

# Established methods and new opportunities for pore water stable isotope analysis

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## **Abstract**

The vadose zone plays a crucial role in the water cycle for storing water, providing water to vegetation and transporting solutes or degrading contaminants. Earth scientists have long acknowledged the importance of the vadose zone and numerous methods have been developed to better understand and predict hydrological processes within this “critical zone”. For several decades, stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) of pore water are used as environmental tracers to gain insights into vadose zone water movement and other processes. To determine the pore water stable isotopic composition various sampling procedures have been developed. We present the procedure and the accompanied advantages and drawbacks of each method. We further discuss possible opportunities and limitations regarding the scale of interest and the pore space that is sampled. The methodological review reveals that the choice of the sampling method is crucial for the interpretation of pore water stable isotopes in the vadose zone, but a thorough comparison between the different methods is yet missing. Spiking experiments, where water of known isotopic composition is added to oven-dried soil, have shown to be questionable, since the extracted water is usually depleted compared to the standard water. A comparative study analyzing soil samples with the recently developed direct water-vapor equilibration method and the widely used cryogenic extraction shows deviations, which can only be partly explained, but discloses the need for a more thorough experimental comparative study. Especially promising are developments of continuous isotope measurements based on laser-based spectrometry that will open up new opportunities of analyzing pore water isotopes with higher temporal and spatial resolutions, revealing new insights into hydrological processes across various temporal and spatial scales.

## 1. Introduction

Almost 60 years ago, Zimmermann et al. (1966) introduced water isotopes of pore water as a “tracer to determine movement of soil moisture and evapotranspiration”. Since then, pore water stable isotopes have found various applications in the multidisciplinary context of the vadose zone: Recently, they were used for example to study flow paths at hillslopes (Stumpp and Hendry, 2012; Garvelmann et al., 2012; Mueller et al., 2014; Windhorst et al., 2014; Peralta-Tapia et al., 2014), determine mixing processes over the soil depth (Thomas et al., 2013; Geris et al., 2015; Orłowski et al., 2015), estimate transit times in soil profiles (Stumpp et al., 2009a; Timbe et al., 2014; Sprenger et al., 2015), infer root water uptake pattern (Kulmatiski and Beard, 2013; Rossatto et al., 2014; Meißner et al., 2014; Bertrand et al., 2014; Bachmann et al., 2015), and separate between soil evaporation and transpiration fluxes (Dubbert et al., 2014). These studies (among numerous others) show that the vadose zone plays a special role in the hydrological cycle due to its role as a mediator in the groundwater-vegetation-atmosphere continuum. The vadose zone is defined by Hopmans and van Genuchten (2005) as the unsaturated zone between the soil surface and the groundwater table, where complex time-dependent, nonlinear physical, chemical, and biological processes take place interacting with the groundwater and the atmosphere. Depending on the boundary conditions, the vadose zone depths can span from several centimeters to dozens of meters, and far beyond the organic A, B and C soil horizons. In catchment hydrology, streamflow data is seen as an integrated signal of catchments, which is likely to be overemphasized by near stream processes and interactions with groundwater (Hewlett and Hibbert, 1967; Anderson et al., 1997; Geris et al., 2014), while the signal from the landscape-scale is blurred by the different flow paths (Kirchner et al., 2001). Thus, a better understanding of the vadose zone processes within the catchment is needed to challenge our perception of the hydrological processes and its implementation in hydrological models at different scales (McDonnell et al., 2010; Zehe et al., 2014). Stable isotopes of water ( $^{18}\text{O}$  and  $^2\text{H}$ ) are seen as ideal tracers to reveal the relevant processes within a catchment – including the vadose zone, since they are part of the water molecule itself (Kendall and McDonnell, 1998). The isotopic composition of a water sample is its ratio between heavy to light isotopes (e.g.  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ ) and is reported relative to the ratio of the Vienna

Standard Mean Ocean Water (VSMOW). This relation between water sample and standard is given in ‰ for the  $\delta$ -notation. Over the years, several different ways have been established to measure the isotopic composition of pore water in soils. An overview of the recent developments in the analysis methods is missing so far. Though, each method holds assumptions that need to be acknowledged in their application for hydrological studies. Therefore, we present the currently available methods and discuss their opportunities and drawbacks, which come with the application of each method.

## **2. Methods of pore water stable isotope analyses**

The different methods for pore water stable isotope measurement can be grouped according to (a) the way to access the information (extraction of pore water in the field (section 2.1), in the laboratory (section 2.2) or via equilibration (section 2.3)), (b) the related pore sizes that are sampled and (c) the type of the information (resident or flux concentration) (Table 1). The methods and their measurement accuracies, required sample volume or mass, advantages and disadvantages, and exemplary studies will be presented in the following sections and are summarized in Table 2. In addition, all methods are classified according to the sampled pore size distribution (Fig. 1) and the different water pools in the vadose zone (Table 1).

### **2.1. Water extraction in the field**

#### **2.1.1. Lysimeters**

Early application of water stable isotope studies derived time series of flux concentrations of the isotopic composition from the outflow of lysimeters (Eichler, 1966), which is depending on the sampling interval and potentially restricted to a seasonal recharge (Darling and Bath, 1988). Lysimeters hold the advantage of controlled boundary conditions. Evapotranspiration (ET) can be estimated with weighted lysimeters (Sutanto et al., 2012) and also soil moisture and matrix potential can be monitored (Maciejewski et al., 2006) or internal water samples can be extracted (Mali et al., 2007; Sutanto et al., 2012). However, the installation of lysimeters is cost- and time-intensive highly depending on the size ranging from 0.15 m (Lindström and Rodhe, 1992) to maximum 4 m (Mali et al., 2007). Lysimeter

studies are often site specific, neglect lateral fluxes, and are limited in depth (usually about 2 m). However, they help to disentangle the influence of specific drivers influencing the water flow through the vadose zone, such as vegetation (Stumpp et al., 2009a; Stumpp et al., 2009b; Pangle et al., 2013) or fertilization (Stumpp et al., 2012).

### **2.1.2. Zero tension lysimeters**

Zero tension lysimeters are water collectors in the soil collecting free draining water (Ebermayer, 1873; Jordan, 1968). They are installed by using soil pits or trenches and coarse material assures a connection to the soil above the lysimeters to generate seepage flow boundary conditions (Weihermüller et al., 2007). The installation procedure can result in enhanced bypass flow for soils of small pore sizes or under dry conditions due to water divergence (Jemison and Fox, 1992). Some isotope studies comparing zero tension lysimeters with suction lysimeters showed no significant difference between both methods (Dewalle et al., 1988; Anderson et al., 1997; O'Driscoll et al., 2005), while others found occasionally (Wenner et al., 1991) or systematically significant differences with zero tension lysimeters samples being more similar to the rain water (McGuire et al., 2002). The sampling is either event based (Wenner et al., 1991; Anderson et al., 1997) or pooled over weeks (Asano et al., 2002) and usually limited to the upper 100 cm soil.

### **2.1.3. Wick samplers**

Wick samplers extract soil water via fiberglass wicks that develop a suction of 50 to 60 hPa, depending on the wick length (Holder et al., 1991; Brandi-Dohrn et al., 1996) and the prevailing flux in the soil (Louie et al., 2000). Possible bypass flow can be limited by extension tubes and the flow rate can be measured via a tipping bucket (Gee et al., 2003) enabling flux concentration estimates. Wick samplers result in higher collection efficiencies than suction cup (Brandi-Dohrn et al., 1996) and zero tension lysimeters (Zhu et al., 2002). A sprinkling experiment with  $^{18}\text{O}$  enriched water showed that wick samplers mostly sampled event water (95 %), while the suction lysimeters sampled a mixture containing 15 % - 30 % event water (Landon et al., 1999). Hence, wick samplers should be used in pore

water isotope studies that are interested in sampling the mobile soil water (Timbe et al., 2014; Windhorst et al., 2014). However, the applicability of wick samplers is usually limited to the upper 1.5 m of the soil.

#### **2.1.4. Suction Lysimeters**

In suction lysimeters a partial vacuum is applied to extract the freely draining water and slightly bound pore water (Briggs and McCall, 1904). The applied suction varies in the pore water isotope studies between 133 hPa (Kabeya et al., 2007) and 8,000 hPa (Li et al., 2007a). The applied suction directly influences the pore space of which the water will be sampled (Fig. 1). However, the suction induces a temporary head field, which evolves around the lysimeters and produces a gradient that drives water flow in all pore sizes (Grossmann and Udluft, 1991) and also influences the sampling volume of the soil (Warrick and Amoozegar-Fard, 1977; Morrison and Lowery, 1990). Suction lysimeters can be run in a discontinuous or a continuous operation mode (Weihermüller et al., 2007), either applying a suction at some time or changing the suction in accordance to the actual matric potential. Both operation modes have advantages and disadvantages, whereas it is always difficult to relate the extracted water to a precise sampling time (Weihermüller et al., 2007). Suction lysimeters hold limitations in event based sampling because of the integrated signal (Anderson et al., 1997) and during periods of low soil water contents, when sampling is impossible, resulting in fragmented time series (e.g. Wenner et al., 1991; Yano et al., 2006; Kabeya et al., 2007). The actual movement of water through the porous cup of a suction lysimeters does not cause isotopic fractionation (Wenner et al., 1991). Suction plates, instead of suction cups of limited sampling area, can improve the sampling efficiency and flux concentration estimates (Kasteel et al., 2007). Besides these limitations, numerous pore water stable isotope studies make use of suction cup lysimeters installed in depths reaching down to 4 m (Table 2), arguing that the extracted water is more tightly held than gravitational water and therefore possibly the relevant water regarding hydrological and biological processes (Wenner et al., 1991).

## **2.2. Water extraction in the laboratory**

Geologic samples for pore water stable isotope analysis are usually drawn from unsaturated core samples taken manually, with a percussion or manual drill, or a rotary drilling rig. Depending on the scale of interest and the desired sampling interval the soil sampling takes place within few decimeters (David et al., 2013) to several hundred meters (Hendry et al., 2013). According to our experiences, the unsaturated core samples need to be thoroughly checked for cross contaminations (e.g. due to drill mud) and potentially, the outer diameter or parts of the core need to be discarded. If subsequent drilling is applied to reach greater depth into the subsoil than the soil core length, the subsequently taken cores need to be carefully checked for backfilled material. If the desirable sampling interval is smaller than the core size, the core sample needs to be divided into subsamples. Furthermore, the compression of the unsaturated core samples caused by the drilling needs to be accounted for in order to get the correct depth relation for each sample. For drilling with fluids to reach deep depths, contamination with the drilling fluid needs to be considered, which is more likely for permeable than for fine-textured geologic media (Hendry et al., 2015). Dry sonic methods for drilling should be avoided because of kinetic fractionation due to heating during sonic coring (Hendry et al., 2015). In general, the geologic samples need to be stored immediately at low temperature in air tight containers without air to prevent isotopic fractionation due to evaporation. Appropriate containers are unsaturated core samples sealed with caps and paraffin tape, glass vials or plastic bags. Comparisons among several bag types showed that laminated coffee bags (e.g. by Weber Packaging, Güglingen, Germany) are most tight. In our experience these coffee bags, filled with 250 g of moist soil do not lose more than 0.15 % of water over 30 days when heat sealed, while the weight loss reaches almost 1 % if freezer bags are used. However, Hendry et al. (2015) showed that freezer bags (Ziploc™) are applicable when storage is limited to 10 days of storage. Tedlar gas sampling bags are also a good alternative, but they are much more expensive than the coffee bags. Which container is most practical also depends on the applied extraction method. The extraction and isotope analysis should be done as soon as possible to prevent further alteration of the isotopic signal due to evaporation or microbial activity. If geologic samples cannot be analyzed shortly after the sampling, sterilization to inhibit microbial activity is recommended

(Hsieh et al., 1998b). Sterilization methods that apply heat (e.g. Autoclaving, dry heat, microwaves) or toxic chemicals, which need to be evacuated if gaseous (e.g. chloroform, ethylene and propylene oxide) and/or alter the pore water chemical or physical composition (e.g. sodium azide, mercuric chloride) (Trevors, 1996) are not suitable. Therefore, irradiation with gamma rays is recommended, since it leaves no chemical contamination and minimum effects on the physical composition of soil samples (Trevors, 1996; McNamara et al., 2003). Hsieh et al. (1998b) showed that soil samples sterilized with  $\gamma$ -radiation with a dosage of 24 kGy at room temperature resulted after 4 weeks incubation in about 2 ‰ less depleted  $\delta^{18}\text{O}$  values than unsterilized samples. Thus, possible influences on the  $^{18}\text{O}$  concentration in the soil water by  $\text{CO}_2$ -using or  $\text{CO}_2$ -exhaling microorganisms can be repressed.

### **2.2.1. Mechanical squeezing**

Squeezing was used in the early pore water isotope studies (Eichler, 1966). While squeezing can successfully extract pore waters from sandy to silty soils of as low as 6 % volumetric water content (VWC) (Moncur et al., 2013), for clayey soils, just about 50 % of the total water content is extracted, despite a squeezing pressure of 400,000 hPa for 24 h (Kelln et al., 2001). Consequently, the water squeezed out of the soil represents resident concentrations of mobile to loosely bound soil water. However, the mechanical squeezing is too labor intensive to analyze a large number of samples (Kelln et al., 2001).

### **2.2.2. Centrifugation**

In early studies, water of known isotopic composition was added in order to extract enough soil water via centrifugation (Zimmermann et al., 1967). Jusserand (1980) estimated that pores of  $>3 \mu\text{m}$  could be drained by centrifugation. However, even after a centrifugation with 14,000 rpm, 5-15 % of water remained in chalk soils (Edmunds and Bath, 1976). Immiscible heavy liquids may enhance the efficiency of the centrifugation (Sacchi et al., 2001). In comparison to mechanical squeezing and azeotropic distillation with toluene (Section 2.2.3.1), centrifugation with up to 10,000 rpm for up to 48 h resulted

in lowest water extraction volumes for clay rich soil samples (Kelln et al., 2001). A sprinkling experiment on soil cores by Figueroa-Johnson et al. (2007) supported the limitation of centrifugation to bigger pores: The water extracted via centrifugation resulted in an isotopic signal close to the loosely bound water extracted with suction lysimeters in the top soil with large pore sizes, but closer to the tightly bound water extracted by azeotropic distillation in the subsoil with smaller pore sizes.

### **2.2.3. Distillation methods**

#### **2.2.3.1. Azeotropic distillation**

Azeotropic distillation uses organic compounds that build at high temperatures an azeotropic mixture with water to decrease the boiling point (Revesz and Woods, 1990). Originally, azeotropic distillation with toluene was introduced to determine water content (Bidwell and Sterling, 1925) and its applicability for isotope studies was discovered years later (Allison and Hughes, 1983). Different organic solvents were used for the azeotropic distillation resulting in different corresponding boiling point temperatures: The azeotrope of water and toluene starts boiling at 84.1 °C (Revesz and Woods, 1990), with xylene at 90 °C (Hendry, 1983), with petroleum ether at 120 °C (Shatkay and Magaritz, 1987), and with kerosene at 185 °C (Walker et al., 1994). Mixing the water with the organic solvent does not result in any isotopic fractionation (Allison and Hughes, 1983; Shatkay and Magaritz, 1987; Revesz and Woods, 1990), traces of toluene need to be removed by reheating the extracted mixture with paraffin wax before the isotope analysis (Allison and Hughes, 1983) making the procedure time consuming (Kelln et al., 2001). Traces of the organic solvent left in the extracted water can cause inaccuracy, if laser spectrometry is applied for the isotope analysis (Brand et al., 2009). The isotopic signal of the extracted water can be altered due to extraction of hygroscopic water in gypsum (Revesz and Woods, 1990) or by reaction with clay minerals (Ingraham and Shadel, 1992; Izbicki et al., 2002). Because both effects will have a higher influence if the soil water content is low, azeotropic distillation is not applicable for soils with water contents below 5 % (Revesz and Woods, 1990; Ingraham and Shadel, 1992; Izbicki et al., 2002). A comparative study showed that azeotropic distillation provides

different results with different organic compounds and recommended to use toluene or petroleum ether at 110 °C or 120 °C, respectively (Walker et al., 1994). The precision of the method ranges between 0.2 and 0.3 ‰ for  $\delta^{18}\text{O}$  and 1.2 and 3 ‰ for  $\delta^2\text{H}$  (Table 2) and is very much dependent on the yield of the pore water, which increases with the applied temperature, extraction time (minimum 20 min) (Revesz and Woods, 1990), and pore size (Leaney et al., 1993). Since the pore water is extracted by heating, Rayleigh type evaporation processes occur, describing the relation between the isotopic composition of a liquid reservoir and the evaporating vapor (Dansgaard, 1964). Therefore, isotopic fractionation occurs if the pore water is not fully extracted. The resulting differences between the original pore water isotopic composition and the isotopic composition of the vapor ( $\Delta\delta$ ) is described as (Araguás-Araguás et al., 1995):

$$\Delta\delta = \frac{\frac{1}{F\alpha - F}}{F - 1} 1000 \quad \text{Eq. (1)}$$

where  $F$  is the pore water fraction that was not extracted and  $\alpha$  is the temperature dependent liquid-vapor isotopic fractionation factor (Majoube, 1971). At an extraction temperature of 90 °C, an extraction of 99 % of the water is sufficient to keep the error within the accuracy of isotope-ratio mass spectrometry (IRMS) (Fig. 2). A comparison between water extracted by azeotropic distillation, suction lysimeters, and wick samplers showed that the fraction of precipitation from the previous two months was 5 %, 53 %, and 95 % for the methods, respectively (Landon et al., 1999), revealing that the distillation extracts more tightly bound waters. Figueroa-Johnson et al. (2007) support these findings with column experiments that showed pore water extracted via azeotropic distillation gives in comparison to water extracted by suction lysimeters or centrifugation a different signal than the introduced sprinkling water. These differences were more pronounced for a silty loam than for fine sand with 2-7 ‰ and 0.25 ‰ in  $\delta^{18}\text{O}$ , respectively. Consequently, the pore water isotope studies using the azeotropic distillation will measure a resident concentration of loosely and tightly bound waters in the soil.

### **2.2.3.2. Microdistillation**

In microdistillation, a soil sample is heated between 100-200 °C or up to 800 °C and the water vapor is reduced to hydrogen over hot zinc (Turner and Gailitis, 1988) or uranium (Brumsack et al., 1992). The deuterium of the vapor is afterwards determined with an IRMS. With hot zinc extraction, 30 samples can be analyzed in a day and the accuracy of 0.7 ‰ for  $\delta^2\text{H}$  is sufficient, but a source of a bias occurs due to hydrogen exchange with the glass walls of the reaction vessels (Kendall and Coplen, 1985). Nowadays, microdistillation is not used anymore, but its concept could be applied in combination with laser-based spectrometry, which allows direct isotope measurements of a continuous flow of water vapor (see section 2.2.3.5).

### **2.2.3.3. Cryogenic vacuum extraction/distillation**

The vacuum distillation was introduced to study isotope exchange and isotopic fractionation with hydroxyl groups in clays (Stewart, 1967). Stewart (1967) heated the soil samples of different clay minerals to 105-730 °C and the extracted water was collected in a cold trap. The potential of this procedure for pore water isotope studies was shown in a comparative study by Jusserand (1980), where the vacuum distillation was applied by heating the soil sample to 80 °C at a vacuum of 1330 hPa for 2-4 h. The vacuum distillation was also successfully used at 80 °C (Münnich, 1983), 50-60 °C (Saxena and Dressie, 1984), 110 °C (Ingraham and Shadel, 1992), or 100-160 °C (Walker et al., 1994; Araguás-Araguás et al., 1995), but the 3-7 h extraction was time consuming. The method allowed to extract 98.5 % (Jusserand, 1980; Araguás-Araguás et al., 1995) to almost 100 % (Saxena and Dressie, 1984) of the water added to oven dried soil. The standard protocol introduced by West et al. (2006) suggesting an extraction at 0.08 hPa at 100°C made cryogenic extraction with a feasible extraction time of 30 to 40 min possible. The minimum extraction time of 30 min was confirmed for different soils at a vacuum of 0.003 hPa and 90 °C by Orłowski et al. (2013). A modified vacuum extraction method where the extraction tubes were replaced by Exetainer® vials requires an extraction time of only 15 min at 0.031 hPa and 90 °C to get a reliable precision (Koeniger et al., 2011). Orłowski (2010) showed that purging the extraction line with high-purity nitrogen does not change the isotopic composition, but reduces

the isotopic variability of the results (Table 2). The high temperatures in the distillation methods are likely to mobilize both hygroscopic (Koeniger et al., 2011) and biologically bound water. Errors due to isotopic fractionation processes as a consequence of incomplete extraction seem to be overcome for cryogenic vacuum extraction methods, since the recovery rate of introduced waters are >99 % (West et al., 2006; Koeniger et al., 2011; Orłowski et al., 2013), indicating that the changes are within the measurement accuracy of the IRMS (Fig. 2). However, there are still studies where a high d-excess indicates that the pore water was not fully extracted by the cryogenic vacuum method (e.g. Munksgaard et al. (2014)). The relatively short extraction time and high accuracy of the vacuum extraction method facilitated its application in numerous studies to extract water from soils, leaves or tree samples (Table 2).

#### **2.2.3.4. Batch distillation**

Vendramini and Sternberg (2007) introduced a batch distillation technique that does not require a vacuum, but the pore water is extracted from a soil sample in a closed ampoule that is heated (100 °C) on one side and cooled on the other. The extraction of up to 72 samples takes place over night in parallel without further supervision. However, the sealing of the ampoules prior to and after the extraction requires some glass-blowing skills and time. A comparison with cryogenic extraction showed acceptable comparability between both methods, with slightly depleted values for the batch distillation, probably caused by condensation at the glass walls (Vendramini and Sternberg, 2007).

#### **2.2.3.5. Microwave extraction–isotope ratio infrared spectroscopy**

The microwave extraction–isotope ratio infrared spectroscopy technique uses microwave power to extract pore water at 60-80 °C and a vacuum of 970 hPa over 10 min (Munksgaard et al., 2014). The extracted water vapor is carried via dry air to a condensation chamber at 18 °C. From there, the air flow is led to a laser-based spectrometer to analyze both water isotopes in the vapor phase. In contrast to the other extraction methods, the microwave extraction method does not work with IRMS, but applies continuous flow laser-based spectrometry. The precision of the microwave extraction method

is 2 ‰ for  $\delta^2\text{H}$  and 0.3 ‰ for  $\delta^{18}\text{O}$  (Munksgaard et al., 2014). To account for instrument drift and to get the isotopic composition in relation to VSMOW, filter papers wetted with water of known isotopic composition analyzed along the soil samples need to be carried out for calibration. A comparative experiment by Munksgaard et al. (2014) showed that incomplete distillation with the cryogenic extraction resulted in more depleted  $\delta^{18}\text{O}$  values for soil samples compared to the results with the microwave extraction method. Due to the fact that the analysis are done in a single process within 15 min, resulting in the determination of the isotopic composition of up to 18 unknown samples during a working day, the microwave extraction method is a promising tool that has not been widely applied in pore water isotope studies yet.

#### **2.2.3.6. He-purging distillation**

Another recently introduced distillation technique uses Helium (He) as a carrier gas to enhance vaporizing the pore water over 180 min at 95 °C (Ignatev et al., 2013). In split sample analysis, the He-purging distillation resulted in an enrichment of 0.03 ‰ for  $\delta^{18}\text{O}$  and 1.1 ‰ for  $\delta^2\text{H}$  compared to cryogenic extracted pore water (Ignatev et al., 2013). Nevertheless, the correlation coefficient between both methods was above 0.99. With a standard deviation (SD) of 0.08 ‰ and 0.7 ‰ for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively, the method introduced by Ignatev et al. (2013) is an alternative to other distillation methods. However, the analysis are with an extraction time of 180 min quite time consuming.

#### **2.2.3.7. Accelerated solvent extraction technique**

Recently, the accelerated solvent extraction (ASE) technique, which is usually used to extract organics from soil samples, was tested for its applicability for pore water stable isotope analysis (Zhu et al., 2014). The pore water was extracted in an ASE stainless steel cell with dichloromethane as a solvent for extraction over 10 min at 100°C and 103,000 hPa, which needs to be repeated three times (Zhu et al., 2014). The analysis is time and labor intensive, because it requires repetitive cycles and solvent removal via centrifugation followed by solid phase extraction before IRMS. The accuracy is given with

a SD of 0.37 ‰ for  $\delta^{18}\text{O}$  and 0.89 ‰ for  $\delta^2\text{H}$  and spiking experiments resulted in disproportionate enriched results (-2.12 ‰ to -4.58 ‰ for  $\delta^2\text{H}$ ), which need to be addressed in further analysis (Zhu et al., 2014).

## **2.3. Equilibration methods**

The isotopic composition of two neighboring water pools will approach an average concentration over time (Urey, 1947). Thus, in an equilibrated state between soil sample and surrounding atmosphere or liquid water, the headspace or water can be directly analyzed, making a physical extraction of the water or high temperatures unnecessary. The equilibration methods generally make use of the activity of isotopologues to derive the isotopic composition of the soil sample of interest (Kendall and McDonnell, 1998). Since salts alter the activity of isotopes, equilibration methods that yield isotope activity ratios need to be corrected in order to derive reliable isotope ratios. This “salt effect” occurs for brine samples (Horita and Kendall, 2004) and is therefore of minor relevance for the vadose zone. However, similar isotopic fractionation effects cause from water–solid interactions in clay rich soils (Oerter et al., 2014). Kaolinitic minerals are not as labile to exchange with the vapor phase as adsorbed water on montmorillonite and illite surfaces (Stewart, 1972). Such cation fractionation effects can result in  $\delta^{18}\text{O}$  values determined via equilibration methods that are depleted by up to 1.55 ‰ for dry soils (5 % VWC) and 0.49 ‰ for wet soils (30 % VWC) of homoionic montmorillonites (Oerter et al., 2014).

### **2.3.1. Laboratory equilibration methods**

#### **2.3.1.1. $\text{CO}_2$ and $\text{H}_2$ equilibration**

The potential of the  $\text{CO}_2$  equilibration method (Epstein and Mayeda, 1953) to measure  $\delta^{18}\text{O}$  pore water in soil samples was shown by Jusserand (1980) and further developed by Scrimgeour (1995) to determine both  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ . For the  $\delta^{18}\text{O}$  analysis, the soil samples equilibrate at 22 °C for 3 days in a  $\text{CO}_2$  atmosphere, which is then analyzed via IRMS.  $\delta^2\text{H}$  was determined in a hydrogen ( $\text{H}_2$ ) atmosphere that equilibrated at 20 °C for 4 days with a platinum catalyst for the  $\text{H}_2$  reduction. The

reported precision of the method was with a SD of  $\pm 15$  ‰ for  $\delta^2\text{H}$  not acceptable, but with  $\pm 0.5$  ‰ much better for  $\delta^{18}\text{O}$  with soils of at least 5 % VWC (Scrimgeour, 1995). Improved precisions for  $\delta^{18}\text{O}$  of 0.4 ‰ for a clayey loam and 0.3 ‰ for a coarse sandy loam were found after sterilization of the samples and equilibration times of 12 - 48 h, with shorter equilibration times for soils of higher water contents and coarser particle sizes (Hsieh et al., 1998b). An improved precision ( $\pm 1$  ‰) was achieved for  $\delta^2\text{H}$  by an equilibration for 4 h at 25 °C with a Pt-doped styrene-divinylbenzene copolymer as catalyst (Koehler et al., 2000). Subsequent  $\delta^{18}\text{O}$  analysis via  $\text{CO}_2$  equilibration of the same soil sample resulted in a repeatability of  $\pm 0.3$  ‰, but with an offset of about +0.5 ‰ compared to azeotropic extraction (Koehler et al., 2000). The major drawback of the methods that use  $\text{H}_2$  or  $\text{CO}_2$  equilibration that not both water stable isotopes can be analyzed simultaneously.

### **2.3.1.2. Diffusive $\text{H}_2\text{O}$ mixing cells**

The isotopic equilibration over 40 days between water of unknown isotopic composition in a porous medium and a fluid of known isotopic composition was introduced as the radial diffusion cell method by van der Kamp et al. (1996). Rbel et al. (2002) modified the method in a way that an equilibration between a standard water and the soil water was reached after 2.5 days. From the isotopic changes of the standard water, the pore water stable isotope composition was derived by mass balance calculations. Comparisons of this method with the cryogenic vacuum distillation showed that the latter results in more depleted isotopic compositions, possibly due to incomplete extraction (Rbel et al., 2002; Savoye et al., 2006).

### **2.3.1.3. Direct water-vapor equilibration**

A direct equilibration method was first proposed by Wassenaar et al. (2008), where the pore water of soil samples equilibrates with dry air in a closed system under constant room temperature in heat-sealed bags to avoid non-equilibrium isotopic fractionation processes. A survey of mass losses of heat-sealed laminated bags showed that almost no ( $< 0.15$  %) pore water leaves the closed system within 30 days. The equilibration time was shown to vary from 15 h (Garvelmann et al., 2012; Mueller et al.,

2014) to 48 h (Sprenger et al., 2015) or 7 days (Hendry et al., 2013). After equilibration, the water vapor of the saturated headspace is directly sampled with a needle connected to a continuous flow laser-based spectrometer that measures the vapor  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  composition. Within a few minutes, a constant water vapor level is reached and the isotope measurements of the subsequent two minutes are averaged. To calibrate the data to reference concentrations (VSMOW) and to account for isotopic drift of the instrument, standard waters of known isotopic composition need to be analyzed along with the soil samples. These standard waters can be either each put into a bag solely (Wassenaar et al., 2008) or together with oven dried soil material (Garvelmann et al., 2012). The latter might include possible isotopic fractionation effects of the soil matrix, but in contrast, it could potentially influence the organics in the sample. This is of interest because cations in the soil can cause isotopic fractionation (Oerter et al., 2014) and organics can interfere the measurements via laser spectrometry (Brand et al., 2009; West et al., 2010). With regard to the measurement precision, we observed an average standard deviation (SD) during the two-minute constant water vapor content measurement for 1,600 soil samples of 0.31 ‰ for  $\delta^{18}\text{O}$  and 1.16 ‰ for  $\delta^2\text{H}$ . While the SD of  $\delta^{18}\text{O}$  increased with higher water vapor contents in the headspace ( $r = 0.51$ ,  $p < 0.01$ ), the measurement of  $\delta^2\text{H}$  was less sensitive ( $r = -0.09$ ,  $p < 0.01$ ) in the water vapor range between 24000 and 33000 ppmv. Isotope analysis with laser spectrometer can be influenced by methane ( $\text{CH}_4$ ) (Hendry et al., 2011), methanol and ethanol (Brand et al., 2009) or other organic chemical components (West et al., 2010) in the soil sample, because these compounds absorb the laser light in a similar wavelength as  $^1\text{H}_2^{18}\text{O}$  or  $^2\text{H}_2^{16}\text{O}$  do. Since laser-based spectrometers also measure  $\text{CH}_4$  concentrations, the isotope measurements can be corrected for the influence of  $\text{CH}_4$  (Hendry et al., 2011).  $\text{CH}_4$  and also hydrogen sulfide ( $\text{H}_2\text{S}$ ) are more likely to occur in anaerobic conditions, which is usually not the case in the vadose zone. Nevertheless,  $\text{CH}_4$  and  $\text{H}_2\text{S}$  can develop from microbiological activity during equilibration. Thus, there is a tradeoff between sufficient time to reach isotopic equilibrium and keeping the equilibration time as short as possible to minimize the influence by microbial activity. We experienced that due to the strong odor of  $\text{H}_2\text{S}$  and a strong effect on the d-excess value, affected samples can be easily recognized and discarded. While Wassenaar et al. (2008) reported a limited applicability for geologic samples of at least 5 % of

gravimetric water content, Hendry et al. (2015) showed that also samples of <5 % gravimetric water content can be sampled, when the sample size is increased to ensure 3 g of water in the sample when analyzed in 1 L sample bags. Examples using the direct equilibration method are found for unsaturated core samples on the large scales of paleohydrology (Hendry et al., 2013), at the hillslope scale to study mixing processes (Garvelmann et al., 2012; Mueller et al., 2014), and at the pedon scale to study transit times (Sprenger et al., 2015).

### **2.3.2. In-situ equilibration**

The pore water vapor was already subject of isotope studies decades ago (Thoma et al., 1979), since it was observed that pore water vapor is in equilibrium with the liquid pore water. Water vapor was extracted from the vadose zone by vacuum pumping and later analyzed in the laboratory (Saxena and Dressie, 1984; Allison et al., 1987; Tang and Feng, 2001). The precision of such methods was 2 ‰ and 0.2 ‰ for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , respectively (Izbicki et al., 2000). The laser-based spectrometry, allowing for continuous measurements of water vapor isotopologues (Gupta et al., 2009), makes a direct measurement of the soil water vapor possible. The in-situ determination of the pore water vapor via gas-permeable tubes connected to a laser-based spectrometer was tested in the laboratory by Rothfuss et al. (2013). They pointed out the importance of measuring standards along with the soil water vapor to account for temperature effects during equilibration and to get reliable isotope composition relative to VSMOW. The in-situ equilibration was shown to have an accuracy within the desired range of  $\pm 0.2$  ‰ and  $\pm 1$  ‰ for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , respectively, for soil samples of VWC between 9 % and 38 % (Rothfuss et al., 2013). Volkmann and Weiler (2014) developed a field application for in-situ measurements with porous probes, which eliminates possible condensation of water along the sampling line by dilution with  $\text{N}_2$ , and reported good agreement with the destructive direct equilibration method. Also, commercially available soil gas probes connected to a laser spectrometer were found to be applicable for sampling in-situ the pore water isotopic composition with a reasonable accuracy (Gaj et al. 2015). Such in-situ techniques of pore water stable isotope analysis at a sufficient accuracy in time intervals of four minutes disclose new opportunities on studies of the soil water and

plant water interactions during irrigation experiments with isotopically enriched waters (Volkman et al., 2013). The scale of the application of in-situ equilibration methods is limited due to the length of the tubes that route the soil water vapor from the sample location to the laser spectrometer. Furthermore, the measured signal is less clear when long tubes are applied, because of mixing and diffusion in the tubes.

#### **2.4. The problem of spiking experiments for accuracy determination using distillation methods**

A common way to determine the accuracy of pore water isotope analyzes are spiking experiments, where water of known isotopic composition is added to oven-dried soil and afterwards extracted. In such experiments, the extracted water was often found to be depleted in isotopes compared to the added water (Fig. 3, Turner and Gailitis, 1988; Walker et al., 1994; Araguás-Araguás et al., 1995; Braud et al., 2009; Koeniger et al., 2011; Orłowski et al., 2013; Meißner et al., 2014). Rayleigh fractionation due to not to fully extracting water from small pores or by non-equilibrium isotopic fractionation occurring at different temperatures during heating might explain some of these differences (Ingraham and Shadel, 1992; Walker et al., 1994; Araguás-Araguás et al., 1995). To account for errors due to incomplete extraction, corrections via the Rayleigh-type law in Equation 1 were applied (Mathieu and Bariac, 1996; Braud et al., 2009). However, incomplete recovery effects can be excluded for the newly developed vacuum extraction systems (West et al., 2006; Koeniger et al., 2011; Orłowski et al., 2013), because they extract more than 99 % of the introduced water (Fig. 2).

Another explanation of the isotopic depletion for the added water in spiking experiments is interaction between the water molecule and the soil minerals. It is proposed that the added water becomes partly bound to soil minerals (clay hydroxyls), which is then not released again during the extraction or just partly released because not all the hydroxyls bound and release water during the distillation (Stewart, 1967). This explains that the differences between added and extracted water in  $\delta^{18}\text{O}$  (Jusserand, 1980) and  $\delta^2\text{H}$  (Turner and Gailitis, 1988) are higher for soils with kaolinite minerals, which consist to 14 % of hydroxyls. The bias introduced by interactions with the mineral surfaces could be corrected by

calibrating with standards (Turner and Gailitis, 1988). Possible influence of isotopic fractionation due to carbonates can be lowered by a treatment with hydrochloric acid (HCl), which led Meißner et al. (2014) to observe less depleted signals for  $\delta^{18}\text{O}$  ( $\sim 1.3\text{ ‰}$ ). The effect of isotopic fractionation due to hydration is more pronounced when only little water is added (Ingraham and Shadel, 1992; Walker et al., 1994; Lautenschlager, 1999; Braud et al., 2009; Meißner et al., 2014). At higher water contents, the water volume affected by hydration is small compared to the extracted water, which is why hydration has no effect on the analysis. The effect of hydration is higher for high clay contents, as shown by more depleted values for higher clay contents (Turner and Gailitis, 1988; Leaney et al., 1993; Walker et al., 1994; Figueroa-Johnson et al., 2007; Koeniger et al., 2011; Orłowski et al., 2013; Meißner et al., 2014). One explanation is that surfaces of clays can absorb 2 to 15 % of their dry weight (Jusserand, 1980). Since the deviation of the cryogenic extracted water from the spiked water cannot yet be explained, it is questionable, if spiking experiments are the best way to validate pore water stable isotope methods. The deviation could be due to the drying of the soil material, where the structure is changed and possibly not all water removed, or due to the rewetting, where water might be tightly bound to the mineral surfaces and not remobilized during the extraction procedure. Thus, we propose to use split samples of well mixed soil material rather than spiking experiments to ensure an identical isotopic signal in their pore waters. The following section gives an example of a method comparison based on split samples.

## **2.5. Comparing the equilibration method with the extraction methods**

Our review shows that a comparison between the current benchmark, the cryogenic extraction (CE) method, and the direct equilibration (DE) method is missing. So far, Jusserand (1980) and Hsieh et al. (1998b) compared CE with the  $\text{CO}_2$  equilibration and found that nine out of ten soil samples had depleted values for the CE. Also in comparisons of the CE with the diffusive  $\text{H}_2\text{O}$  mixing cells the CE resulted in depleted values (Rübel et al., 2002; Savoye et al., 2006).

We present, as a first attempt, the results of an analysis using both the CE and the DE method for 25 disturbed soil samples that were each divided into two subsamples. The CE was conducted as

described in section 2.2.3.3 with 0.07 hPa at 90 °C for 90 – 240 min depending on the water content of the sample. Afterwards, the isotopic composition of the extracted water was determined by laser-based spectrometry. The DE was done as described in section 2.3.1.3. The 25 soil samples, each of about 300 g of sandy to loamy material, were taken from several depths between 0.3 - 1.45 m in the beginning of June 2014 at different locations within the Attert catchment in Luxembourg. In the laboratory, 10 g of each sample was separated for the analysis with CE and the remaining material was used for DE analysis. The isotopic composition derived with the CE was on average depleted by -1.35 ‰ for  $\delta^{18}\text{O}$  and -8.33 ‰ for  $\delta^2\text{H}$  compared to the results from the DE. The differences between DE and CE ranged from -0.42 to -2.37 ‰ for  $\delta^{18}\text{O}$  and -5.29 to -12.93 ‰ for  $\delta^2\text{H}$  (Fig. 4a), which is very similar to findings by Rübél et al. (2002). The deviation between both methods appears to be linear, but there is a higher scatter in the relation for  $\delta^{18}\text{O}$  than for  $\delta^2\text{H}$ . A comparison of the d-excess values against the gravimetric water content of the samples reveals that the differences are not just offset, but the results from the CE when compared to the results from the DE, were more depleted in  $\delta^{18}\text{O}$  than in  $\delta^2\text{H}$  (Fig. 4b). The d-excess is significantly correlated to the water content of the samples for the CE method, but not for the DE method. We assume that both split samples have the same pore water isotopic composition. However, the actual value is unknown and thus we cannot discard one or the other method. Nevertheless, we know that the pore water consists of rain water, which can be isotopically described by the Local Meteoric Water Line (LMWL). The results mapped in a dual-isotope plot show that often, the isotopic composition of the split samples plot parallel to the LMWL (Fig. 4c). Thus, the analyses with the two different methods do potentially both represent the pore water, but probably different fractions of the pore spaces. The variability of the slope of a line between the split samples is correlated to the differences in the d-excess (Fig. 4d). Biggest deviations from the slope of the LMWL are given for samples with low d-excess of the CE and high d-excess of the DE. There are three possible explanations for the observed differences:

- 1.) Different pore sizes are sampled and the water in these pores is not in isotopic equilibrium. Therefore, if CE extracts more tightly bound water than DE (Fig. 1), water in the smaller pores would have a more depleted signal than water in the bigger pores.
- 2.) Not all the water is extracted in the CE method leading to higher d-excess values due to Rayleigh fractionation. However, the remaining (not extracted) water would need to be about 10 % (Fig. 2). This effect seems to be more pronounced for samples with higher soil moisture, possibly due to a limited amount of water that can be extracted (Fig. 4b).
- 3.) Within the equilibration time of two days in the DE method, equilibrium between the pore water and the headspace is not reached and some vapor was lost via evaporation, which caused isotopic fractionation (lower d-excess) (Fig. 4b, d).

However, these processes cannot explain the subsamples, which show a lower d-excess for CE than for DE, with slope >8 (Fig. 4d). Effects due to isotopic fractionation with cations (Oerter et al., 2014) or due to organics (West et al., 2010) can be excluded for the DE, because the samples had >7.5 % GVC and little to no organic material. The cation isotope fractionation effect would lead to a depletion in  $\delta^{18}\text{O}$  (Oerter et al., 2014) and not to an enrichment, which was observed in the results of the DE compared to the CE. Hence, a final assessment is not possible yet.

### **3. Summary and conclusion**

The pore water stable isotope analysis methods differ in various ways, with consequences for their scale of applicability and the interpretation of the resulting isotope signals:

- 1.) The application of methods that extract the pore water or water vapor in the field is generally limited to the upper meters of the vadose zone. Soil sampling with subsequent pore water isotope analysis in the laboratory is not limited to the upper 4 m of soil, but can potentially reach depths that are limited by the drilling possibilities.
- 2.) Some methods sample big volumes of soil samples that give an integral signal of the volume, while other methods need small samples, which allow replicates in split samples.

- 3.) The water extraction in the field potentially allows derivations of flux concentrations, while the waters from soil samples hold generally information of resident concentrations.
- 4.) The pore spaces that are sampled with the different methods vary, which has consequences for the data interpretation, because the sampled water is either limited to the mobile water or includes immobile waters.
- 5.) For the methods sampling soil water below field capacity, the limitation regarding tightly bound water is yet unknown. Comparative studies are needed to understand the differences between these methods that are currently widely applied.
- 6.) Pore waters extracted in spiking experiments, where water with known isotopic signal is added to oven-dried soil, deviate substantially from the spiked water and the deviation is more pronounced, the higher the clay content and the lower the water content of the soil.
- 7.) Split samples of field soils seem to represent a good base for comparative studies, since they represent the same isotopic signal under natural conditions; however, the true isotopic signature is unknown.
- 8.) New opportunities to sample pore water stable isotopes in high spatio-temporal resolution based on laser-based spectrometry are now available. Such in-situ measurements can be expanded to the catchment scale to study spatial variability of the propagation and alteration of the rainwater isotopic signal in the soil.

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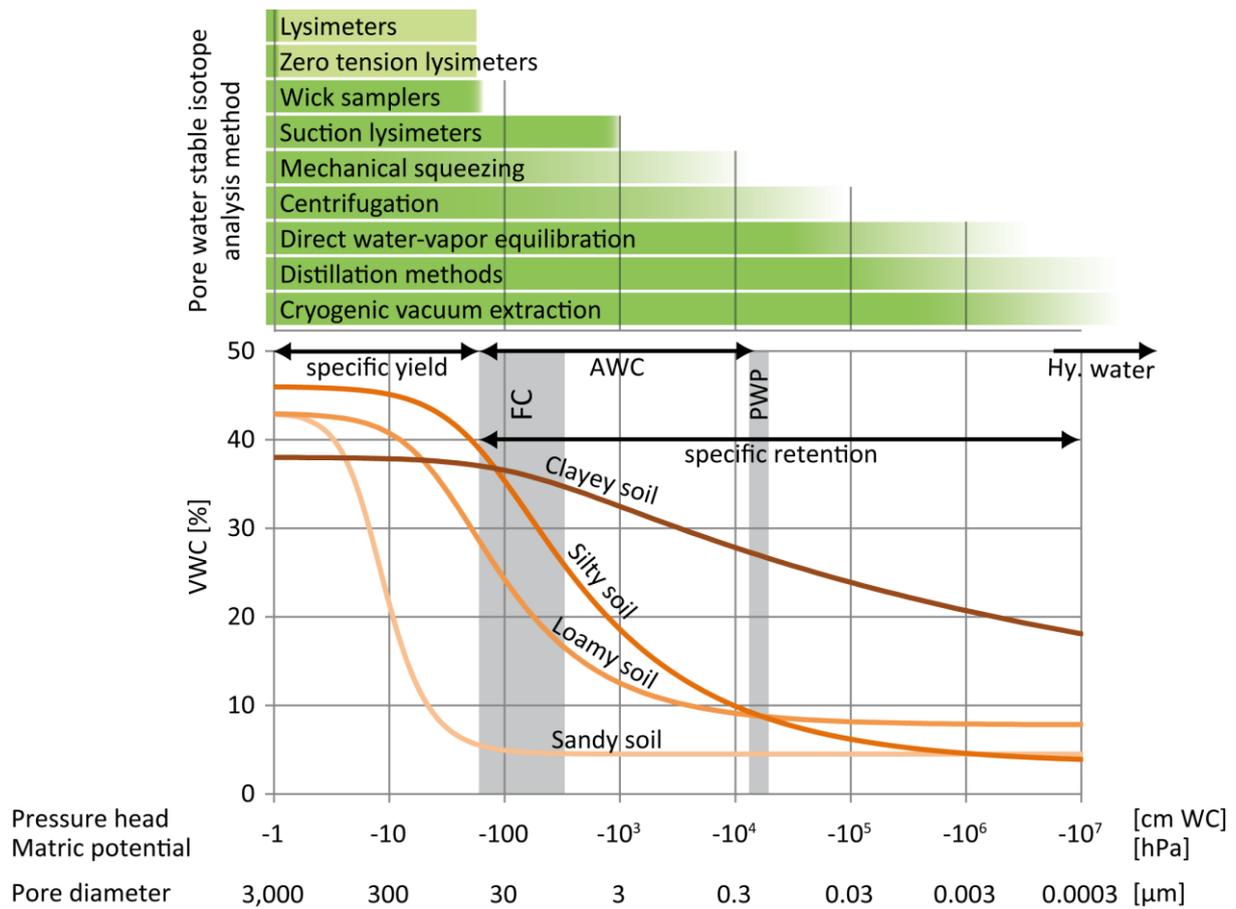


Figure 1: Bottom: Exemplified water retention curves for four different soil textures, the respective pore diameter described by Schjonning (1992) and characteristic water potentials as defined by Scheffer et al. (2002): VWC= volumetric water content, FC = field capacity (grey area), AWC= plant available water capacity, PWP = permanent wilting point, Hy. water = hygroscopic water. Top: The most widely used pore water stable isotope analysis methods and their range of pore water extraction in relation to matrix potential and pore diameter

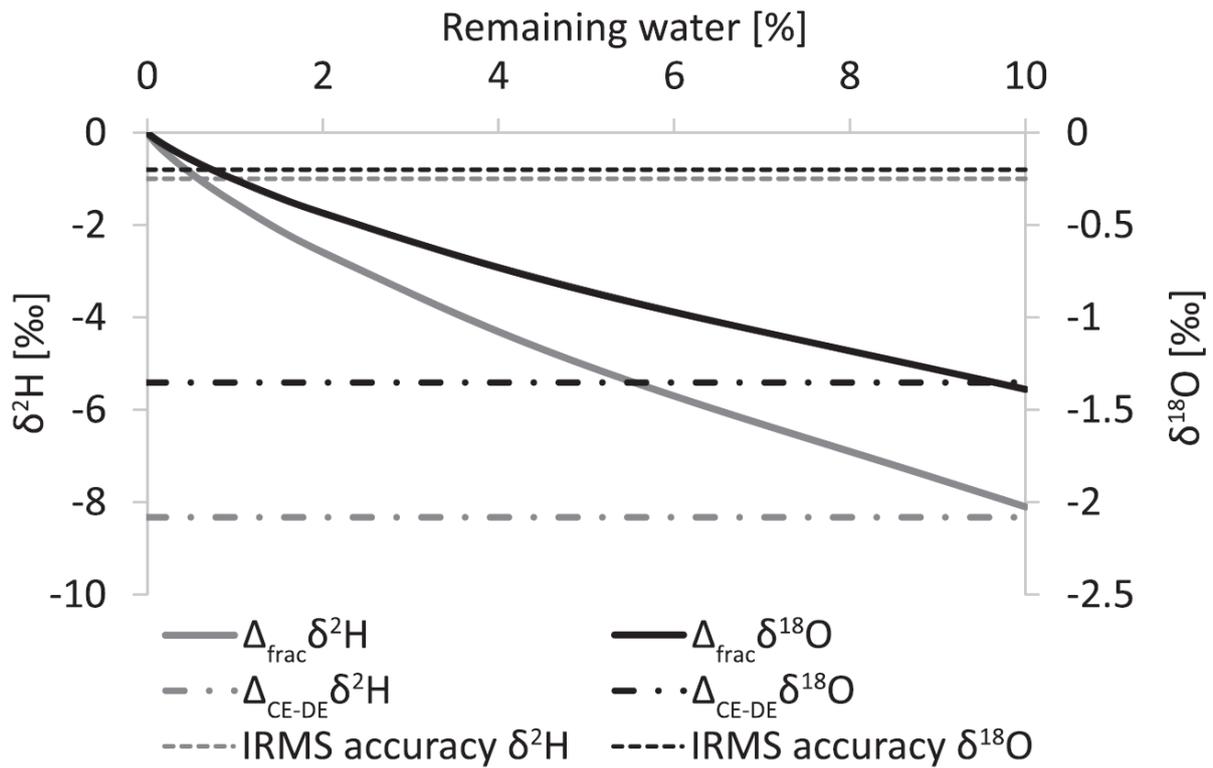


Figure 2: The effect of Rayleigh-type processes ( $\Delta_{\text{frac}}$ ) on the extracted water as a function of remaining (not extracted) water (Equation (1)) for a distillation processes at 90 °C. The mean deviation between the cryogenic extraction and the direct equilibration method as presented in the Section on Comparing the Equilibration Method with the Extraction Methods ( $\Delta_{\text{CE-DE}}$ ), and measurement accuracy for isotope ratio mass spectrometry is shown as reference.

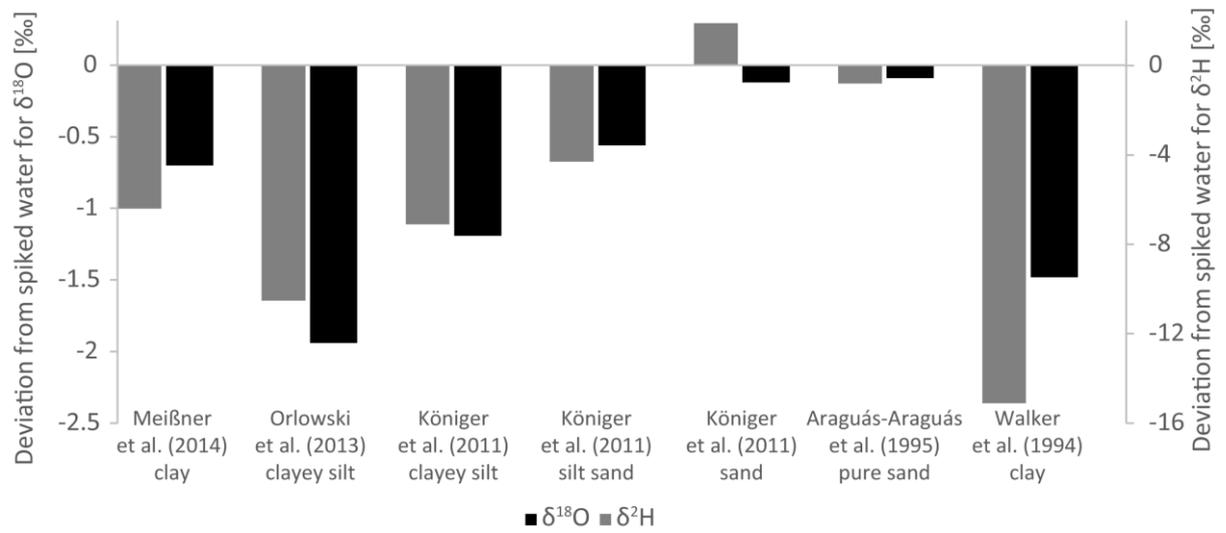


Figure 3: Deviation of cryogenic extracted pore water from water of known isotopic composition added in spiking experiments to oven-dried soil samples for  $\delta^{18}\text{O}$  (black) and  $\delta^2\text{H}$  (grey)

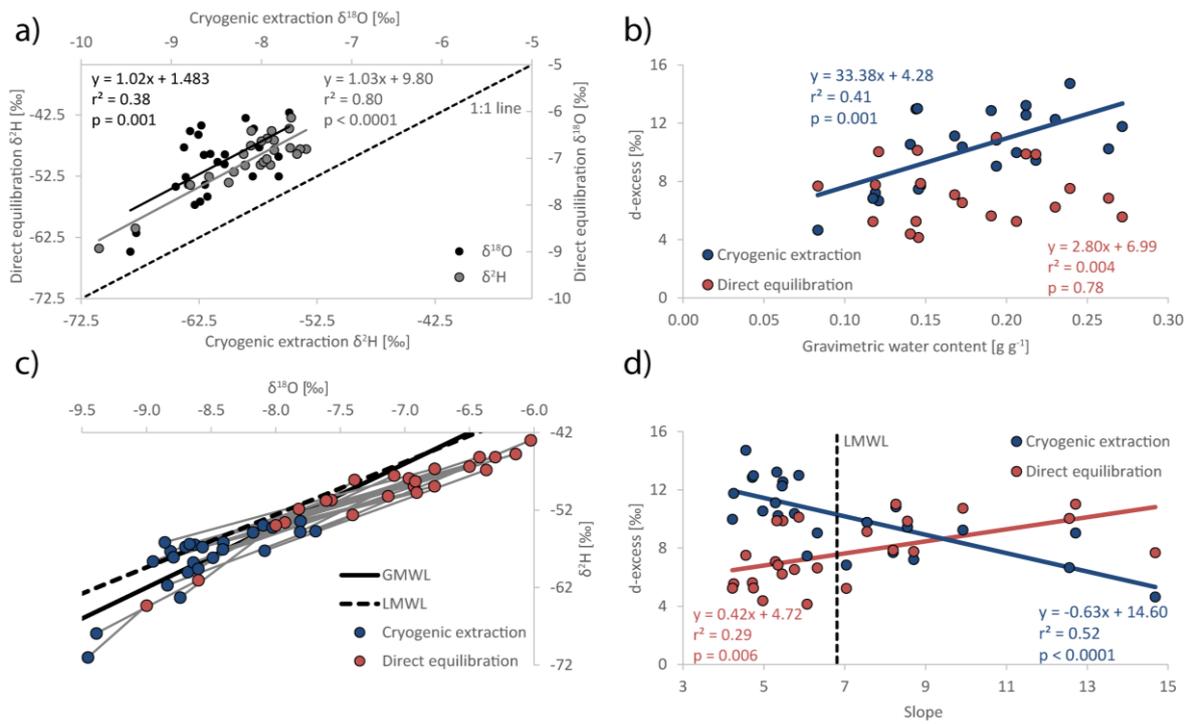


Figure 4: Comparison of the pore water isotope analysis methods of cryogenic extraction and direct equilibration for 25 split samples with regard to (a) the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values [the axes of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are scaled according to the Global Meteoric Water Line], (b) the d-excess as a function of the gravimetric water content, (c) the location in a dual-isotope plot and (d) the d-excess as a function of the slope between the samples in the dual-isotope plot (grey lines in c)

Table 1: Overview of pore water stable isotope analysis methods.

Method	Sampling dry soil (VWC<10%)	Resident concentration	Flux concentration	Mobile water	Immobile water	Hygroscopic water	Crystallization water
Lysimeters	no	no	yes	yes	no	no	no
Zero tension lysimeters	no	no	yes	yes	no	no	no
Wick samplers	no	no	yes	yes	no	no	no
Suction lysimeters	no	no	yes	yes	no	no	no
Mechanical squeezing	yes	no	no	yes	no	no	no
Centrifugation	no	no	no	yes	no	no	no
Azeotropic distillation	yes	yes	no	yes	yes	yes	no
Microdistillation	yes	no	no	yes	yes	yes	no
Cryogenic vacuum extraction	yes	yes	no	yes	yes	yes	no
Microwave extraction	yes	yes	no	yes	yes	yes	no
He-purging distillation	yes	yes	no	yes	yes	no	no
Accelerated solvent extraction	yes	yes	no	yes	no	no	no
CO <sub>2</sub> / Hydrogen equilibration	yes	yes	no	yes	yes	no	no
Direct water-vapor equilibration	yes	yes	no	yes	yes	no	no

yes

no

?

Table 2: Each pore water stable isotope analysis method and their reported accuracies, required mass or volume of the soil sample for the analysis, information if laser spectrometry is needed or not, advantages, disadvantages, and exemplary studies that used the method. The letters in brackets indicate the reference in the last column.

Method	Accuracy as standard deviation [%o VSMOW]		Required soil mass or volume	Laser spectrometry need?	Scale of application	Advantages	Disadvantage	Examples of pore water isotope studies
	$\delta^{18}\text{O}$	$\delta^2\text{H}$						
Lysimeters	NA	NA	NA	No	Max. 4m	Controlled boundary conditions (e.g. weighing, choice of material, additional sensoric)	Unnatural lower boundary condition, cost intensive, only 1D flow	Eichler (1966), Darling and Bath (1988), Foerstel et al. (1991), Lindström and Rodhe (1992), Maloszewski et al. (2006), Mali and Urbanc (2006), Mali et al. (2007), Sutanto et al. (2012), Stumpp et al. (2009a), Stumpp et al. (2009c), Stumpp et al. (2012)
Zero tension lysimeters	NA	NA	NA	No	Max. 1 m	Solely mobile water (well defined)	Water divergence leading to bypass flow (low flow collection efficiencies), disturbance of flow lines, no data during dry conditions, maintenance costs	Wenner et al. (1991), Anderson et al. (1997), Asano et al. (2002), McGuire et al. (2002), O'Driscoll et al. (2005)
Wick samplers	NA	NA	NA	No	Max. 1.6 m	Little disturbance of flow lines, flux concentration	No data during dry conditions, maintenance costs	Landon et al. (1999), Timbe et al. (2014), Windhorst et al. (2014)
Suction lysimeters	NA	NA	NA	No	Max. 4m	Possibly the hydrological/biological relevant water	Bypass flow, no data during dry conditions, unknown sampling	Vandor et al. (1977), Leopoldo et al. (1984), Stewart and McDonnell (1991), Wenner et al. (1991), Anderson et al.

							volume/area, unknown fluxes, no resident nor flux concentration, influence of flow field, cost-intensive continuous suction lysimeter, maintenance costs	(1997), DeWalle et al. (1997), Landon et al. (2000), McGuire et al. (2002), O'Driscoll et al. (2005), Yano et al. (2006), Kabeya et al. (2007), Li et al. (2007a), Lee et al. (2007), Figueroa-Johnson et al. (2007), Vogel et al. (2010), Kabeya et al. (2011), Muñoz-Villers and McDonnell (2012), Kim and Jung (2014), Kim (2014), Peralta-Tapia et al. (2014), Geris et al. (2014), Tetzlaff et al. (2014), Geris et al. (2015)
Mechanical squeezing	NA	NA	172 cm <sup>3</sup> [a]	No	> 100 m	Variable pressure (=variable pore sizes)	Labor intensive, restricted to sandy to silty soils	Eichler (1966), [a] Kelln et al. (2001), Jusserand (1980)
Centrifugation	0.025 [b]	0.30 [b]	117 cm <sup>3</sup> [a]	No	> 100 m	Variable pressure (=variable pore sizes)	Labor intensive, water of fine pore water cannot be extracted	Zimmermann et al. (1967b), Jusserand (1980), Darling and Bath (1988), [a] Kelln et al. (2001), Figueroa-Johnson et al. (2007), [b] Kudo et al. (2013)
Azeotropic distillation	0.5 [c] 0.5 [d] 0.2 [e] 0.3 [f] 0.3 [g] 0.2 [h]	2 [c] 1 [d] 2 [e] 1.2 [f] 3 [g] 1.9 [h]	80 g [c], 100-300 g [h]	No	> 100 m	Bulk pore water	Complete extraction needed, extraction of hygroscopic water, limited to >5 % VWC, several steps (extraction + removal of the organic compound + analysis), toxic materials	[c] Allison and Hughes (1983), [d] Allison et al. (1983), Shatkey and Magaritz (1987), [e] Revesz and Woods (1990), Ingraham and Shadel (1992), [f] Walker et al. (1994), [g] Araguás-Araguás et al. (1995), Kelln et al. (2001), [h] Izbicki et al. (2002), Brandes et al. (2007), Koeniger et al. (2010), Kallioras et al. (2012)
Micro-distillation	NA	0.7 [i] 0.2 – 0.7 [j]	0.1-0.3 g [j]	No	> 100 m		Limited to <sup>2</sup> H, toxic catalysts, mobilization of	[i] Kendall and Coplen (1985), [j] Turner and Gailitis (1988), Brumsack et al. (1992)

							crystallization water (if extraction temperature is > 450 °C), time consuming	
Cryogenic vacuum extraction	0.15 [k] 0.3 [l] 0.1 [l] With N <sub>2</sub> purging 0.4 [n]	0.69 [k] 1.46 [l] 0.49[l] With N <sub>2</sub> purging 3 [n]	250 g [m] 4-53 g [o]	No	> 100 m	Bulk pore water (mobile and immobile water) samples, applicable for leaves and stem samples, little sample volume required	Complete extraction needed, extraction of hygroscopic water, two steps (extraction + analysis), vacuum needed	Bengtsson et al. (1987a), Dawson (1993), Mathieu and Bariac (1996), Dawson (1996), Gehrels et al. (1998), Jackson et al. (1999), Li et al. (2006), [k] West et al. (2006), Li et al. (2007b), Braud et al. (2009), [l] Orłowski (2010), [m] Adomako et al. (2010), Wang et al. (2010b), Rothfuss et al. (2010), Brooks et al. (2010), Wang et al. (2010b), Liu et al. (2011), [n] Koeniger et al. (2011), Zhang et al. (2011), Goldsmith et al. (2012), Meißner et al. (2012), [o] Ignatev et al. (2013), Hao et al. (2013), David et al. (2013), Meißner et al. (2014), Dubbert et al. (2014b), Bachmann et al. (2015)
Batch distillation	NA	NA	≤8 g (limited by vial) [p]	No	> 100 m	No vacuum needed, no supervision of the extraction	Glass-blowing skills needed, isotopic fractionation due to condensation at glass walls	[p] Vendramini and Sternberg (2007), Rossatto et al. (2012), Kulmatiski and Beard (2013), Ellsworth and Sternberg (2014)
Microwave extraction	0.3 [q]	2 [q]	0.5-1 g [q]	Yes	> 100 m	Analysis within 15 min, single process, <sup>2</sup> H and <sup>18</sup> O measured in parallel, little sample volume required	Organics interfere with laser-based spectrometry, requirement of standards to derive VSMOW	[q] Munksgaard et al. (2014)

He-purging	0.08 [o]	0.7 [o]	1-3 g [o]	No	> 100 m	Little sample volume required	Time consuming (180 min for the extraction + analysis)	[o] Ignatev et al. (2013)
Accelerated solvent extraction	0.37 [r]	0.89 [r]	18 g [r]	No	> 100 m	Labor intensive due to three processes (extraction + solvent removal + water analysis)	Disproportionate enriched in doping experiments	[r] Zhu et al. (2014)
CO <sub>2</sub> and H <sub>2</sub> equilibration	0.6 [s] 0.5 [t] 0.4 [u] 0.3 [v] 0.3 [w] 0.1 [x] 1.03 [z]	15 [t]     1 [x]	2-3 cm <sup>3</sup> [t] 6-10 g [u] 5-6 g [w] 8 cm <sup>3</sup> [x] 4 cm <sup>3</sup> [y]	No	> 100 m	No mobilization of hygroscopic water (heating)	No parallel analysis of <sup>2</sup> H and <sup>18</sup> O possible, time for equilibration (0.5 to 3 days), interaction with cations	Jusserand (1980), [s] Hesterberg and Siegenthaler (1991), [t] Scrimgeour (1995), Hsieh et al. (1998a), [u] Hsieh et al. (1998b), [v] Miller et al. (1999), [w] Koehler et al. (2000), [x] McConville et al. (2001), [y] Kelln et al. (2001), Hendry et al. (2004), Ferretti et al. (2003), Gazis and Feng (2004), [z] Robertson and Gazis (2006), Kelln et al. (2007), Oerter et al. (2014)
Diffusive H <sub>2</sub> O mixing cells	1 [A] 0.1 [B]	3 [A] 1 [B]	1 cm <sup>3</sup> [A] 104 cm <sup>3</sup> [B]	No	> 100 m	No mobilization of hygroscopic water (heating)	Time for equilibration (2.5 to 40 days), interaction with cations, mass-balance calculation needed	van der Kamp et al. (1996), [A] Rübél et al. (2002), [B] Savoye et al. (2006), Waber et al. (2012), Bensenouci et al. (2013)
Direct water-vapor equilibration	0.3 [C] 0.15 [D] 0.3 [E] 0.4 [F] 0.31 (This study)	0.7 [C] 1.03 [D]  1-2 [F] 1.16 (This study)	Ca. 100 g [C] 110-240 g [E]	Yes	> 100 m	No mobilization of hygroscopic water (heating), biologically available water	Interaction with cations, organics interfere with laser-based spectrometry, requirement of standards to derive VSMOW	[C] Wassenaar et al. (2008), Stumpp and Hendry (2012), Garvelmann et al. (2012), Klaus et al. (2013), Hendry et al. (2013), [D] Volkmann and Weiler (2014), [E] Mueller et al. (2014), [F] Bertrand et al. (2014), Sprenger et al. (2015)

In-situ equilibration	0.2 [G] 0.16 - 0.43 [D] (depending on standards or field soil) 0.46 [E]	1 [G] 1.15 - 3.06 [D] (depending on standards or field soil) 1.8 [E]	NA	Yes	< 3 m	No mobilization of hygroscopic water (heating), High resolution (ca. 5 min), in-situ	Interaction with cations, organics interfere with laser-based spectrometry, requirement of standards to derive VSMOW	[G] Rothfuss et al. (2013), Volkmann et al. (2013), [D] Volkmann and Weiler (2014), Rothfuss et al. (2015), [E] Gaj et al. (2015)
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