Intercomparison of soil pore water extraction methods for stable isotope analysis and interpretation of hillslope runoff sources

Natalie Orlowski1,2,3 | Dyan L. Pratt4 | Jeffrey J. McDonnell2,5

1Faculty of Environment and Natural Resources, Hydrology, University of Freiburg, Freiburg, Germany
2Global Institute for Water Security, School of Environment and Sustainability, University of Saskatchewan, Saskatoon, Canada
3Institute for Landscape Ecology and Resources Management (ILR), Research Centre for BioSystems, Land Use and Nutrition (IFZ), Justus Liebig University Giessen, Giessen, Germany
4Global Institute for Water Security and Department of Civil and Geological Engineering, University of Saskatchewan, Saskatoon, Canada
5School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, UK

Correspondence
N. Orlowski, Faculty of Environment and Natural Resources, Hydrology, University of Freiburg, Freiburg, Germany.
Email: natalie.orlowski@hydrology.uni-freiburg.de

Funding information
NSERC

Abstract
Intercomparison of soil pore water extraction methods for stable isotope analysis has been a focus of recent studies in relation to plant source waters, which found a wide isotopic variance depending on the extraction method. Few studies have yet explored extraction effects for mobile pore waters that relate to hillslope runoff. This is because it is extremely difficult in natural systems to control the boundary conditions in order to assess and compare impacts of pore water extraction on resulting hillslope flow. With our new semicontrolled experiments on outdoor mini-hillslopes, we studied mixing and runoff processes by means of stable isotopes of water and quantified relations between pore water extraction methods. We tested the null hypothesis that nondestructive and destructive pore water sampling methods sample the same soil water pool. Three hillslopes were mounted on load cells, filled with loamy sand textured soils from the Landscape Evolution Observatory at Biosphere 2, equipped with soil moisture and temperature sensors, a bottom outflow, and a surface runoff gauge for isotope sampling. We followed the precipitation isotopic composition over and through the soil profile. One hillslope was instrumented with suction cups, on the second we installed sampling ports for in-situ soil water vapour measurements, and the third hillslope was sampled destructively for applying the centrifugation and vapour equilibrium methods. All hillslopes were sampled at four depths (0–10, 10–20, 20–30, and 30–40 cm) at three different downslope positions. 2H and 18O analyses were performed via laser spectroscopy. We found no isotopic differences between rainfall, surface runoff, and bottom outflow. The in situ vapour ports' soil isotope data showed the widest spread over all hillslope positions and depths. Centrifugation's and suction cups' isotope results plotted closest to the local meteoric water line and within the range of hillslope runoff and bottom outflow data. Hillslope position did not influence the soil isotope results. These results suggest caution be used in the field when selecting an extraction technique for matching soil waters to runoff waters. Soil suction lysimeters and centrifugation appeared to be the most appropriate tools in this regard.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
© 2019 The Authors Hydrological Processes Published by John Wiley & Sons Ltd

Hydrological Processes. 2019;33:2939–2954.
Stable isotopes of water ($\delta^2$H and $\delta^{18}$O) are useful tools to study mixing and runoff processes across multiple scales. Because early work by Zimmermann, Ehlalt, and Muennich (1968), there have been numerous studies that applied hydrogen and oxygen stable isotopes to trace water from precipitation through the unsaturated zone. In subsurface hydrology, stable isotopes of water have been used to study evaporation processes (Allison, Barnes, & Hughes, 1983; Barnes & Allison, 1988; Mathieu & Bariac, 1996; Rothfuss et al., 2015), the depth of plant water uptake (Evaristo, McDonnell, Scholl, Bruijnzeel, & Chun, 2016; Martin-Gómez, Serrano, & Ferro, 2016; Orlowski, Winkler, McDonnell, & Breuer, 2018; Volkmann, Haberer, Gessler, & Weiler, 2016), or infiltration and runoff generation processes (Zha, Tang, Zhao, Wang, & Tang, 2013). For a general overview of isotope hydrology in soils and the vadose zone, the reader is referred to reviews by Soderberg, Good, Wang, and Caylor (2012) and Sprenger, Herbstritt, and Weiler (2015); Sprenger, Leistert, Gimbel, and Weiler (2016).

The application of stable isotopes of water as natural tracers relies on accurate, high-precision measurements (Wassenaar et al., 2012). However, isotope effects during the extraction of water from soils triggered by their physicochemical properties (e.g., clay minerals, soil organic carbon content, and water content) can occur (Araguás-Araguás, Rozanski, Gonfiantini, & Louvat, 1995; Gaj et al., 2017; Meißner, Köhler, Schwendenmann, Hölscher, & Dyckmans, 2014; Oerter et al., 2014; Orlowski, Frede, Brüggemann, & Breuer, 2013) and extraction method issues itself (Orlowski, Pratt, & McDonnell, 2016, Orlowski, Breuer, et al., 2018), which lead to difficulties in reliably removing water from the soil matrix (Oerter, Perelet, Pardyjak, & Bowen, 2017).

Although extraction intercomparisons have shown quite wide variance in values depending on the method of extraction of the pore waters (Orlowski et al., 2016; Orlowski, Breuer, et al., 2018), few studies have yet explored extraction effects for the mobile pore waters that relate to hillslope runoff or the linkages between different hydrological compartments. That is because it is extremely difficult in natural systems to control the boundary conditions in order to assess and compare the impact of pore water extraction on resulting hillslope flow and isotopic composition. Hillslopes are fundamental landscape units (Bachmair, Weiler, & Troch, 2012) that shape water availability on land (Fan et al., 2019). Hillslope runoff is crucial to understand in relation to its source end members because hillslopes modulate how precipitation becomes runoff and are therefore of major importance for many Earth system processes (van den Heuvel et al., 2018). Profound process knowledge of hillslope hydrological dynamics is, therefore, essential for flood prediction and understanding transport of material, slope stability, and soil-vegetation-atmosphere feedback processes (Bachmair et al., 2012). However, our knowledge of the subsurface is extremely limited and we do not know where water is stored (supporting vegetation) and released to stream baseflow (supporting aquatic ecosystems; Fan et al., 2019).

To date, spiking experiments have been the method of choice for comparing different soil water extraction techniques or systems among each other (Orlowski et al., 2016; Orlowski, Breuer, et al., 2018). For such experiments, soil samples are oven-dried and rehydrated with water of known isotopic composition to a certain water content. Afterwards, the added water should be recaptured via a water extraction method without isotope fractionation. However, more and more studies (Gaj, Kaufhold, & McDonnell, 2017; Newberry, Prechsl, Pace, & Kahmen, 2017; Sprenger et al., 2015) question the usefulness of such an approach, where remoistening of oven-dried soil samples might be the major problem leading to artificially modified soil water pools and isotopic exchange processes. Furthermore, such experiments are usually performed on disturbed soil cores, which make it challenging to compare isotope results to soils under natural conditions. Thoma, Frentress, Tagliavini, and Scandellari (2018) highlight the need for soil water extraction methods not only under laboratory conditions but also under natural conditions in the field.

We build on past work that has examined different soil pore water extraction methods for isotope analysis (see the review by Sprenger et al., 2015). Some of these tools have already been compared against each other at the soil core scale (e.g., Figueroa-Johnson, Tindall, & Friedel, 2007; Kelln, Wassenaar, & Hendry, 2003; Landon, Delin, Komor, & Regan, 1999; Orlowski et al., 2016; Thoma et al., 2018; Walker, Woods, & Allison, 1994). But to date, the destructive vs. nondestructive pore water extraction techniques have not been intercompared so far and certainly not in relation to the hillslope runoff signal. For hydrological system testing, we compare in situ water vapour ports and suction cup lysimeters as nondestructive methods and centrifugation and direct vapour equilibration as destructive pore water sampling techniques on a mini-hillslope system. Three-dimensional hillslopes have the advantage that they can represent field-scale infiltration and lateral flow processes (Pratt & McDonnell, 2017).

Centrifugation and direct vapour equilibration have shown similar results in a previous study by Orlowski et al. (2016) but have not been intercompared to in situ pore water extraction methods under semi-controlled conditions outdoors. In situ water vapour ports (as per Pratt, Lu, Barbour, & Hendry, 2016) were chosen as this method can provide high-frequency soil water vapour isotope data in real time when coupled to a portable laser spectroscopy for isotope
measurements. Suction cups (alternatively called suction lysimeters or suction cup lysimeters) are low-cost pore water samplers that are commonly applied in field studies (e.g. Brooks, Barnard, Coulombe, & McDonnell, 2010; Hervé-Fernández et al., 2016; Zhao et al., 2013).

The null hypothesis guiding this work was that destructive and nondestructive extraction methods installed in the mini-hillslopes sample isotopically the same soil water pool (low tension, mobile water), which further generates runoff. The larger context for this work is understanding of the linkages between compartmentalized storage and runoff (McDonnell, 2017). However, the contrasting methodologies we use to sample the different soil water compartments (mobile versus tightly bound waters) contributing to flow may affect our process interpretations. To better address some of this, we further investigate the following research questions:

1. Do rainfall, soil water (examined by our four techniques), surface runoff, and hillslope subsurface stormflow differ in their isotopic composition and what does this tell us about mixing and runoff processes?
2. How does hillslope position and depth affect the obtained isotopic results of the different extraction methods?

2 | MATERIAL AND METHODS

2.1 | Hillslope experimental setup and sampling

Three mobile, tiltable, mini-hillslopes (0.63 m wide, 1.78 m long, and 0.43 m deep; slope: 10°; Fig. 1) were filled (bulk density: 1.5 g/cm³) with inert, sterilized ground basaltic tephra with a loamy sand texture (originated from Landscape Evolution Observatory [LEO] at Biosphere 2, University of Arizona, USA). Bulk density is gravity settled under saturation conditions. This soil material was chosen as it has already been used in comparable hillslope studies at LEO (Biosphere 2; e.g., Niu et al., 2014; Pangle et al., 2015). Table 1 provides general soil property information. In addition, the soil water retention curve and the fractional mineral composition for this soil type are given in Pangle et al. (2015).

The soil porosity, \( \varepsilon \) (cm³/cm³), was calculated from the bulk density data, assuming a soil particle density of 2.65 g/cm³ (Minasny, McBratney, & Bristow, 1999; Prima et al., 2017).

The three hillslopes were placed outdoors to use the natural isotopic composition of precipitation as tracer entering the hillslopes. Other than spiking experiments, this approach better reflects the application of the respective soil pore water extraction methods under natural field conditions. To observe outdoor micro-climatic conditions, we installed a climate station (WS600, Lufft, Fellbach, DE), which recorded data on precipitation amounts, air temperature, relative humidity, wind speed and direction, and air

![FIGURE 1](image_url) (a) Photo of the three outdoor mini-hillslopes and (b) sketch of the experimental setup of the hillslopes. Z1–Z3 stand for the three sampling positions on the hillslopes.
pressure. Flux into and out of the system due to precipitation events, or evaporation, was monitored with a system of load cells (RSB6-500kg, Loadstar Sensors, Fremont, CA, USA). Pratt and McDonnell (2017) proved the accuracy of the hillslope load cell system. Hillslopes were further equipped with soil moisture and temperature sensors (STM, Decagon, USA; accuracy: ±0.03 m³/m³), a bottom outflow and a surface runoff gauge for isotope sampling. Soil moisture and temperature sensors were calibrated to the respective soil type.

At the beginning of our experiment, soils in the mini-hillslopes were hydrated to ponded water saturation with Saskatoon tap water of known isotopic composition (measured on an IWA-45EP Analyzer [Los Gatos Research Inc., Mountain View, USA]: δ²H: −125.4±2.0‰ and δ¹⁸O: −15.5±0.4‰) on 28 July 2016 and allowed to equilibrate and fill material allowed to settle for the following 5 days.

In order to check whether soils were entirely saturated at the beginning of our experiment, the calculated soil porosity of 0.43 cm³/cm³ was assumed to coincide with saturated soil water content \( \varepsilon \) (θs, \( \varepsilon = \varepsilon_s \)), as suggested by many authors (e.g., Di Prima, 2015; Minasny et al., 1999; Prima et al., 2017). This approach assumes a low to medium spatial variability for both \( \varepsilon \) and bulk density (Di Prima, 2015). However, the measured volumetric water contents at the beginning of the experiment were higher than the expected saturated conductivity on the basis of the soil textural characteristics alone.

To intercompare pore water isotopic compositions, hillslopes were instrumented with destructive (centrifugation and vapour equilibration method) and nondestructive pore water sampling methods (suction cups and in situ vapour ports). To test the effect of hillslope position on the isotope results, we divided the hillslopes into three zones: upslope, midslope, and downslope position (1–3). Hillslope 1 was instrumented with suction cups (IR-Lys, Irrometer; MMM tech, DE) at three depths (10, 20, and 30 cm). In the second hillslope, we installed sampling ports for direct in situ measurements of soil water vapour isotopic composition (as per Pratt et al., 2016) at four depth intervals (0–10, 10–20, 20–30, and 30–40 cm). The third hillslope was sampled destructively via soil coring for the application of centrifugation and vapour equilibrium methods to evaluate the soil’s isotopic composition over the same depth intervals. Hillslopes 2 and 3 were sampled at the same four depths at three different downslope positions (1–3; Fig. 1), whereas hillslope 1 was sampled in three depths at two downslope positions (hillslope position 1 and 3). We conducted six sampling campaigns for pore water isotope analysis between 31 July 2016 and 5 November 2016. Rainfall, surface runoff, and bottom outflow amounts were recorded, and isotope samples were taken when water was present (Fig. 2). Event-based precipitation was conducted using a rainfall totalizer situated in direct proximity to the hillslopes. Isotope sampling followed IAEA standards with respect to evaporation prevention against isotope fractionation, representativeness of the sample, storage, and sample preparation (IAEA, 2014).

2.2 | Destructive and nondestructive water extraction methods

2.2.1 | Destructive pore water sampling

The centrifugation set-up and tubes were prepared following di Bonito, Breward, Cruot, Smith, and Young (2008) and Orlowski et al. (2016). Two 15-ml tubes were prepared as "filter tubes" for each sample, with Whatman® Grade 1 filter paper placed over the exit hole of the first tube containing the soil sample. The second tube acts as a collection tube placed directly under the filtration tube containing the soil sample. The filter tube assembly is then placed and capped inside a 50-ml centrifuge tube. Destructively taken soil samples were spun at 5,000 rpm for 30 min on a Beckman Coulter centrifuge (Avanti JXN-26, Beckman Coulter Inc., DE). Relative centrifugal force was converted to soil water tensions using transformations based on simple soil physics (Edmunds & Bath, 1976; Figueroa-Johnson et al., 2007). A calculated tension of approximately 30 kPa was applied to all soil samples.

Centrifugation was chosen as it showed the highest proficiency in our previous intercomparison study (Orlowski et al., 2016) for a silty sand and a clayey loam soil type and both isotopes (δ²H and δ¹⁸O). It further comes with the advantage that it is time-efficient and therefore large numbers of samples (8–24 samples depending on rotor size and extraction time) can be processed daily (Orlowski et al., 2016).

Direct vapour equilibration followed protocols outlined by Hendry, Schmeling, Wassenaar, Barbouir, and Pratt (2015) and Wassenaar, Hendry, Chostner, and Lis (2008). About 400 g of soil was placed into a Ziploc® medium-sized freezer bag and was inflated with dry air, sealed, and allowed to equilibrate at room temperature (22 °C) for 72 hr prior to isotope analysis. Analysis was performed via off-axis integrated cavity output spectroscopy (OA-ICOS) using the vapour sampling mode. Same as for extracted liquid water, in-house standards, calibrated against Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Antarctic Precipitation 2 (SLAP2), were run as samples to allow the results to be reported against VSMOW (Nelson, 2000).

A major advantage of the direct vapour equilibration method is that it is the least expensive and least time consuming choice (Orlowski et al., 2016). However, previous studies have shown that trade-offs in accuracy are sacrificed with this method, especially in low water content soils (<5% gravimetric water content of less than 3 g of water in the sample) and consolidated shales (Hendry et al., 2015; Wassenaar et al., 2008). Additionally, sample storage time and storage containers play a crucial role (Orlowski et al., 2016).

2.3 | Nondestructive pore water sampling

For nondestructive pore water sampling, we used suction cup lysimeters. Suction cups are tubular-shaped with a tip of porous material (e.g., ceramic, sintered metal; Thoma et al., 2018). For pore water extraction, a vacuum is applied and water is pulled from the soil into the suction cup body or a peripheral collection device (Thoma et al.,
In our study, a pressure of 60 kPa was applied to each suction cup. Suction cups were allowed to equilibrate for a minimum of 3 hr prior to pore water sampling. For comparison, Geris et al. (2015) sampled only for 10–30 min to collect soil water via suction cups. The presumed advantage of the porous cup method is that the disturbance of the surrounding soil is negligible after installation, which results in only minor changes in natural percolation behaviour induced by the suction cups (Grossmann & Udluft, 1991). Suction cups have been widely used to assess movement of solutes through the unsaturated zone due to the ease of installation, simplicity of design, and low costs (Hart & Lowery, 1997). A serious limitation, however, resides in the fact that the sampling volume and the imposed changes in matric potential during sampling on the natural flow pattern are not well known (Hart & Lowery, 1997; Weihermüller, Kasteel, Vanderborght, Pütz, & Vereecken, 2005). For a detailed assessment on water extraction with suction cups, see Grossmann and Udluft (1991) and Weihermüller et al. (2005).

In situ vapour ports were installed at the time of hillslope filling. About 5-cm porous ceramic filters were attached to lengths of 7-mm high-density polyethylene (HDPE) tubing. The HDPE tubing has proven to be suitable for in situ soil vapour collection (Pratt et al., 2016). The filters were installed horizontally at each depth of interest upon filling the hillslopes with soil. The HDPE tubing was then routed to the hillslope surface for sampling. Others have used similar in situ probes with a LGR isotope analyzer also at shallow soil depth (e.g., Gaj et al., 2016). HDPE tubing was tightly capped when not in use for vapour sampling. Sampling of vapour ports included a pre-evacuation procedure to flush the sampled lines of any residual vapour and liquid equilibration method by adding 10 ml of standard water into a Ziploc bag and inflating with dry air (Pratt et al., 2016). These standards were measured after four samples to correct for instrument drift and to normalize the results to the VSMOW scale. Flow rates were kept low (85.8 ml-min⁻¹) as suggested by Thoma et al. (1978) to maintain a zone of influence representative of water vapour at the depth of the in-situ ports (Pratt et al., 2016). We applied the following correction protocol by Pratt et al. (2016) to obtain the pore water isotopic composition: the isotopic composition of the vapour sample was first corrected for relative humidity effects (δRH) based on the method of Schmidt et al. (2010). Then, the ratio between the known standard water value and the measured vapour value was calculated (Δ1). Afterwards, the theoretical ratio of the vapour and liquid composition of the standard samples (Δ2) was calculated for laboratory temperatures based on equilibrium fractionation using equilibrium fractionation factors from Majoube (1971). The theoretical equilibrium fractionation of a standard water at the in-situ temperature was calculated and the ratio was then calculated against the measured vapour value (Δ3). Finally, the in-situ pore water isotopic composition was obtained using the sample vapour measurements (corrected for relative humidity) and Equation (1).

\[
\delta_{\text{corrected}} = \delta_{\text{SH}} + \Delta_1 + (\Delta_2 - \Delta_3)
\]  

This correction protocol utilized the in-situ and ambient temperature data obtained from both the soil moisture/temperature probes and the outdoor weather station.

### 2.4 Isotope analyses

All liquid water samples collected from each respective extraction method (centrifugation and suction cups) were filtered (0.45 µM-Corning PTFE Syringe Filter) and analyzed via OA-ICOS on an IWA-45EP Analyzer (Los Gatos Research Inc., Mountain View, USA). The accuracy of OA-ICOS analyses was ±0.5‰ for δ²H and ±0.2‰ for δ¹⁸O (LGR, 2013). For direct water vapour analyses (vapour equilibration technique and in situ vapour ports), LGR’s ultraportable water-vapour isotope analyzer (U-WVIA, 915-0034, Los Gatos Research Inc., Mountain View, USA; flow rate: 85.8 ml/min) was used with an accuracy of ±2.0‰ for δ²H and ±0.3 for δ¹⁸O determined by repetitive measurements.

All isotope ratios are reported in per mil (‰) relative to VSMOW (δ²H or δ¹⁸O=(Rsample/Rstandard−1)×1,000‰), where R is the isotope ratio of the sample and the known reference (i.e., VSMOW; Craig, 1961). All runs include three in-house standards. In-house standards, calibrated against VSMOW2 and SLAP2, were run as samples to allow the results to be reported against VSMOW (Nelson, 2000).

OA-ICOS isotope data of soil water extracts were checked but not corrected for spectral interferences (caused by potentially coextracted organics such as methanol or ethanol) using the Spectral Contamination Identifier post-processing software (LWIA-SCI, Los Gatos Research Inc.) when measured via OA-ICOS. This software compares recorded spectra from unknown samples with those from known noncontaminated samples (standards) to produce a metric of contamination from either narrow-band (e.g., methanol [MeOH]) or broad-band (e.g., ethanol [EtOH]) absorbers, which indicates the likelihood or degree of spectral interference (Schultz, Griffis, Lee, & Baker, 2011). However, so far, there does not exist an overall correction scheme or protocol for samples potentially contaminated by organics. In our study, no sample was found to be contaminated.

### 2.5 Data analyses and statistical evaluation

For statistical analyses, we used IBM SPSS Statistics (Version 25, SPSS Inc., Chicago, IL, USA). All graphical plots were done using Origin 2018 (OriginLab Corporation, Northampton, MA, USA). For quantifying differences between runoff, surface runoff and baseflow (also between the three hillslopes), extraction method differences, and effect of hillslope position on the isotopic composition, all data were tested for normality using the Shapiro-Wilk test. Homoscedasticity was tested using either the Levene’s test for normally distributed data or the Fligner–Killeen test for non-normally distributed data. Outlier
analysis was performed (2.2IQR), and outliers were removed for further analyses. Depending on the type of data (normally distributed and homoscedastic), either Kruskal–Wallis rank sum tests or analyses of variances were applied and posthoc tests (i.e., Tukey-B tests or Dunnett-T3) were run to determine which groups were significantly different ($p\leq0.05$). We further analyzed linear relationships between rainfall, surface runoff, and bottom outflow isotope data, as well as between these water sources and the soil isotope data obtained via the different extraction methods.

For each soil water extraction method, rainfall, surface runoff, and bottom outflow samples, we further calculated the line-conditioned excess (lc-excess) as suggested by Landwehr and Coplen (2004):

$$lc\text{-excess} = \left[\delta^{2}H - a\delta^{18}O - b\right],$$  \hfill (2)

where $a$ and $b$ are the slope and $y$-intercept of Saskatoon’s local meteoric water line (LMWL; $\delta^{2}H=7.7x\delta^{18}O-1.7\%$), respectively. The degree of the offset of lc-excess calculated with Equation (1) enables the assessment of whether or not rainfall waters have undergone evaporative processes in soil when the offset is negative and greater than the standard deviation of the LMWL. Lc-excess values reflect both source water differences as well as the full complexity of physical processes that produce surface waters (Landwehr and Coplen, 2006). Generally, the lc-excess of the precipitation input is about 0‰ and shows relatively little seasonal dynamics in comparison to $\delta^{2}H$, $\delta^{18}O$, and $d$-excess (Sprenger, Tetzlaff, & Soulsby, 2017). We used t tests to determine whether the average soil water lc-excess of each method and hillslope position deviated significantly from zero.

We calculated daily potential evaporation rates ($ET_o = \text{evaporation loss in the present study}$) with the FAO Penman-Monteith method (Doorenbos & Pruitt, 1977) from our recorded climate data.

3 | RESULTS

3.1 | Temporal and isotopic variability of rainfall, surface runoff, and bottom outflow

Figure 2 summarizes the temporal variability of mobile water’s isotopic composition as well as microclimatic conditions (precipitation, volumetric water content and hillslopes’ weights, soil and air temperature, and evaporation rates).

Surface runoff followed the isotopic trend of the precipitation input (Fig. 2a). Bottom outflow was not always present and was isotopically slightly more depleted than precipitation and surface runoff. The introduced tap water isotopic composition was on average the most depleted. $\delta^{2}H$ values of precipitation were more positive at the beginning of the experiment in summer than in autumn where temperature temporarily dropped below zero.

FIGURE 2 Temporal variability of (a) rainfall amounts (grey bars), amount-weighed $\delta^{2}H$ values of rainfall (blue triangles), surface runoff (light blue triangles), and bottom outflow (blue hexagons). For reference, soil sampling dates (red asterisks) and the Saskatoon tap water’s $\delta^{2}H$ value $\pm SD$ is given as dotted orange line; (b) volumetric soil water contents of hillslope 2 (hillslope position 2; blue lines) and load cell data of hillslopes 1–3 (grey lines); and (c) daily mean air (red line) and soil temperatures (hillslope 1: orange line, hillslope 2: green line; SD shown as grey shaded areas) and evaporation (light orange line) over the course of the experiment. Note that due to logger malfunctioning, no load cell data is available after 22 August.
Statistically, no significant differences were observed between rainfall, surface runoff, and bottom outflow isotopic composition. Rainfall and surface runoff of the three hillslopes even showed linear correlations among each other (e.g. for $\delta^{18}O \ R^2=0.9-1.0$). In terms of differences between the sampled hillslopes, surface runoff did not significantly differ statistically between the three hillslopes ($p\leq0.05$). Significant differences were observed between the bottom outflow of hillslope 1 and 3 for $\delta^{18}O$ ($p=0.022$), but mean differences between the two were ±0.28, which lies within the accuracy of OA-ICOS analyses of ±0.2‰ for $\delta^{18}O$.

Because the hillslopes were flooded with Saskatoon tap water of known isotopic composition at the start of the experiment, homogeneous soil water contents over depths were observed (Fig. 2b). Following the approach of Prima et al. (2017), we could prove that soils were fully saturated (>0.5 Vol-%) at the start of the experiment and again at the end. From mid-August to the end of September, volumetric water contents continuously decreased. This was related to higher air and soil temperatures over summer (on average 16.3°C) and little rain. The decrease in soil water content led to a steady weight loss of the hillslopes (Fig. 2b). At the end of September, some major precipitation events occurred (>5 mm/day) saturating the soils until soil water contents reached initial values again (0.52–0.55 Vol-%; Fig. 2b). Soil temperatures of hillslope 1 and 2 were almost identical and generally followed air temperature trends. Standard deviations of soil temperatures ranged between 0.1 and 3.8 over the course of the experiment (Fig. 2c). Towards the end of the experiment, air and soil temperatures dropped respectively, and ranged between 0 and 10°C. Evaporation rates continuously decreased from 2.8 mm/day to close to zero at the end of the experiment. Little evaporation, lower temperatures, and some major rain events led to a refill of the soil water storage towards the end of October.

Table 2 compares evaporation rates, precipitation amounts, and volumetric soil water contents on the dates of soil isotope sampling, seven and 14 days prior to the samplings as well as averaged precipitation lc-excess values from the three antecedent rain events.

The antecedent evaporation rates ($ET_7$ and $ET_{14}$) did not differ significantly from the evaporation rates on the date of the soil isotope sampling. Highest evaporation rates occurred for the samplings in August (3 August: 2.6 mm/day and 22 August: 2.1 mm/day, respectively). For the last sampling on 3 November, no evaporation was recorded, even $ET_{14}$ was low (0.1 mm/day).

Except for the last two samplings, there was no rain on the sampling day and we finished collecting soil isotope data before the rain event occurred mid-day for the sampling on 17 October. The antecedent rain indices defined as rainfall amount during the 7 and 14 days prior to the soil sampling differed for the six soil isotope samplings (Table 2). The sampling days that showed high evaporation rates also corresponded the highest $P_7$ and $P_{14}$ values (3 and 22 August and 17 October). The volumetric soil water contents were different for every sampling campaign and also varied for the four sampling depths. The two pore water samplings conducted in September showed the lowest volumetric soil water contents of all samplings. Whereas for the first and last two samplings, soils were fully saturated. Interestingly,

| Soil sampling date | $ET_0$ [mm/day] | $ET_7$ | $ET_{14}$ | $P_7$ | $P_{14}$ | lc-excess [%] | $\delta^{18}O$ (‰) | $\delta^{18}O$ (‰) | $\delta^{18}O$ (‰) | $\delta^{18}O$ (‰) |
|--------------------|-----------------|------|---------|------|------|-------------|-----------------|-----------------|-----------------|-----------------|
| 03/09/2016         | 2.64            | 2.50 | 2.61    | 0.0  | 20.0 | -4.60       | 0.12            | -4.60            | 0.12            | -4.60            |
| 22/08/2016         | 2.11            | 2.16 | 2.07    | 0.0  | 13.2 | -3.85       | 0.53            | -3.85            | 0.53            | -3.85            |
| 06/09/2016         | 1.21            | 1.61 | 1.68    | 0.0  | 4.2  | -3.62       | 0.36            | -3.62            | 0.36            | -3.62            |
| 07/09/2016         | 1.05            | 1.14 | 1.22    | 0.0  | 4.4  | -1.40       | 0.31            | -1.40            | 0.31            | -1.40            |
| 20/09/2016         | 1.09            | 1.14 | 1.22    | 0.0  | 4.4  | -1.40       | 0.31            | -1.40            | 0.31            | -1.40            |
| 17/10/2016         | 0.32            | 0.44 | 0.48    | 0.0  | 14.8 | 3.26        | 0.50            | 3.26             | 0.50            | 3.26             |
| 03/11/2016         | 0.00            | 0.02 | 0.06    | 0.2  | 4.0  | 8.40        | 0.51            | 8.40             | 0.51            | 8.40             |
$\theta_o$ at 7 cm did not show the lowest values and the sensor at 28-cm soil depth did not exhibit the highest $\theta_o$ values when compared with the other depths (Table 2 and Fig. 2b).

3.2 Isotopic differences between extraction methods and hillslope positions

The plots presented in Figure 3 illustrate the data variability in dual isotope space of each method per hillslope position and depth with respect to rainfall, surface runoff, bottom outflow, and tap water.

Soil isotope data obtained via the in situ vapour ports showed the widest spread over all hillslope positions and depths and plotted furthest away from the LMWL (Fig. 3). Standard deviations for $\delta^{18}O$ ranged from ±3.1 to ±4.8‰ for hillslope positions 1–3. For comparison, smallest standard deviations for $\delta^{18}O$ were obtained for the suction cup method for hillslope position 1 and 2 of ±1.8 and ±1.4‰, respectively. Isotope results of the centrifugation and suction cup method plotted closest to the LMWL and within the range of rainfall, surface runoff, and bottom outflow data. When comparing $\delta^{18}O$ and $\delta^2H$ values of the same method between the three sampling positions on the hillslopes (1–3), none of the extraction methods showed significant differences between the hillslope positions ($p>0.05$; Fig. 3). In terms of differences between the extraction methods, $\delta^{18}O$ values of the in situ vapour port method differed significantly from all other methods (when compared with centrifugation $p=0.05$, $p=0.001$ for suction cups, and 0.17 for the vapour equilibration method, respectively; Fig. 3). The same was true for the $\delta^2H$ values ($p=0.000$). Centrifugation versus vapour equilibration isotope results showed 1:1 relationships for all three hillslope positions ($R^2=0.6–0.8$), exemplarily depicted for $\delta^{18}O$ in Figure 4. This indicates that those methods are able to produce similar soil isotope results.

The lc-excess describes the deviation of the sample’s $\delta^2H$ value from the LMWL (Landwehr, Coplen, & Stewart, 2014). Negative lc-excess values may indicate nonequilibrium kinetic fractionation processes due to evaporation after precipitation, whereas positive values may accord with a sample arising from several sources including relatively newly evaporated moisture (Landwehr et al., 2014). When comparing lc-excesses between the soil pore water extraction methods in our study, centrifugation and suction cup data showed the smallest standard deviations over all hillslope positions and plotted closest to zero, which indicates similarities to rainfall inputs (plotting along the LMWL; Fig. 3 and 5). However, both methods deviated significantly from zero ($p<0.05$), separately tested for each hillslope position. The vapour equilibrium technique showed slightly more negative lc-excess values, especially for hillslope position 1 suggesting evaporative isotopic fractionation. Mean lc-excess values were also statistically different from zero for all hillslope positions ($p=0.000$). Lc-excess of the in situ vapour port method showed the greatest variation (11.1±26.2) over all hillslope positions and depths (Fig. 5). Nevertheless, mean lc-excess values were not statistically different from zero for hillslope positions 1 and 3 of the in situ vapour port technique but for hillslope position 2 ($p=0.019$). For comparison, mean rainfall lc-excess was 2.1±6.8 over the entire sampling period and differed significantly from bottom outflow lc-excess values of hillslope 1–3 ($p=0.000$). Bottom outflow lc-excess values (-9.1±1.6) were further significantly different to surface runoff (2.4±8.0) lc-excesses of hillslope 1–3 ($p=0.004$; Fig. 5).

Comparing the extraction methods’ soil isotope results to rainfall, surface runoff, and bottom outflow, we found no significant differences for pore water sampled via centrifugation and vapour equilibration (Fig. 3). We further tested whether $\delta^{18}O$ and $\delta^2H$ data of the respective soil depth and hillslope position, correlated with the preceding rainfall $\delta^{18}O$ and $\delta^2H$ data. Not surprisingly, we found linear correlations between rainfall and $\delta^{18}O$ values or $\delta^2H$ values for some of the extraction methods, but only a few were statistically significant. $\delta^{18}O$ and $\delta^2H$ data obtained by suction cups were significantly different from bottom outflow data of hillslope 3 ($p=0.035$ for $\delta^{18}O$ and

![FIGURE 3](image-url)  Dual isotope plots of rainfall, surface runoff, bottom outflow, tap water, destructive, and nondestructive water extraction methods for hillslope positions 1–3 over depths (0–10, 10–20, 20–30, and 30–40 cm). For comparisons, the local meteoric water line (LMWL; blue line) and global meteoric water line (GMWL; dashed line; GMWL: $\delta^2H=8.2x\delta^{18}O+11.3$‰, as defined by Rozanski et al., 1993) are plotted. Plots include lc-excess diamond plots for each pore water extraction method and hillslope position (small insets).
$p = 0.032$ for $\delta^2$H. Soil isotope data obtained via the in-situ vapour ports differed significantly from bottom outflow data of hillslope 1 for $\delta^{18}$O ($p = 0.042$) and for $\delta^2$H of hillslope 1–3 ($p \leq 0.001$). Surface runoff data ($14.4 \pm 5.1$ for $\delta^{18}$O and $110.9 \pm 37.4$ for $\delta^2$H) showed similar variations as rainfall isotope data ($14.4 \pm 5.1$ for $\delta^{18}$O and $111.0 \pm 36.3$ for $\delta^2$H) over the entire sampling period (Fig. 3) and bottom outflow isotope data had the smallest standard deviation among this group ($13.9 \pm 0.5$ for $\delta^{18}$O and $118.3 \pm 2.2$ for $\delta^2$H). However, the sample size for bottom outflow was rather small ($N = 30$) as it was not always present. This indicates that surface runoff was not affected by isotopic evaporative enrichment and we were able to sample it shortly after rainfall events. This is supported by the fact that both surface runoff and rainfall mean lc-excess values were similar and above zero. On average, surface runoff $\delta^{18}$O values deviated by $\pm 0.8$‰ from rainfall

**FIGURE 4** 1:1 plots for centrifugation $\delta^{18}$O values versus vapour equilibration $\delta^{18}$O values for hillslope positions 1–3. A 1:1 line is given for comparison (dashed line). Note that outliers (2.2xIQR) were removed for statistical analyses and plots.

**FIGURE 5** lc-excess depth profiles of the destructively (centrifugation and vapour equilibration) and nondestructively (suction cups and in situ vapour ports) obtained results (different colours represent different methods) from hillslope positions 1–3 (different symbols). For comparisons, mean rainfall, surface runoff, and bottom outflow lc-excess values are included. Note that the depth-plot for the in situ vapour port method has a different x-axis scale.
over all hillslopes and by ±4.9‰ for δ²H and showed linear correlations for the three hillslopes with rainfall isotope data.

3.3 Can we observe isotopic differences over depth and hillslope positions via the different extraction methods?

Regarding the depth distribution of δ²H values of the different pore water extraction methods, the most negative δ²H values were observed at a depth of 15 cm for centrifugation and vapour equilibration (Fig. 6). From 5 to 15 cm, isotopic compositions obtained via centrifugation and vapour equilibration were even more depleted than rainfall and surface water isotopic compositions. However, with increasing depth, δ²H values fell within the range of bottom outflow values for those two methods. Soil water δ²H sampled by suction cups showed the exact opposite trend with least enriched values at 5 cm and most enriched values at 15 cm soil depth. Further, δ²H values at a depth of 15 cm plotted closest to bottom outflow data. However, no pore water could be extracted for hillslope position 2 at 5 cm because of malfunctioning suction cups. The lowest standard deviations for suction cup δ²H data were achieved in a depth of 25 cm (±3.6 and ±2.3 for hillslope positions 1 and 2, respectively) over the entire sampling period. For centrifugation and vapour equilibration, lowest standard deviations occurred below 25 cm depth, where θ₀ values ranged between 0.19 and 0.55 Vol-% (Table 2). For all extraction methods, centrifuged data from hillslope position 2 achieved the lowest standard deviations over all depths (±1.5 to ±3.9). δ²H pore water values of the in situ vapour port method fell in the range of all water sources (rainfall, surface runoff, and bottom outflow) for 5–15 cm over all hillslope positions. This is not surprising because standard deviations were generally higher for this method in comparison to the others. However, for the deepest soil depth (35 cm), deviations were highest for δ²H generated by this technique for hillslope position 1 (standard deviation of ±36.5).

4 DISCUSSION

4.1 Mixing and runoff processes at the hillslope scale

Typically, as precipitation infiltrates into the soil profile, macropore and mesopore are filled and soil micropores are recharged through adsorption or capillarity (Or & Tuller, 1999; Tuller, Or, & Dudley, 1999; Phillips, 2010; Brooks, 2015). During our observation period, surface runoff followed the isotopic trend of the precipitation input and showed linear correlations for the three hillslopes with rainfall isotope data. In comparison, bottom outflow was episodic and isotopically more depleted than precipitation and surface runoff. Nevertheless, it did not differ significantly from rainfall and surface runoff isotope data. This suggests that “recharge” into our hillslopes was dominated by higher magnitude rainfall events (as per Jasechko, Wassenaar, & Mayer, 2017). It further suggests that our hillslope systems must have been well mixed and drainage water was not affected by isotopic fractionation effects as all mobile water sources plotted along the LMWL. Nevertheless, we observed differences in the δ¹⁸O values between hillslope 1 and 3 for the bottom outflow, which was not the case for δ²H values or surface runoff isotopic composition. However, total weights of hillslopes 2 and 3 were slightly higher than hillslope 1. As soil volumetric water contents decreased continuously from mid-August to the end of September, one might have expected distinctly different bottom outflow isotopic composition and surface runoff that might have been altered by evaporation, but neither was the case.

FIGURE 6 δ²H depth profiles of the destructively (centrifugation and vapour equilibration) and nondestructively (suction cups and in-situ vapour ports) obtained results (different colours represent different methods) from hillslope positions 1–3 (different symbols). For comparisons, mean rainfall, surface runoff, and bottom outflow δ²H values are included. Note that the depth-plot for the in situ vapour port method has a different x-axis scale.
Similarly, others have shown relationships in hillslope systems where isotopic composition of surface and deeper layers are not constrained solely by mobility of the evaporated/enriched surface layer water, that is, shallow bulk soil water demonstrated less mobility into the subsurface than what is represented isotopically in deeper bulk soil water (Shuler, 2018). What controls this process phenomenon? One would assume that pulse inputs from precipitation would produce a mixed breakthrough of isotopically enriched surficial waters that would be represented in the drainage water, but more commonly, we are seeing something completely different. Although our study represents observed processes on a reconstructed, small-scale hillslope, on average, mixing processes represented here show an isotopically fairly well-mixed system (not observable by the in situ vapour port method). Some have suggested that hillslope antecedent conditions directly affect discharge relationships in the way that the wetter the hillslope at the start of a precipitation event, the more likely the discharge or drainage water will follow the isotopic composition of the input signal (Pangle et al., 2017). Although this was not necessarily a target question for our study, we observed similar trends during wetter periods throughout the summer.

Other studies utilizing the same parent material from the Biosphere 2 LEO laboratory (University of Arizona; USA) have demonstrated unique physical characteristics that may affect the storage and water holding capacity of these reconstructed hillslopes (van den Heuvel et al., 2018). The soil water retention curve of this material demonstrates strong matric potential differences between saturated and unsaturated states. However, the existence of fine pore structures may cause more water retention and a larger capillary fringe. This capillary fringe of effectively saturated soil water may increase mixing processes throughout the hillslope and negate any evaporative enriched shallow soil water as the quantity of water in the near surface is quantitatively smaller than in the subsurface. Gaj et al. (2019) showed that the degree of transport, mixing and fractionation of water stable isotopes within the unsaturated zone under drought is controlled by the composition of the biogeochemical interface, soil tension, and wettability. Especially the use of stable isotope signatures of soil water and water vapour at the dry end of the water retention curve (around wilting point) is largely unexplored, but nevertheless important, because these dry conditions occur preferentially at the shallow soil depths, where evaporation into the atmosphere occurs (Gaj & McDonnell, 2019). However, the strength of the relationship between mobility and isotopic composition remains poorly constrained (Shuler, 2018).

4.2 Method performance

For our intercomparison study, we went beyond the typical soil core approach and tested commonly used destructive and nondestructive soil pore water extraction methods on a larger 3-D-hillslope scale. Because we conducted our experiment under natural outdoor climate conditions, we were able to use the individual rainfall isotopic compositions as tracers. Previous lab intercomparisons on different extraction methods spiked various types of soils with water of known isotopic composition (spiking approach) to examine the method performance. We followed the rainfall isotopic composition over and through the soil profiles over a period of 3 months and could show that even for nonspiked soils, the four extraction methods exhibited significant differences among each other.

During our method evaluation, the in situ vapour ports showed the poorest results with isotope data having the widest spread over all hillslope positions and depths and differing significantly from the other applied methods. Even though, the in situ port method is considerably faster and nondestructive (once installed), its analytical performance was not convincing in our study. This method exhibited the largest standard deviation, which is most likely caused by a combination of effects induced by water content, porosity, and exchange with atmospheric water vapour. The soil substrate used in this study is known for having a large capillary fringe, and it is relatively porous (compare Delleur, 1998), which in itself, would demonstrate intermixing of waters and vapour sources depending on the hillslope position. Tested zones in our hillslope using this method present the possibility of intermixing of different water vapour sources due to the zone of influence dictated by this analytical technique. Others have successfully demonstrated that this technique works with an older version of a LGR and a Picarro laser spectroscope (e.g., Gaj et al., 2016). For our study, implementing in situ vapour ports utilizing an LGR U-WVIA in such shallow, porous material seemed to be problematic due to the analyzer’s zone of influence. As the laser spectroscope is pulling air from the vapour ports at approximately 86 ml/min, after 10 min, nearly a litter of vapour has been pulled from the respective zone, with a porosity of 0.43 cm²/cm³, this equates to a zone of approximately 1.3 L or a radius of influence of 13 cm. With a port spacing of 10 cm, the zones of influence overlap in our hillslope, most likely creating a vertically mixed isotope vapour signal. This might explain some of the large standard deviation discrepancies of this method for our hillslope application. We further hypothesize that the sampled soil water vapour may have interacted with atmospheric water vapour at the shallowest depth (top vapour port) causing the wider spread of the data, which can also be explained by the zone of influence. It is suggested that as an improvement to the method, in order to pull less vapour from the respective zone, and therewith reduce the zone of influence, to reroute the waste air dump of the LGR analyzer back down to the port to provide a recirculated vapour atmosphere at each zone. Other discrepancies may arise from condensation in the sampling lines, which is impossible to detect at depth, yet a critical piece of the analytical puzzle that may offer a change in how the vapour port system is installed and serviced prior to sampling. To overcome this issue, we suggest using an electronic valve at the port inlet to keep soil vapour from entering the sampling line before sampling. We preevacuated the sampled vapour port lines (3-5 pore volumes of sample vapour) prior to soil water vapour sampling to flush of any residual water and thus memory effects. However, the condensation problem seems to be quite common, not only for this method but also for similar soil water vapour sampling techniques, for example, the method described by Rothfuss, Vereecken, and Brüggemann (2013) and applied by Quade et al. (2018). The in
The suction cup method showed smallest standard deviations over the entire study period, but some suction cups showed malfunctions and eventual clogging by the porous media. Landon et al. (1999) compared stable isotopic composition of soil water collected from suction lysimeters, wick samplers, and cores in a sandy unsaturated hillslope position and stated that each sampling method collected different fractions of the total soil-water reservoir. They concluded that suction lysimeter samples contained a higher proportion of more mobile water (15–95%) than samples from cores (5–80%) at the same depth. Because isotope results obtained from suction cups in our study plotted closest to the LMWL and fell within the range of rainfall, surface runoff, and bottom outflow data, we conclude that they also sampled the more mobile soil water pool. The same was true for isotope data generated by centrifugation. The applied pressure for centrifugation was 30kPa, whereas 60kPa were applied to the suction cups for water extraction. Kelln et al. (2001) used water isotope data from a piezometer installed in a clay-rich till for an extraction method comparison. Their data suggested that each tested method (direct equilibration, centrifugation, mechanical squeezing, and azeotropic distillation) showed small differences in $\delta^{18}O$ in comparison to the piezometer water. They further concluded that each method collected different fractions of the clay-water reservoir. In their comparison, the direct evaporation method, which is comparable to our vapour equilibration method, produced the most accurate results. However, because our soil material only contained 3.2% clay, we assume that the fraction of potential interlayer water is rather small.

In our study, we did not find evidence for systematic differences obtained by the centrifugation and vapour equilibration method in terms of measuring water vapour, which would have indicated a separate ecohydrological pool as per McDonnell (2014). Our results even plotted on a 1:1 line for the centrifugation and vapour equilibration method, and for some of the extraction methods, we were able to identify significant linear correlations between rainfall and $\delta^{18}O$ values or $\delta^2H$ values. Similar results were found by Orlowski et al. (2016), who compared isotope results of two different soil types and three different water contents using the spiking approach. This suggests either that there was no isotopic segregation between soil water pools in our hillslope systems or that all methods except for the vapour ports technique gave values that were representative of the soil water as a whole. Similar conclusions were drawn by Oerter et al. (2017), who compared the water vapour probe method with a direct evaporation method and vacuum extraction at a series of four study sites in a managed desert agroecosystem in the eastern Great Basin of North America. The authors demonstrated close agreement between isotope values measured by all three methods suggesting that all techniques sampled the same soil water pool.

From our previous and current intercomparison work, we could prove the reliability of the centrifugation method over different soil types from the lab to the hillslope scale. However, the vapour equilibration method exhibited larger isotopic discrepancies during the intercomparison on spiked soils (Orlowski et al., 2016) than under outdoor conditions on the hillslope scale. Fractionation effects caused by interactions between soil water and surfaces of clay minerals (Gaj et al., 2017; Newberry et al., 2017; Oerter et al., 2014) could be excluded for our study, because clay contents were low in the sampled soils (Table 1).

We could further show that none of the extraction methods exhibited significant isotopic differences between the three sampling positions on the hillslopes (hillslope positions 1–3), indicating that the hillslopes’ water pool must have been isotopically well mixed. For most of the samplings, soils were even close to saturation and water content effects (as per Meißner et al., 2014; Orlowski et al., 2016) were of minor relevance for our study.

### 4.3 Take home messages and next steps

Our work demonstrated at the mini-hillslope scale that hydrological processes measured utilizing stable isotopes of water exhibited considerable discrepancies across extraction and collection methods. Nevertheless, centrifugation and direct vapour equilibration showed consistent results over our sampling period. Whereas, the largest standard deviations were observed for the in situ vapour port technique, which is most likely caused by water content effects, porosity, and exchange with atmospheric water vapour. Soil fractionation processes associated with extraction techniques appear to still be an issue for understanding why different results are obtained between methods.

McDonnell (2014) suggested discrete isotopic sampling along the soil moisture release curve to tackle this phenomenon. Some have started the evaluation of this phenomenon suggesting that soil water retention characteristics in the future may be a critical component influencing the soil water isotopic composition (Gaj & McDonnell, 2019), and others are attempting to model bulk water processes versus mobile water processes to further explain fractionation effects and delineate the water pools (Sprenger et al., 2018).

For many past studies, possible fractionation effects associated to the different extraction techniques remain unknown and details on the applied extraction methodological settings are often not indicated (Orlowski et al., 2018; Orlowski, Breuer, et al., 2018). Recent work by Millar, Pratt, Schneider, and McDonnell (2018) used the most common water extraction methods (centrifugation, microwave extraction, direct vapour equilibration, high-pressure mechanical squeezing, and two different CVD systems) for their intercomparison study on spring wheat (*Triticum aestivum* L.) and showed that all methods yielded markedly different isotopic compositions. The various methods also produced differing concentrations of coextracted organic compounds. This highlights that a crucial evaluation of applied extraction techniques is not only important for soil water isotope applications but also plays a major role when water isotopes are used in the ecohydrological context or applied to different compartments of the hydrological cycle. Many current and past meta-analysis on the global
scale that couple ecolhydrological processes are comparing results obtained through a variety of extraction procedures (cryogenic extraction, vapour equilibration, and others), substrates (soil, plant, rock, etc.), and compartments (e.g. atmosphere, saturated, and unsaturated zone; Sprenger et al., 2019). As we gain further insights into extraction techniques and methodologies, it is difficult to discern whether or not we are truly comparing apples to apples.

5 | CONCLUSIONS

This work presents results from a 1.12-m² reconstructed mini-hillslope filled homogeneously with a loamy sand textured crushed basalt. We tested the null hypothesis that destructive and nondestructive pore water extraction methods installed in three hillslopes sample isotopically the same soil water pool (low tension and mobile water), which further generates runoff. We concluded that yet again, not all methodological techniques sample the same water pool or produce the same isotopic result. However, all method isotopic results fell within the range of precipitation and runoff. Like previous studies, we demonstrated that centrifugation and direct vapour equilibration produced comparable results and directly correlated with each other statistically. Over the course of our experiment, the 3-D hillslopes were exposed to both rainfall and evaporative processes and achieved varying points of soil water saturation. From a basic hydrology standpoint, hillslope wetness and antecedent saturation coincided with both baseflow and runoff isotopic phenomena observed by other, large-scale studies. From a method-based extraction standpoint, the pore water extraction approaches utilized in our study most likely sampled only the more mobile soil water pool.

We argue that stable isotopes of water should be used in conjunction with other tracers to overcome methodological issues and to gain a holistic view on the linkages between different compartments of the hydrological cycle.

New continuous, in situ measurements of soil and plant water isotopic composition might overcome isotope fractionation, and zone of influence issues we observed with the various soil water extraction techniques across different scales and compartments of the hydrological cycle.

ACKNOWLEDGMENTS

We thank Kim Janzen, Chris Dogniez, and Cody Millar for their laboratory support. Dominic Demand is thanked for fruitful discussions. This research was supported by an NSERC Discovery Grant and Accelerator Award to J. J. McDonnell.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Natalie Orlowski https://orcid.org/0000-0003-4368-4580
Dyan L. Pratt https://orcid.org/0000-0003-4706-3765

REFERENCES

Allison, G. B., Barnes, C. J., & Hughes, M. W. (1983). The distribution of deuterium and δ18O in dry soils 2. Experimental. Journal of Hydrology, 64(1), 377–397. https://doi.org/10.1016/0022-1694(83)90078-1
Aragüés-Araguás, L., Rozanski, K., Gonfiantini, R., & Lourvat, D. (1995). Isotope effects accompanying vacuum extraction of soil water for stable isotope analyses. Journal of Hydrology, 168(1–4), 159–171. https://doi.org/10.1016/0022-1694(94)02636-P
Bachmair, S., Weiler, M., & Troch, P. A. (2012). Intercomparing hillslope hydrological dynamics: Spatio-temporal variability and vegetation cover effects. Water Resources Research, 48(5). https://doi.org/10.1029/2011WR011196
Barnes, C. J., & Allison, G. B. (1988). Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen. Journal of Hydrology, 100(1–3), 143–176. https://doi.org/10.1016/0022-1694(88)90184-9
Brooks, J. R. (2015). Water, bound and mobile, Science, 349(6244), 138–139. https://doi.org/10.1126/science.aac4742
Brooks, J. R., Barnard, H. R., Coulombe, R., & McDonnell, J. J. (2010). Ecohydrologic separation of water between trees and streams in a Mediterranean climate. Nature Geoscience, 3(2), 100–104. https://doi.org/10.1038/ngeo722
Craig, H. (1961). Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science, 133(3467), 1833–1834. https://doi.org/10.1126/science.133.3467.1833
Delleur, J. W. (1998). Handbook of groundwater engineering. chp. 16 (pp. 15–16). Heidelberg, Germany: Springer Science & Business Media.
Di Bonito, M., Breward, N., Crout, N., Smith, B., & Young, S. (2008). Overview of selected soil pore water extraction methods for the determination of potentially toxic elements in contaminated soils: Operational and technical aspects. In B. de Vivo, H. E. Belkin, & A. Lima (Eds.), Environmental Geochemistry: site characterization, data analysis and case histories (pp. 213–249). London, UK: Elsevier. https://doi.org/10.1016/B978-0-444-53159-9.00010-3
Di Prima, S. (2015). Automated single ring infiltrometer with a low-cost microcontroller circuit. Computers and Electronics in Agriculture, 118, 390–395. https://doi.org/10.1016/j.compag.2015.09.022
Doorenbos, J., & Pruitt, W. O. (1977). In Land and Water Division (Ed.), Environmental engineering: site characterization, data analysis and case histories. pp. 213–249. London, UK: Elsevier. https://doi.org/10.1016/B978-0-444-53159-9.00010-3
Edmunds, W. M., & Bath, A. H. (1976). Centrifuge extraction and chemical analysis of interstitial waters. Environmental Science & Technology, 10(5), 467–472. https://doi.org/10.1021/es60116a002
Evaristo, J., McDonnell, J. J., Scholl, M. A., Bruijnzeel, L. A., & Chun, K. P. (2016). Insights into plant water uptake from xylem-water isotope measurements in two tropical catchments with contrasting moisture conditions. Hydrological Processes, 30(18), 3210–3227. https://doi.org/10.1002/hyp.10841
Fan, Y., Clark, M., Lawrence, D. M., Swenson, S., Band, L. E., Brantley, S. L., ... Yanazaki, D. (2019). Hillslope hydrology in global change research and Earth system modeling. Water Resources Research, 55, 1737–1772. https://doi.org/10.1029/2018WR023903
Figueroa-Johnson, M. A., Tindall, J. A., & Friedel, M. (2007). A comparison of δ18O composition of water extracted from suction lysimeters, centrifugation, and azeotropic distillation. Water, Air, and Soil Pollution, 184(1–4), 63–75. https://doi.org/10.1007/s11270-007-9399-8
Gaj, M., Beyer, M., Koeniger, P., Wanke, H., Hamutoko, J., & Himmelsbach, T. (2016). In situ unsaturated zone water stable isotope (δ2H and δ18O) measurements in semi-arid environments: A soil water balance.
Wassenaar, L. I., Hendry, M. J., Chostner, V. L., & Lis, G. P. (2008). High resolution pore water δ2H and δ18O measurements by H2O (liquid)–H2O (vapor) equilibration laser spectroscopy. Environmental Science & Technology, 42(24), 9262–9267. https://doi.org/10.1021/es802065s

Weihermüller, L., Kasteel, R., Vanderborght, J., Pütz, T., & Vereecken, H. (2005). Soil water extraction with a suction cup. Vadose Zone Journal, 4(4), 899. https://doi.org/10.2136/vzj2004.0156

Zhao, P., Tang, X., Zhao, P., Wang, C., & Tang, J. (2013). Identifying the water source for subsurface flow with deuterium and oxygen-18 isotopes of soil water collected from tension lysimeters and cores. Journal of Hydrology, 503, 1–10. https://doi.org/10.1016/j.jhydrol.2013.08.033

Zimmermann, U., Ehhalt, D., & Muennich, K. O. (1968). Soil-Water Movement and Evapotranspiration: Changes in the Isotopic Composition of the Water. In Isotopes in Hydrology (pp. 567–585). Vienna, Austria: International Atomic Energy Agency.

How to cite this article: Orlowski N, Pratt DL, McDonnell JJ. Intercomparison of soil pore water extraction methods for stable isotope analysis and interpretation of hillslope runoff sources. Hydrological Processes. 2019;33:2939–2954. https://doi.org/10.1002/hyp.13539