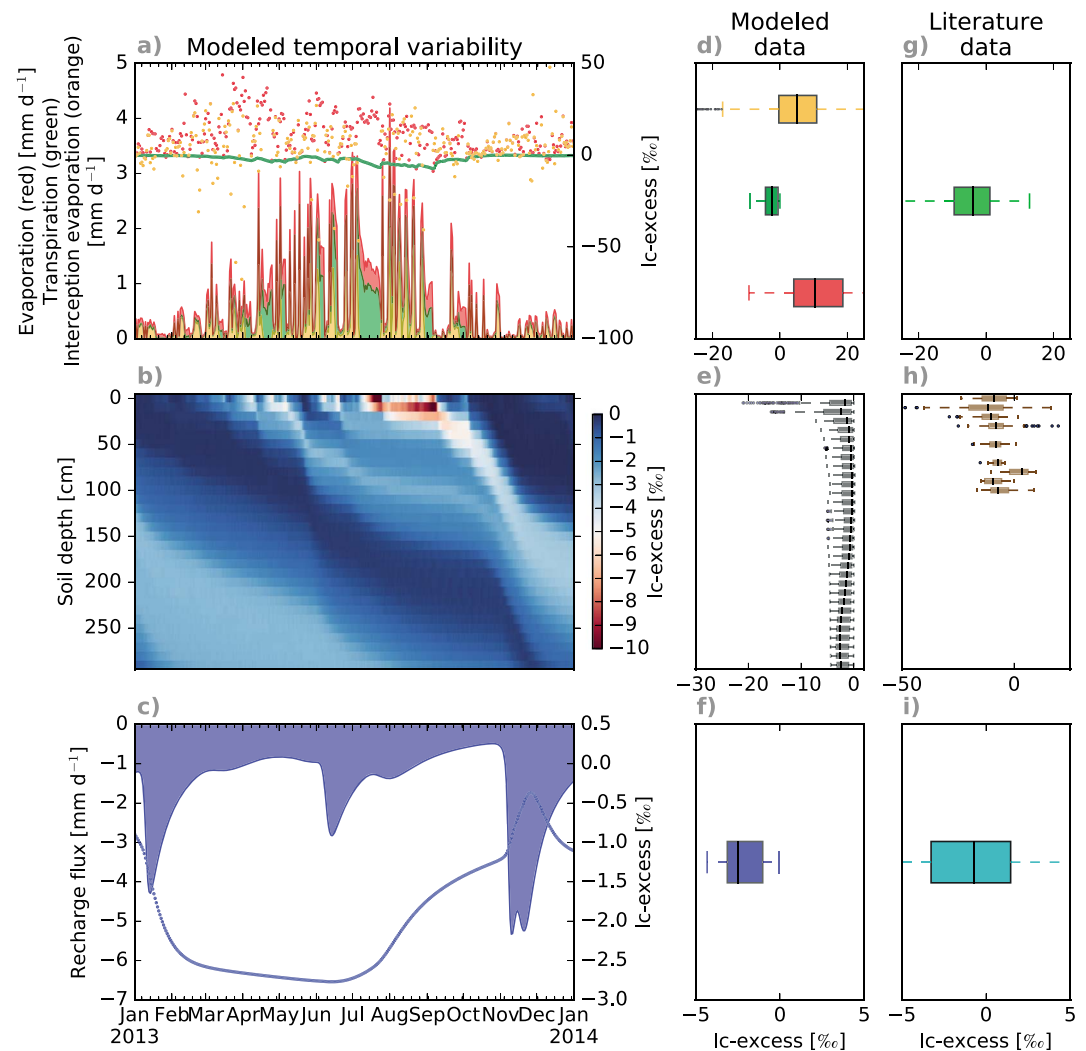


Figure 9. Simulated temporal dynamics of lc -excess for a forested plot with a sandy soil for the year 2013. (a) Fluxes into the atmosphere by soil evaporation, interception evaporation, and transpiration (lines) and the accompanied lc -excess (points). (b) lc -excess of the soil water across a 3 m soil profile. (c) Recharge flux and its lc -excess. (d–f) Range of the simulated lc -excess for each compartment for the simulation period January 2011 to June 2014. (g–i) Range of the lc -excess in the literature. Xylem data from a temperate forest [Bertrand et al., 2012], soil data from soil water isotope studies in temperate forests [Jia et al., 2012; Rong et al., 2011; Wang et al., 2010b; Berry et al., 2014; Brooks et al., 2010; Sun et al., 2008; Bertrand et al., 2012; Sprenger et al., 2016b], and groundwater data from the global meta-analysis by Evaristo et al. [2015]. Note that the y axis for Figure 9e and 9h represent the soil depth and thus the same as for Figure 9b.

were simulated on a daily basis with the Richards equation and according to the advection-dispersion equation. For a detailed description on the model, we refer to Mueller et al. [2014]. The soil hydraulic parameters were derived from Wessolek et al. [2009]. The model further considered evapotranspiration, estimated with the Hargreaves equation [Hargreaves and Samani, 1982]. Evapotranspiration was partitioned into evaporation and transpiration as a function of the leaf area index. Transpiration decreased linearly over the rooting zone (upper 70 cm) and depended on the water content and porosity according to the implementation in TOPMODEL by Menzel [1997]. While transpiration did not alter the isotopic composition, soil evaporation led to isotopic fractionation. The equilibrium fractionation was derived in accordance to Majoube [1971] as a function of the soil temperature and the kinetic fractionation taking the humidity into account estimated according to Gonfiantini [1986].

The simulation results show that the signal of isotopically enriched water due to soil evaporation in the upper soil is not passed on to greater depth. We show the temporal dynamic of the evaporation fractionation signal

($\delta^{18}O$ -excess) in the different compartments for the simulation for a sandy soil in Figures 9a–9f. The pore water being isotopically fractionated during dry periods becomes diluted with newly introduced (unfractionated) rainwater, and the fractionation signal expressed as $\delta^{18}O$ -excess fades with proceeding percolation depth (Figure 9b). As outlined above, the volume of water affected by evaporation fractionation in the upper 30 cm is relatively low compared to the water volume below 30 cm soil depth. For our simulations, the topsoil contains only between 10 and 30% of the water volume between –30 and –200 cm (data not shown). The water that is taken up by the vegetation—usually sampled as xylem water—will show the fractionation signal during dry periods but varies also according to the isotopic composition of the rainfall input (Figures 9a and 9d). As outlined above, unfractionated precipitation volumes are relatively high compared to the potentially fractionated pre-event water. For our simulations, 73% of the total precipitation volume infiltrates into a soil that stores less than the event water in the upper 30 cm of soil. The simulated recharge water in 3 m depth shows very little variation of the $\delta^{18}O$ -excess due to the mixing processes of fractionated pore water with unfractionated rainfall input (Figures 9c and 9f). Nevertheless, in our simulations, the root water uptake and the recharge water do not necessarily originate from two different pools of subsurface water.

The presented simulations are within the range of the $\delta^{18}O$ -excess as reported for xylem water in a temperate climate [Bertrand *et al.*, 2012] (Figure 9g) and globally reported for groundwater [Evaristo *et al.*, 2015] (Figure 9g). The variation of the simulated soil water $\delta^{18}O$ -excess is within the range of the isotopic composition of soil water published in studies in temperate forests (Figure 9h). The simulations cover the lower range of the $\delta^{18}O$ -excess values observed in the literature. However, the evaporation and the accompanied isotopic fractionation were simulated in a parsimonious manner to keep the required input data and the number of parameters low and the model was not calibrated to specific sites.

Our simulations and the conceptual model can explain the general concept of the suggested subsequent fractionation fading effect that might explain why the top soil and xylem water show an evaporative fractionated isotopic composition, while the stream water and groundwater show no evaporation signal. Furthermore, the subsequent mixing effect and the involved dilution of the evaporation fractionation signal are supported by high-frequency measurements in a soil column by Rothfuss *et al.* [2015], who showed that intensively fractionated water of the top soil immediately shifts its isotopic composition toward the GMWL after irrigation. Such high-frequency measurements are yet missing under field conditions but will give new insights into the mixing patterns within the topsoil, while the deeper soil with its low dynamic of the isotopic composition is already relatively well studied.

Good *et al.* [2015] found in their global isotope mass balance analysis that the soil evaporation (and its partitioning in evaporation from bound and mobile soil waters) has direct influence on the isotopic signal in the continental runoff: The higher the fraction of evaporation from bound waters, the more isotopically depleted will be the continental runoff. This evaporation partitioning into bound and mobile waters correlates with the hydrological connectivity between bound and mobile water, resulting in a more depleted isotopic signal in the continental runoff when more preferential flow occurs, while translatory flow would lead to isotopically enriched continental runoff. Good *et al.* [2015] concluded for their global analysis that 62% of water entering the streams is hydrologically disconnected (i.e., preferential flow) from the bound soil water.

Our concept of the subsequent fading of fractionation effects does not support the findings by Good *et al.* [2015], because mixing with unfractionated rain water and dispersion during the percolation brings the isotopic signal of the recharging water close to the signal of the precipitation input making the stream water signal less sensitive to soil water fractionation.

In addition, the reviewed studies showed that the vegetation can adapt to water availability in the soil, indicating that the water uptake by roots is preferably in areas or pore spaces which are relatively easily accessible. Thus, it is questionable if ecohydrological separation is actually taking part or if instead the soil water undergoes isotopic changes over space (e.g., depth) and time (e.g., seasonality) leading to distinct isotopic signals between the top soil and subsoil, which will directly affect the isotopic signal of the root water.

7. Future Work

Our review showed that water stable isotopes are increasingly used to study the soil-vegetation-atmosphere interface. However, especially where disciplines like hydrology, soil science, and ecology overlap, a better

understanding of the interactions between water, minerals, and vegetation remains challenging. As such, we see three major aspects for future work.

First, the different pore water stable isotope analysis methods and the problem of defining their sampled pore space or comparing their precision and applicability needs to be better understood [Orlowski *et al.*, 2016a; Sprenger *et al.*, 2015a]. The influence of soil texture [Meißner *et al.*, 2014; Oerter *et al.*, 2014; Orlowski *et al.*, 2016b; Oshun *et al.*, 2016] and organic material [West *et al.*, 2010] on the pore water stable isotope analysis is increasingly acknowledged. Also, the composition of carrier gas was shown to have an influence on the isotope analysis with laser spectrometry by altering the ^2H to ^{18}O ratio [Gralher *et al.*, 2016]. Thus, soil samples analyzed with the direct equilibration method can be affected by the carrier gas and gases developed by microbial activity (e.g., CO_2 or CH_4) [Gralher *et al.*, 2016]. Nevertheless, how to account for these issues for the pore water isotope sampling methods is currently up for debate and probably needs a combined effort to systematically compare methods, analysis systems, and approaches from several groups around the world.

Second, in situ measurements of water stable isotope signals have shown to provide valuable insights due to high-frequency sampling of precipitation input [Berman *et al.*, 2009; Herbstritt *et al.*, 2012; Pangle *et al.*, 2014], soil water infiltration [Volkman *et al.*, 2016a], soil water evaporation [Gangi *et al.*, 2015; Gaj *et al.*, 2016; Rothfuss *et al.*, 2015], and vegetation transpiration [Dubbert *et al.*, 2014a; Volkman *et al.*, 2016a, 2016b; Wang *et al.*, 2012b]. These methods allow for higher sampling intervals in time to study short-term responses within the soil and vegetation on the one hand, but the in situ measurements provide also the means for a high spatial sampling of the isotopic signal in the soil-vegetation-atmosphere interface. The inclusion of the pore water stable isotope data for the calibration of numerical models as shown by, e.g., Sprenger *et al.* [2015b, 2016b] or [Huang *et al.*, 2015], provide a promising perspective for modeling soil processes [Vereecken *et al.*, 2016].

Lastly, the progress made in pore water stable isotope analysis enables a higher spatial coverage of the soil water isotope sampling. Thus, replicates to account for the subsurface heterogeneity allow supporting a more general picture of the spatial variability [Brooks *et al.*, 2010; Sprenger *et al.*, 2016b; Thomas *et al.*, 2013]. This is especially true for vadose zone transit time studies, where repeated measurements are rather an exception than the rule (Table 1). Spatial information of the pore water isotopic signal over an area and in depth could be applied for soil water isoscapes [Bowen, 2010; Bowen and Good, 2015] and allow benchmarking hydrological models [Birkel *et al.*, 2014; Sprenger *et al.*, 2016b]. This way, a multiobjective parameterization including hydrochemical data and hydrometric data, as widely applied for catchment outlet data, can be extended to vadose zone data to account for processes within catchments than rather concentrating on the integrated signal in the discharge.

8. Conclusion and Summary

Our review shows that there is an interplay of various processes that alter the pore water isotopic composition and the dominant factors being controlled by the climate, soil texture, soil structure, and land use. Thus, a multidisciplinary approach is required, where the interactions of the soil with the atmosphere, groundwater, and vegetation are considered to understand the isotopic composition of the vadose zone. The application of pore water stable isotope analyses can be adjusted depending on the research question, but the multidisciplinary character of the pore water data needs to be considered nevertheless. As shown in this review, the use of pore water stable isotopes is continuously increasing due to the technical developments in the last two decades making the analyses more time and cost efficient. However, many aspects regarding the physical processes affecting the pore water isotopic composition are still poorly understood. Especially, the hydroecological interactions are challenging to study with spatial scales ranging from small soil pores, where water is tightly bound and possibly taken up by roots, to large catchments, where the vegetation cover governs the partitioning between soil evaporation and transpiration. Also, the temporal dynamics in the flow and mixing of water with different isotopic composition has not been observed and studied in the necessary details yet.

Based on the presented studies in this review, we propose to consider the following points when pore water stable isotopes are being used: (1) Knowledge about the past precipitation inputs is indispensable to interpret pore water stable isotope data. (2) Consideration of both ^{18}O and ^2H (or the d-excess and lc-excess)

reveals important insights into evaporation processes in the topsoil. (3) The hydroecological feedbacks are not restricted to the topsoil but influence also the travel times of the recharge flux (e.g., preferential seasonal root water uptake and evaporation). (4) Recharge water that is not isotopically fractionated does not necessarily imply that the vegetation, which xylem water shows a fractionated isotopic signal, uses a different pool of pore water. (5) The choice of the pore water stable analysis method may determine the pore space that is sampled, which is directly related to the mobility of the soil water. (6) The sampling frequency of rainfall input and pore waters needs to be adapted in space and time with regard to the addressed research question. (7) Replicates of pore water samples strengthen the explanatory power and allow inferring generalizable conclusions for the highly heterogeneous vadose zone.

Glossary

Deuterium excess (d-excess) is the deviation from the global meteoric water line defined as: $d\text{-excess} = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$ [Dansgaard, 1964].

Dual-isotope plot describes the relation between two isotopes. Here we limit the concept on the relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

Equilibrium fractionation for water stable isotopes is given when the phase change in any direction (e.g., liquid to vapor or vapor to liquid) does not alter the ratio of the water isotopes in a closed system at a constant temperature at 100% humidity.

Evaporation line is a regression line that describes the enrichment of heavy isotopes due to evaporation fractionation in open water or soil water.

Global meteoric water line (GMWL) describes the global relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation water [Craig, 1961]. This relationship is given as [Rozanski et al., 1993]

$$\delta^2\text{H}_{\text{VSMOW}} = 8.2 \delta^{18}\text{O}_{\text{VSMOW}} + 11.27$$

Isotope delta (δ notation) is the relative difference in the ratio of heavy to light isotopes (e.g., $^2\text{H}/^1\text{H}$ for deuterium and $^{18}\text{O}/^{16}\text{O}$ for oxygen-18) of a water sample to a standard water, the Vienna Standard Mean Ocean Water; for ^{18}O : $\delta^{18}\text{O}_{\text{VSMOW}} = \left[\frac{R(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{R(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} - 1 \right]$ and for ^2H : $\delta^2\text{H}_{\text{VSMOW}} = \left[\frac{R(^2\text{H}/^1\text{H})_{\text{sample}}}{R(^2\text{H}/^1\text{H})_{\text{VSMOW}}} - 1 \right]$.

Kinetic fractionation describes the fact that the ratio between heavy and light isotopes will get altered during a phase change (e.g., liquid to vapor), because one of the isotopes is less likely to do the phase change due to the differences in mass of the isotopes.

Line-conditioned excess (lc-excess) is the deviation from the local meteoric water line defined by Landwehr and Coplen [2006] as $lc\text{-excess} = \delta^2\text{H} - a \cdot \delta^{18}\text{O} - b$, with a and b being the slope and interception of the LMWL, respectively. Negative lc-excess indicates that the water sample experienced evaporation fractionation processes.

Local meteoric water line (LMWL) describes the local (regionally limited) relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation water.

Travel time (or transit time) is the time a water particle takes to pass through a hydrological system [McDonnell et al., 2010].

Vadose zone is as the unsaturated soil/sediment between soil surface and groundwater table [Hopmans and van Genuchten, 2005].

Vienna Standard Mean Ocean Water (VSMOW) is a standard water of defined $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ ratios; used as a reference for the calibration of the measurements of stable isotopes of water to ensure a comparability [Craig, 1961; Gonfiantini et al., 1995].

Xylem water is the water transported in the transport tissues (xylem) of vegetation.

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