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ADVANCED REVIEW

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Toward a common methodological framework for the sampling, extraction, and isotopic analysis of water in the Critical Zone to study vegetation water use

Natalie Ceperley[1] | Teresa E. Gimeno[2] | Suzanne R. Jacobs[3] | Matthias Beyer[4] | Maren Dubbert[5] | Benjamin Fischer[6] | Josie Geris[7] | Ladislav Holko[8] | Angelika Kübert[9] | Samuel Le Gall[10] | Marco M. Lehmann[11] | Pilar Llorens[12] | Cody Millar[13] | Daniele Penna[14,15] | Iván Prieto[16] | Jesse Radolinski[17,18] | Francesca Scandellari[19] | Michael Stockinger[20] | Christine Stumpp[20] | Dörthe Tetzlaff[21,22] | Ilja van Meerveld[23] | Christiane Werner[24] | Oktay Yildiz[25] | Giulia Zuecco[26,27] | Adrià Barbeta[28] | Natalie Orlowski[29,30] | Youri Rothfuss[10]

Correspondence
Youri Rothfuss, Institute of Bio- and Geosciences - Agrosphere (IBG-3), Forschungszentrum Jülich, 50425 Jülich, Germany.
Email: y.rothfuss@fz-juelich.de

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Abstract

The analysis of the stable isotopic composition of hydrogen and oxygen in water samples from soils and plants can help to identify sources of vegetation water uptake. This approach requires that the heterogeneous nature of plant and soil matrices is carefully accounted for during experimental design, sample collection, water extraction and analyses. The comparability and shortcomings of the different methods for extracting water and analyzing isotopic composition have been discussed in specialized literature. Yet, despite insightful comparisons of extraction methods and benchmarking methodologies of laboratories worldwide, the community still lacks a roadmap to guide sample collection, extraction, and isotopic analyses, and many practical issues for potential users remain unresolved: for example, which (soil or plant) water

Abbreviations: CEC, cationic exchange capacity; CRDS, cavity ring down spectroscopy; CVD, cryogenic vacuum distillation; CZ, Critical zone; HPMS, high-pressure mechanical squeezing; IAEA, International atomic energy agency; IRIS, isotope-ratio infrared spectrometer; IRMS, isotope-ratio mass spectrometer; LMWL, local meteoric water line; OA-ICOS, Off-axis integrated cavity output spectroscopy; PCSs, passive capillary samplers; RWU, root water uptake; SPC, Scholander pressure chamber; SWC, soil water content; SWP, soil water potential; WATSON, WATer isotopeS in the critical zONe: from groundwater recharge to plant transpiration; $\delta^{18}O$, The $^{18}O/^{16}O$ abundance ratio in a sample relatively to that of V-SMOW (in ‰); $\delta^{2}H$, The $^{2}H/^{1}H$ abundance ratio in a sample relatively that of a standard (namely the Vienna Standard Mean Oceanic Water, V-SMOW) (expressed in ‰).

Natalie Ceperley, Teresa E. Gimeno, and Suzanne R. Jacobs shared first authorship.

Adrià Barbeta, Natalie Orlowski, and Youri Rothfuss shared last authorship.

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pool(s) does the extracted water represent? These constitute a hurdle for the implementation of the approach by newcomers. Here, we summarize discussions led in the framework of the COST Action WATSON ("WATer isotopeS in the critical zONe: from groundwater recharge to plant transpiration"—CA19120). We provide guidelines for (1) sampling soil and plant material for isotopic analysis, (2) methods for laboratory or in situ water extraction, and (3) measurements of isotopic composition. We highlight the importance of considering the process chain as a whole, from experimental design to isotopic analysis to minimize biased estimates of the relative contribution of different water sources to plant water uptake. We conclude by acknowledging some of the limitations of this methodology and advice on the collection of key environmental parameters prior to sample collection for isotopic analyses.

This article is categorized under:

Science of Water > Hydrological Processes

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isotopic analysis, sampling techniques, soil–plant interactions, water extraction techniques, water stable isotopes

1 | INTRODUCTION

The Critical Zone stretches from the top of the vegetation canopy to the active groundwater (Fan, 2015). This thin layer sustains all terrestrial life and understanding its functioning is essential to quantify and predict freshwater storage and dynamics (Brooks et al., 2015). The stable isotopes of hydrogen and oxygen are useful tracers for studying the spatio-temporal patterns of water movement and storage in the Critical Zone (Orlowski et al., 2023), as well as changes in vegetation water-use in response to climate, environmental and human-induced changes (e.g., Miguez-Macho & Fan, 2021; Penna et al., 2018; Querejeta et al., 2021; Sprenger et al., 2016; Tetzlaff et al., 2014). Here, we focus on the application of isotopic analyses to study changes in water storage and fluxes in the Critical Zone linked to vegetation water use, in all types of land covers, from agricultural fields to forests, and climates, from semi-arid to humid.

The primary source for plant water uptake is the soil (Rothfuss & Javaux, 2017), although plants can also take up precipitation, dew or fog water directly via foliar uptake (Goldsmith et al., 2017); or bedrock water through their roots (Hahm et al., 2020). The analysis of the abundance of the stable isotopes of hydrogen and oxygen ($\delta^{18}O$ and $\delta^{2}H$) from plant water and its sources can be used to estimate the relative contributions of the different sources to plant uptake. Examples of studies applying this approach have addressed to which extent plant water reflected precipitation (Allen et al., 2019), groundwater (Barbeta & Peñuelas, 2017), stream water (Dawson & Ehleringer, 1991), or tightly bound mineral water (Palacio et al., 2014).

This approach assumes that plant water uptake occurs through the roots and is a non-fractionating process, even though this may not be the case for plants in salty or extremely dry habitats (Ellsworth & Williams, 2007). Limitations to this approach arise from (i) the temporal and spatial variability of the exchange between and within plant and soil water pools (Dubbert et al., 2023), and (ii) the heterogeneity in water availability in plant tissues and soil matrices (Duvert et al., 2022). This complexity leads to uncertainties in the calculation of the relative water uptake contributions (Beyer & Penna, 2021) and has stimulated the development of different methodologies to extract water from plant tissues and soils, and the monitoring of the isotopic composition of such water pools. Nonetheless, despite their wide applications, these methodologies are still subject to debate (Chen et al., 2020; Millar et al., 2022; Orlowski, Breuer, et al., 2016; Zuecco et al., 2022).

Here, we summarize discussions held in the framework of the COST Action WATSON ("WATer isotopeS in the critical zONe: from groundwater recharge to plant transpiration"—CA19120), that resulted in the following guidelines for

(1) sampling plant and soil material in the laboratory, greenhouse, or field; (2) the extraction of water (and other co-extracted substances) from plant tissues and soils in the laboratory and in situ; and (3) the isotopic analysis of water in the laboratory. Such guidelines are, to our knowledge, not compiled elsewhere and complement the protocol for sampling meteoric waters for the specific purpose of isotopic analysis (International Atomic Energy Agency [IAEA], 2007). Here, we do not review the mechanics and underlying theory of how to incorporate water isotopic compositions into multisource mixing models to predict the relative contribution of each source to plant water uptake; for further details on this topic the reader is referred to Rothfuss and Javaux (2017). Our goal is that these guidelines will encourage and facilitate researchers to adopt this methodology to study plant–water relations.

We have organized our guidelines in three sections according to the following steps of the integrated eco-hydrological process chain, namely:

1. "Soil and plant sampling," where we describe the best practices for the sampling of plant and soil material to ensure preservation of the original water $\delta^{18}O$ and $\delta^{2}H$, that is, practical guidance for minimizing sample evaporation and potential for fractionation.
2. "Water extraction techniques," where we present the different extraction methods, their advantages and disadvantages, and the type of plant and soil material from which water can be retrieved.
3. "Isotopic analyses," where we describe the measurement process and provide recommendations for standardization.

2 | SOIL AND PLANT SAMPLING

Most studies that use the stable isotope technique to infer the sources of plant water uptake rely on the extraction of water from soil and plant samples, such as soil cores, small wood cores, stems, branches, leaves, root collars or others. This section focuses on the destructive sampling protocols to collect such samples. More specifically, we provide an overview of the collection of ancillary data and other measurements of plant physiological performance related to plant water uptake (Section 2.1) and of important aspects that need to be taken into account during sampling (Section 2.2). Nondestructive sampling techniques that allow for direct in situ collection of liquid soil water are reviewed in Section 3.2. Recent advancements in laser-based spectroscopy have allowed for the development of continuous in situ measurements of the isotopic composition of plant- and soil-water vapor (e.g., Kübert et al., 2020; Kühnhammer et al., 2022; Landgraf et al., 2022; Marshall et al., 2020; Rothfuss et al., 2013; Volkmann & Weiler, 2014; Werner et al., 2021). These techniques require the deployment of an isotope-ratio infrared spectrometer (IRIS) and access to power in the field, rarely available. These methods are not reviewed here, and the reader is kindly referred to Beyer et al. (2020) for further details.

2.1 | Ancillary data

A series of recent meta-analyses on the water isotopic composition across different compartments of the Critical Zone have highlighted the importance of reporting ancillary data consistently (Amin et al., 2020; de la Casa et al., 2022; Evaristo & McDonnell, 2017; Miguez-Macho & Fan, 2021). These studies show how geophysical and biological characteristics, such as geographic location, climate, topology, geology, vegetation, or soil type determine the isotopic composition of plant and soil water and also influence the choice of sampling, extraction, and measurement methodology. Therefore, reporting this information is crucial to compare results across studies to infer global patterns of vegetation water use. Here, we describe the ancillary data that should accompany the description of a study site, together with additional variables that are helpful for interpreting plant water uptake inferred from the isotopic analyses or for eco-hydrological model parametrization (Smith et al., 2022) (Table 1).

2.1.1 | Soil data

Soil volumetric water content (SWC) and soil matric potential (SWP) of the different layers define the moisture state and the water available for plant water uptake. Soil layers where SWC is very low—or SWP is close to or below the so-called permanent wilting point (Savage et al., 1996) are unlikely to contribute to soil water uptake. Thus, continuous

TABLE 1 Summary of necessary and recommended ancillary data for isotopic studies on plant water uptake.

Data type	Necessary	Recommended
Location and timing	Latitude, longitude, elevation, climate type, sampling dates, irrigation regime (if applicable)	Topology (slope and aspect), land use, and management history, size of the study area
Soil	Soil water content, soil depth, soil texture (mineral fraction), total carbon content and/or soil organic matter (SOM) content	pH, soil type, cation exchange capacity (CEC), soil matric potential, soil temperature, soil agricultural management (if applicable)
Vegetation	Species (including variety and/or rootstock for agricultural studies), phenology and/or length of the growing season, leaf/stem water content	Rooting depth, leaf/stem water potential, transpiration, vegetation structure (height, basal area), radial growth rate, tree water deficit (TWD), wood parenchyma fraction, leaf area index (LAI)
Atmospheric and meteorologic	Isotopic composition of precipitation, irrigation water, throughfall and stemflow (when applicable) (local meteoric water line, LMWL); annual or growth season mean of precipitation and air temperature	Water table depth and isotopic composition of groundwater (if accessible by the vegetation), air relative humidity, solar radiation, cloudiness, snow depth (if applicable), seasonal and/or monthly precipitation and air temperature

monitoring of SWC and SWP along the depth profile is very useful for defining the soil sampling strategy. When continuous SWC and/or SWP data (via monitoring with sensors) are not available, SWC can be calculated from the difference between the measured fresh (M_f) and dry (M_d) sample weights and soil bulk density (BD, i.e., the soil dry mass per unit of soil volume) according to: $SWC = BD * (M_f - M_d)/M_d$. This can be done on independent samples (not meant for isotopic analysis) or on the actual samples collected for isotopic analyses if the water is extracted using cryogenic vacuum distillation (CVD) (see Section 3). Alternatively, discrete measurements of shallow SWC can be taken using hand-held sensors (such as Time Domain Reflectometers) during field sampling campaigns (e.g., Matesanz et al., 2009). In greenhouse studies, SWC can be calculated by regularly measuring pot weight and the amount of water added. SWC can be converted into SWP based on the retention curve for the soil of the investigated site (Richards, 1931). Soil water retention curves can also be determined from the soil texture (sand, silt, and clay fractions), and organic fraction (or total carbon content) using pedotransfer functions (van Looy et al., 2017). Other soil properties such as soil organic or total carbon content, cationic exchange capacity (CEC) and pH are important for the identification of potential methodological artifacts (especially during water extraction, see Section 3). These variables (but not SWC and SWP) are relatively constant over time, so they do not need to be measured repeatedly (Table 1). Among all these properties, we recommend measuring and reporting at least: SWC, soil texture (expressed as fractions, not as soil types) and organic or total carbon content (de la Casa et al., 2022). These are the variables with the largest potential effects (Orlowski, Breuer, et al., 2016) and the most useful for informing studies modeling root water uptake from isotopic data, for example (Couvreur et al., 2020).

2.1.2 | Vegetation data

The depth of soil water uptake depends on the species (Fernández et al., 2008; Kulmatiski et al., 2010). Thus, species composition, of both targeted and surrounding species, must always be reported, and for agricultural studies also the variety and rootstock. Other useful observations and measurements are rooting depth, vegetation structure and growth (plant cover, leaf area index, plant height, basal area, dendrometric measurements), and plant physiological status (leaf and stem water content or water potential, transpiration rate). Estimation of maximum rooting depth is particularly useful, and this is most often done via manual excavation and visual inspection. The determination of rooting depth is challenging in sites where the roots of the vegetation (trees and shrubs mainly) extend beyond 10 or 20 m deep (Canadell et al., 1996). However, this should not discourage the application of water isotopic analyses to study vegetation water use in sites where rooting depth is unknown and deeply rooted species dominate (e.g., Matheny et al., 2017; Miguez-Macho & Fan, 2021). Furthermore, one must be aware that root presence does not necessarily imply active root water uptake (S. F. Wang et al., 2023), but soil layers without roots can be ruled out as potential sources. Leaf and stem water potential, measured commonly with the Scholander pressure chamber, (see Rodriguez-Dominguez et al., 2022 for a detailed experimental review of the methodology, and see also Section 3) provide information on plant water status

and signal stress occurrence (Barbeta et al., 2020; Hahm et al., 2020). For trees, plant water status can be inferred from tree water deficit monitored with continuous band or point dendrometers (Nehemy et al., 2021; Zweifel et al., 2016). Leaf and stem water content also respond to water stress, although less so (Merchant et al., 2007). The advantage is that water contents can easily be calculated from sample weights before and after CVD (Section 3). Transpiration measurements are particularly valuable as they allow the calculation of absolute water uptake rates from fractions (e.g., Deseano Diaz et al., 2023) and are useful to parametrize or calibrate ecohydrological models (Smith et al., 2022). Estimates of transpiration can be obtained from leaf gas exchange measurements (Querejeta et al., 2021) or sap flow measurements (e.g., Muñoz-Villers et al., 2018; Vandegehuchte & Steppe, 2013). Finally, it is useful to provide information on plant traits related to plant water use strategies, such as water-use efficiency, hydraulic conductivity, or specific leaf area (Illuminati et al., 2022; Rosas et al., 2019).

2.1.3 | Atmospheric and meteoric data

A site-specific local meteoric water line (LMWL) should be reported (Table 1). When the isotopic composition of precipitation cannot be obtained locally, data from a nearby site (although often limited to monthly time scale) or published datasets (e.g., IAEA's Global Network of Isotopes in Precipitation) can be used. For studies in agricultural or urban settings, the irrigation regime should be reported, and samples of irrigation water should be collected for isotopic analyses. It is also useful to provide information on the depth of groundwater and its isotopic composition because this can be an important source for plant water uptake (Barbeta & Peñuelas, 2017).

The site description should include typical meteorological data (e.g., air temperature, precipitation amount), which aligns with the sampling interval of plant and soil water sampling (Table 1). Other variables describing atmospheric conditions that are useful for the interpretation of isotope-derived plant water use strategies are air relative humidity and temperature (to calculate the vapor pressure deficit), incoming radiation, wind speed, potential evapotranspiration, cloud cover, and snow cover.

2.2 | Sampling strategy

We recommend that two overarching principles and a series of questions guide the sampling strategies:

i. *the sampling design* should capture the expected variability in water isotopic composition over space and time (Section 2.2.1);
ii. *sample collection* should consider the subsequent sample processing in the laboratory.

In the following subsection, "sample" applies exclusively to those collected for the analyses of δ^2H and $\delta^{18}O$ and "sampling strategy" refers, first, to the *sampling technique* (tools and material used for collection, volume sampled, etc.) and second, to the *design* (sampling duration and frequency, number of replicates, lateral and vertical resolution, extent, etc.). The *sampling technique* will be dictated by the nature of the sampled material and should take into account the methodology used for processing in the laboratory. Meanwhile, the *sampling design* will be driven by the objectives of the study and constrained by the time and financial resources available, site characteristics (e.g., accessibility, climate, and landscape characteristics), and local regulations.

2.2.1 | Sampling design

How often and when to sample?

The number of plant samples and soil profiles collected over the study period will depend on the study's objectives (e.g., discarding the use of stream water, Dawson & Ehleringer, 1991), on the phenology of the dominant vegetation type (e.g., evergreen Nehemy et al., 2022, versus deciduous species, Hahm et al., 2020 or dry-deciduous species, Muñoz-Villers et al., 2018) and on the variability in the vegetation, soil, and hydrological parameters of the system (e.g., groundwater uptake might vary seasonally across species, Cramer et al., 1999). For inferring patterns of vegetation water use, plants and soils need to be sampled concurrently. Collection of soil or plant samples during rainy days

should be avoided. The isotopic composition of shallow (0–30 cm) soil water is more likely to vary over time, as it is subject to evaporative enrichment and mixing during and after small precipitation events than deeper soil water (Barbeta et al., 2019; Xiang et al., 2021). Sampling every 2–4 weeks throughout the growing season (the period of the year when low temperatures, in temperate and boreal regions, and/or water availability, in arid or semi-arid regions, do not impose critical limitations to the physiological activity of the vegetation) should suffice to characterize the temporal variability in the soil and plant water isotopic composition (see, e.g., Yang et al., 2015, where increasing the sampling frequent did not reveal additional temporal variability). The sampling frequency should be adjusted to the local meteorological conditions. During rainy periods and around sporadic precipitation events, sampling should be performed before and as close as possible to each precipitation event, and every 4–7 days during the 2 weeks immediately after a precipitation event, when evaporative enrichment is likely to affect soil water. In contrast, in the middle of prolonged periods without precipitation, evaporative enrichment should not have a large impact (since the upper soil would be dry) and sampling frequency can be reduced to every 3–6 weeks (Barnes & Allison, 1983; Gómez-Navarro et al., 2019; Mahindawansha et al., 2018). In addition, factors such as the frequency, intensity, and type of precipitation (snow vs. rain), the rate of infiltration and percolation, and plant water transit time or sapflow velocity might also be needed to be considered (Nehemy et al., 2022).

The time of the day is not critical for sampling soils for isotopic analyses. This is because soil water isotopic composition depends on incoming precipitation and evaporative enrichment that usually change soil water isotopic composition over several days (Kübert et al., 2020). In contrast, the isotopic composition of plant water pools could vary over a single day (De Deurwaerder et al., 2020; Martín-Gómez et al., 2017). For studies where the goal is to characterize vegetation water use over seasonal scales and beyond (i.e., over weeks, months, or years), we recommend sampling plants between mid-morning (2–3 h after sunrise) and solar midday. During that period, plants have been actively transpiring for a few hours, but leaf and stem water potentials have not reached their minimum and thus remobilization of stored water is less likely, particularly in large trees (Treydte et al., 2021). Ideally, prior knowledge about water transit times (that is of sapflow velocity) and when transpiration flux peaks would help identify optimal time of the day for sampling (Muñoz-Villers et al., 2018).

How to determine the spatial extent and resolution at a sampling site?

The depth of the sampling profile should comprise all soil layers from the surface until the maximum rooting depth, hence all potential sources for relative root water uptake (RWU) (Liebhard et al., 2022), although determining maximum rooting depth is challenging, and nearly impossible in practice for deep-rooted trees species (e.g., Fan et al., 2017). However, indirect proxies of maximum rooting depth can be obtained from the literature, at least for general plant functional types or global regions (Cabon et al., 2018; Stocker et al., 2023). The resolution for vertical sampling should be higher (every 5 or 10 cm) in the upper soil (0–30 cm below the soil surface, de la Casa et al., 2022), where the isotopic composition of soil water is most variable, than in deeper soil layers (every 10 or 20 cm below 30 cm depth). Additional samples might need to be collected from other intermediate depths when changes in soil texture are detected. Albeit at a lower resolution, samples from deeper soil layers should be collected, because they often contribute to RWU (e.g., Muñoz-Villers et al., 2018). Besides, waters from different precipitation events generally mix in the deep soil (although see Sprenger et al., 2019), thus characterizing deep soil isotopic composition is relevant for regions where the isotopic composition of precipitation varies seasonally. Sampling of deep soil water is also important at sites where capillary rise of groundwater can occur (Dawson, 1993). Where the first analyses of the isotopic composition of deep soil water reveal a low intra-horizon variability, the vertical sampling frequency can be reduced in the following sampling campaigns.

The terrain, vegetation cover, and soil heterogeneity, as well as the spatial scale of the study, determine the lateral extent of the sampling, that is, the number of vertical profiles to be collected. One vertical profile may perhaps suffice in a flat grassland with a homogeneous soil and vegetation cover, but to characterize a steep, heterogeneous forest, multiple profiles should be collected from several locations. In many studies, samples are taken from at least 3–5 locations (e.g., under and in between trees, in uphill and downhill locations, or in wet and dry areas in the riparian zone; e.g., Diongue et al., 2023). In heterogeneous landscapes, the variability among soil profiles will be driven by factors such as the preferential entry of isotopically enriched stemflow around superficial roots, tree cover, aspect, microtopography, distance to a stream or a road (e.g., Goldsmith et al., 2018; Moreno-Gutiérrez et al., 2012; Palacio et al., 2017; Pinos et al., 2022; Querejeta et al., 2021). At the beginning of the campaign, it is recommended to collect several (i.e., at least 2–3) replicate samples for each soil profile to characterize the lateral variability in the isotopic composition of the water within each soil layer. For heterogeneous landscapes, the sampling effort could be optimized by having more profiles in

the upper soil than the deeper soil. However, very few studies so far have investigated the number of samples that are needed to characterize the horizontal heterogeneity of soil water isotopic composition (Penna & van Meerveld, 2019).

For vegetation samples, the choice of sampled individuals must be based on the research question and the variability in vegetation at the study site. For example, to characterize the seasonal RWU in an even-aged monospecific forest stand, grassland, or crop, it may suffice to sample five evenly spaced individuals per campaign. Where multiple species/varieties and/or age cohorts coexist, several individuals (3–5) of each group should be sampled. In addition, in heterogeneous landscapes, additional groups of individuals should be sampled if this heterogeneity affects soil water status and isotopic composition (e.g., distance to stream, aspect, or contrasting topography; Goldsmith et al., 2018).

2.2.2 | Sampling techniques

Soil sampling

The hand auger is the most used tool to collect soil samples from a profile. Auger types vary in diameter (typically 25–75 mm) and in whether they include a closed or open bucket system. Both manual and powered augers can be used, depending on soil hardness. However, exposure of the obtained soil samples to the air should be minimized to avoid evaporation, and therefore artificial isotopic enrichment of the soil water. The disturbance to the soil structure is greater when holes or small trenches are dug to obtain soil samples. However, this methodology enables additional measurements, for example, the estimation of rooting depth or installation of sensors to monitor SWC, SWP or soil temperature.

To minimize the number of sample handling steps, and thereby reduce the possibility for isotopic enrichment, the container that is used to store the sample will be, ideally, the same one as the one that will be used during water extraction or measurement (see Section 3) (Millar et al., 2022). For example:

- when using the water-vapor equilibrium technique, the soil should be collected directly into a sealable, inflatable, and evaporation-tight bag (L. I. Wassenaar et al., 2008) (see Section 3.1.2). These bags should be made out of metal-lined plastic (not plastic alone, Millar et al., 2022);
- for the centrifugation method, soil can directly be put in air-tight sealed centrifuge tubes (Adams et al., 2020, see Section 3.1.5);
- for CVD, soil should be collected in the vials that fit into the sample holder that is attached to the vacuum line. It is crucial to select the appropriate vial size as sample holder sizes vary depending on the configuration of the extraction line (e.g., 12 mL exetainer or 50- to 100-mL glass vials, Koeniger et al., 2011, see Section 3.1.1). Vials should never be overfilled to avoid the risk of sample explosion during extraction. In other words, always leave a small headspace in the vial (10%–20% of the vial volume), particularly when sampling very wet soils.

The volume of the soil sample collected at each depth needs to be sufficient to yield an amount of water that can be efficiently extracted and analyzed (or directly measured) in subsequent steps (1–2 mL, Diao et al., 2022). The amount of water will depend on the SWC, so in very dry soils, it may be necessary to sample larger soil volumes. Furthermore, some samples may require reanalyses or additional analyses, for example, to test for the presence of organic compounds, which requires a larger volume. We recommend collecting measurements of SWC prior to sampling to calculate the soil volume necessary to extract an amount of water sufficient for the targeted analyses.

Plant sampling

Here, we assume that the purpose of sampling plant tissues is to determine the isotopic composition of the plant water that reflects the sources of root water uptake (Ehleringer & Dawson, 1992; Rothfuss & Javaux, 2017). Water absorbed through the root cells is transported to the xylem, the conductive plant tissue that transports water and minerals (i.e., sap) from the sites of uptake, the roots, to the sites of evaporation, the leaves. Thus, the goal is to sample tissues, from which we can extract unenriched xylem sap water. Xylem sap water is typically obtained from stems, twigs, or roots that in principle are not subject to evaporative enrichment (although see Martín-Gómez et al., 2017).

The specific plant sampling considerations will depend on the anatomical differences between woody species (trees, shrubs, and other plant functional types with suberized stems) and nonwoody species (grasses, herbs, or nonvascular plants). The amount of plant material sampled needs to be sufficient to extract at least 1–2 mL of water. This becomes especially relevant when CVD is used to extract the water, as samples that yield <0.6 mL can be subject to methodological artifacts (Diao et al., 2022). Again, additional water volumes could be required for reanalyses or for additional

analyses, for example, to test for the presence of organic compounds (Martín-Gómez et al., 2015). Assessing the relative water content of plant samples is a useful practice to ensure adequate volumes of water are available for extraction, but the amount of water extracted will vary with plant water status (Merchant et al., 2007).

Woody species: Xylem sap in woody plant species is enclosed within suberized and/or lignified tissues that physically separate sap from the air and thus prevent evaporative enrichment. Dawson and Ehleringer (1993) established the sampling protocol that is still most widely used. This protocol prescribes that (i) sampled stem segments should be at least 10–15 leaf nodes away from the stem's tip to avoid back-diffusion of enriched leaf water into xylem water, and (ii) phloem and bark should be removed before placing samples into the containers to avoid the inclusion of potentially enriched water. Bark and phloem are also more likely to contain organic compounds that could be co-distilled during the extraction process and result in spectral interference (see Section 4.2.2). Alternatively, for trees and shrubs, one can collect stem wood cores or woody tissues from roots where water is less likely to have undergone evaporative enrichment (Barbeta et al., 2020). However, in tree trunks or in large branches and roots, and especially for ring-porous tree species (Delzon et al., 2004; Poyatos et al., 2007), water transport may occur only in the first millimeters below the bark, thus the central part of the trunk should be avoided. Also, water from individual roots may represent only the water that was accessed by those roots. Hence, when possible, roots from different parts of the plant should be collected. This is particularly important when sampling plants in desert or semi-arid environments, where plants can exhibit hydraulic segmentation (Schenk et al., 2008) and certain branches can be preferentially linked to roots located at specific soil depths (Espino & Schenk, 2009). Further caution is required when sampling small individuals or endangered or protected species, for which sampling roots or stems can damage individuals irreversibly.

Nonwoody species: Nonwoody plants lack protective tissues that isolate xylem water from evaporative enrichment. Therefore, sampling requires either locating nontranspiring tissues or avoiding evaporation prior to sampling. Nonwoody species can be classified into two major groups that differ anatomically: monocotyledonous or monocots (grasses) and dicotyledonous or dicots (forbs, herbs, legumes, and others). For both monocots and dicots, underground tissues, such as root collars, underground runner stems (stolons), tubers, rhizomes, or bulbs that have not undergone evaporative enrichment, should be sampled, when possible. However, some of these (e.g., bulbs, tubers, or rhizomes) serve as storage organs, and thus their isotopic composition can be a mixture of sources that can vary over time. For vegetative (nonreproductive) monocot grasses, the base of the tiller (pseudostem) of the plant should be sampled (see Figure 1 in Liu et al., 2017) and excised from its protecting leaf sheath (Barnard et al., 2006; Hirl et al., 2019). Note that, depending on the vegetative stage, the tiller consists of one or several "stems," which are formed by the addition of nodes (branching points with leaves) and unelongated internodes. In dicot herbs, it is more difficult to access unenriched tissue water since the stem cannot be separated from its leaf sheath. In this latter case, two methodologies are possible and should be tested, preferably simultaneously: (i) sampling of photosynthetically active (i.e., green) material from a stem section (internode) or petiole near the root crown; and (ii) covering a stem section (or petiole) using Parafilm® and aluminum foil to prevent evaporation and sampling that section at pre-dawn a day later (Hirl et al., 2019). Either way, sampling non-woody plants for isotope analysis usually involves destructive harvesting of the individuals.

Leaves: Leaf water is exposed to evaporative enrichment, with the degree of enrichment depending on the leaf's microclimate. This results in a higher spatial and temporal variability, both between and within individuals, compared to xylem water (Goldsmith et al., 2018). More importantly, in the leaf, several pools of water co-exist with mesophyll and vein (xylem) water. Leaf mesophyll water is in contact with the sites of evaporation and therefore its isotopic composition is more strongly affected by kinetic fractionation than leaf vein water (Cernusak et al., 2016). Furthermore, enriched mesophyll water mixes via back diffusion with vein water; therefore, it is not easy to infer source water from bulk leaf water. However, it has been recently proposed that by using the known effect of isotopic enrichment due to evaporation (Craig & Gordon, 1965), plant source water can also be inferred from leaf water (Benettin et al., 2021). This indirect method requires additional input variables (see Benettin et al., 2021, for further details) and parameterization of the processes driving isotopic enrichment within the leaf water pools (Bowen et al., 2018). Therefore, for inexperienced users, we recommend collecting unenriched plant tissues. Only when sampling of twigs, stems or roots is not possible, sampling leaves may be considered an alternative. The high concentration of organic compounds that can be co-distilled when extracting leaf water (see Section 4) means that the use of isotope ratio mass spectrometers (IRMS) instead of laser-based analyzers is recommended when analyzing leaf water for isotopic composition. However, organic compounds can skew measurements conducted with an IRMS as well if the concentrations of these compounds are high (Martín-Gómez et al., 2015).

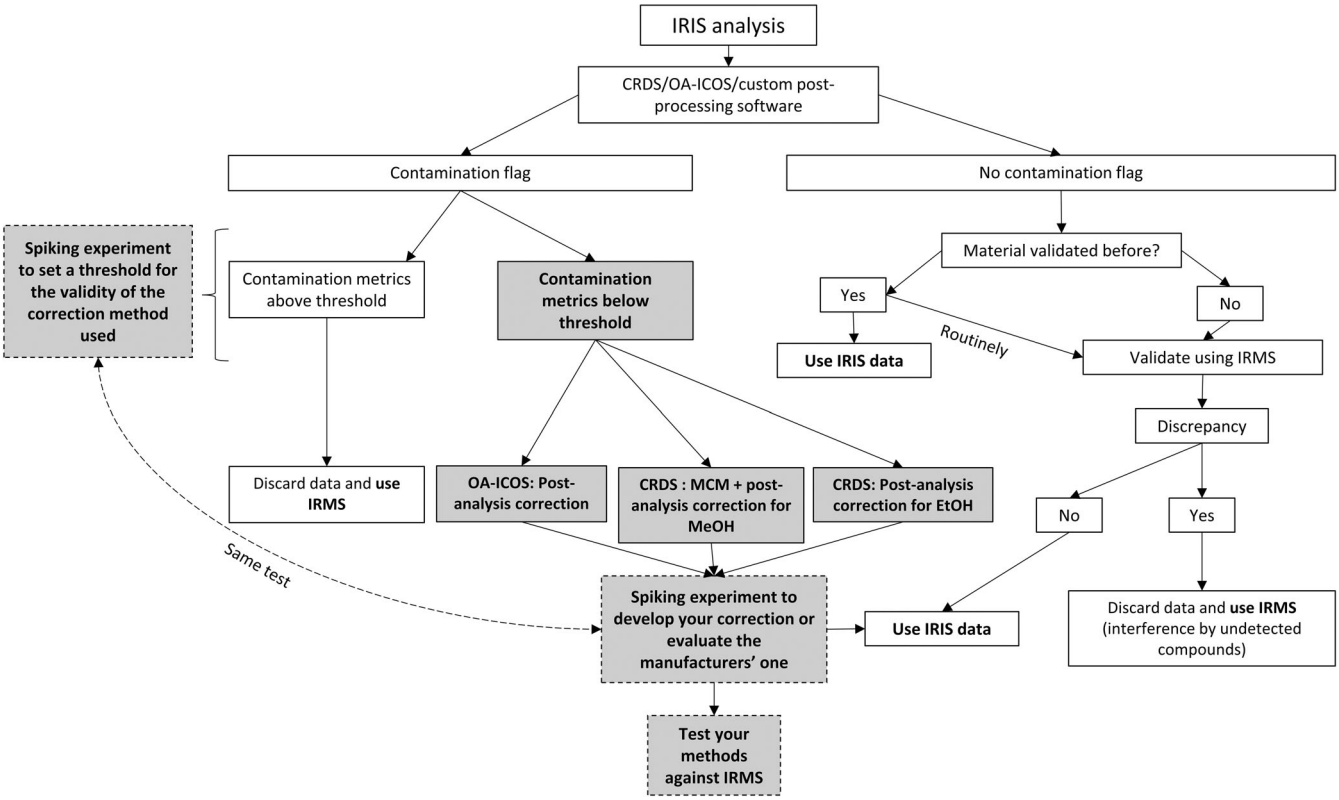

FIGURE 1 Decision-tree or flowchart (updated and based on West et al., 2011), showing the alternative pre- and post-processing steps to deal with spectral interference during isotope-ratio infrared spectrometer (IRIS)-based analysis of liquid water extracted from plant and soil samples. The steps not considered in the flow chart presented by West et al. (2011) are highlighted in bold with a gray background. Boxes depicted with dashed lines indicate steps that require additional experiments beyond the IRIS analyses.

2.2.3 | Storage and transport

On-site (short-term) storage, transport, and long-term storage of the soil and plant samples should be carefully organized to minimize artifacts due to evaporative enrichment (Fischer et al., 2019). The best materials for collection, storage and transport of samples are glass or HDPE plastic vials with polymer screw caps, compatible with the extraction methods of choice. To avoid evaporative enrichment, vial headspace should be minimized (i.e., the ratio of sample to headspace in the sampling vial or bag should be as big as possible), but some headspace is needed to avoid sample explosion during CVD (see Section 2.2.2). The use of an icebox or electric cooler—if power is available on site—is recommended for storage in the field and during transport. Once in the laboratory, traditionally, samples for isotopic analyses are stored at temperatures below zero to stop evaporative enrichment, evaporation and condensation within the sample vial, and biological processes (e.g., fermentation). However, freezing and thawing associated to sample handling can damage soil microstructures and cause plant cell wall bursting, enhancing issues with organic compound extraction (Fischer et al., 2019; Millar et al., 2018). Therefore, we recommend considering storage in a refrigerator at 4–6°C for samples processed within relatively short time-spans (2–8 weeks since their collection in the field). Storage in the refrigerator should be done when we aim to extract specific plant water pools and compare them isotopically (e.g., plant xylem vs phloem water, Nehemy et al., 2022) using adapted methods (e.g., Cavitron vs. Scholander pressure chamber, see Section 3), or when specific sample processing is required (e.g., separation of leaf veins, bark removal, preservation of soil microstructures). Importantly, in the refrigerator, evaporation and condensation can occur within the vial, hence for samples stored in the refrigerator aimed for CVD (see Section 3), the cap of the sample vial might need to be incorporated into the extraction vessel. In contrast, freezing might be more suitable for samples that are meant to be extracted with CVD and need to be stored for longer time periods or that are subject to transformations due to the activity of microorganisms (especially high in samples from warm and wet places). Finally, issues and artifacts associated to storing samples at temperatures below zero are less likely to impact results when water is extracted with CVD and the isotopic composition is measured with IRMS.

3 | WATER EXTRACTION TECHNIQUES

This section describes and evaluates the most common laboratory-based (Section 3.1) and in situ (Section 3.2) water extraction methods for soil and plant samples. Given the differences in the performance of the various extraction techniques (see Sections 3.3 and 3.4, and Table 2), the choice of extraction technique is ideally based on the suitability of that technique for a particular soil and/or plant sample and the type of extracted water (e.g., bulk vs. mobile soil water). In practice, many other factors need to be considered, such as the availability of resources (funding, time, and labor), the number of samples to be analyzed, and the type of equipment available in the laboratory. It is therefore not possible to provide straightforward recommendations for the selection of an extraction technique. CVD and high-pressure mechanical squeezing (HPMS) are, for example, quite cost- and labor-intensive, but may be slightly more suitable for soils with a low water content than the cheaper microwave extraction or the water vapor equilibration technique that generally require a larger sample volume or higher soil water content (SWC). Extraction artifacts exist for all methods, although artifacts have not been studied to the same extent for each of them. Accordingly, additional limitations not listed here could arise, including the co-extraction of organics that can cause spectral interferences (see Section 4). Awareness of the limitations and benefits of the different methods (see Table 2) can help inform the experimental design based on the available resources and equipment.

3.1 | Laboratory-based extraction methods

3.1.1 | Cryogenic vacuum distillation

CVD is the most widely used technique to obtain liquid water from plant and soil samples (Amin et al., 2020). CVD has been applied in many studies, compared across laboratories worldwide, and tested against other extraction methods (Millar et al., 2018, 2019; Orlowski et al., 2018; Orlowski, Pratt, et al., 2016). The protocol for CVD is described in detail in West et al. (2006) and Orlowski et al. (2013), but in short, the sample is placed in an extraction unit (e.g., Exetainer® vial, glass unit) and connected (usually via stainless steel capillaries) to a collection unit (usually a glass-collection tube), where the extracted water is collected. This closed system is evacuated at pressures ranging from 0.13 to 13 Pa to decrease the boiling point of water and to facilitate the sublimation of the bound water (Koeniger et al., 2011; Orlowski et al., 2013). The extraction unit is heated; with a water bath, sand bath, or controllable heating blocks; and the water vapor is collected in the collection unit, which is submerged in liquid nitrogen (cold trap). Since the extraction process follows a Rayleigh distillation process, extraction efficiency needs to be >98% to avoid isotopic fractionation (Araguás-Araguás et al., 1995). Optimally, three to five replicates per sample are extracted (Millar et al., 2018; Orlowski et al., 2013). However, this is challenging in plant types with a low water content, such as grasses. The completeness of the extraction for a particular sample is checked by comparing the sample weight after extraction and subsequent oven drying at 105°C for 24 h (Box 1).

There are multiple ways in which a CVD system can be set up (Amin et al., 2021; Koeniger et al., 2011; Orlowski et al., 2013; West et al., 2006). Furthermore, different studies have used different vacuum pressures, extraction temperatures, and extraction times (Orlowski et al., 2013). These differences can result in substantial differences and limit the reproducibility among laboratories (Orlowski et al., 2018). Reporting these parameters of the extraction setup is thus essential for the interpretation of the results.

Compared to other techniques CVD is generally labor- and cost-intensive (Kübert et al., 2020), sensitive to handling errors and, under certain circumstances, subject to co-extraction of organic contaminants. Research over the past decade has revealed that extraction artifacts can create substantial bias in the obtained isotope values, for both plant and soil samples (Gaj et al., 2017; Millar et al., 2018; Orlowski, Breuer, et al., 2016).

3.1.2 | Water-vapor equilibration technique

The water-vapor equilibration technique, first introduced by L. I. Wassenaar et al. (2008), combines a headspace equilibration method with IRIS. A plant or soil sample is placed in a sealable, inflatable, gas-tight bag (usually a double resealable zipper storage bag or laminated aluminum bag) to create a closed system. The choice of material and closure system are important, as certain bags are not evaporation-proof and allow evaporative enrichment during the

TABLE 2 Overview of characteristics of the most common water extraction techniques and appropriateness of the technique for soil and plant samples.

	Cryogenic vacuum distillation	Water-vapor equilibration technique	Microwave extraction	High-pressure mechanical squeezing	Centrifugation
Labor	●●●	●○○	●○○	●●●	●●○
Costs	●●●	●○○	●○○	●●●	●●○
Required equipment	●●●	●○○	●○○	●●●	●●○
Time per sample	●●○	●●● *Equilibration time can take up to several days, actual measurements are fast*	●●○	●●● *One sample at a time; time depends on initial water content of sample*	●●○
Sample volume and water content required	●○○	●●● *Water content >5%*	●●● *Water content >8%*	●○○	●●○ *Water content >8%*
Extraction artifacts	●●● *Sensitive to handling errors*	*Not known yet*	●●●	●○○	●●●
Co-extraction of organics*	●●●	●●●	●●●	●●●	●●●
Strength of soil water extraction	●●●	●●○	●○○	●●●	●●○
Suitability for soils	●●○ *Less suitable for clayey soils*	●●● *Problematic for soils with low water content; may not work as well for soils rich in silica, aluminum and other clay minerals*	●●○ *Problematic for soils with low water content; lower precision for silty sands and clayey loams*	●●●	●●○ *Distinct differences for clayey soils, but well-suited for silty sands and clayey loams*
Suitability for extraction of xylem water (low = only bulk water extracted)	●●●	●○○	●●○	●●●	●●○ *Depending on method, it allows separate extraction of xylem water*
Suitability for plants	●●○ *High levels of co-extracted organics*	●●○ *Affected by co-extracted organics, short storage times*	●●○ *Low precision (spring wheat)*	●○○ *High levels of co-extracted organics*	●●○ *Unsuitable for plant species with high levels of organics*

Note: ●○○ = low, ●●○ = medium, ●●● = high. The main challenges of the techniques are indicated in italics.

*Too few studies have quantified the risk of co-extracting organics to differentiate between the methods. Further research is required to understand what kind of organics are extracted from plant and soil samples using each extraction technique.

equilibration phase (Gralher et al., 2021; Hendry et al., 2015). The bag is inflated with dry synthetic air and left for a sufficient amount of time at laboratory temperature, usually 3–6 days for soils (Mattei et al., 2019; Orlowski et al., 2019; Orlowski, Pratt, et al., 2016; L. I. Wassenaar et al., 2008) and 24 h for plants (Millar et al., 2018; Santos Pires et al., 2022), to ensure that the liquid water in the sample and the vapor in the headspace are in equilibrium in terms of vapor concentration and isotopic composition. After equilibration, the bag is punctured with a needle (through a previously applied silicon septum) that connects the bag to an IRIS gas inlet port for direct vapor isotope analysis. The

BOX 1 Calculation of the extraction efficiency for cryogenic vacuum distillation

To check whether extraction was complete or whether it is likely that fractionation occurred during extraction, it is good practice to calculate the extraction efficiency. This is a multi-step approach, starting with weighing the sample and container directly after collection in the field (m_{field}). The sample and container are weighed again just before extraction (m_{pre}) to check if any water was lost between collection and extraction (m_{loss}):

$$m_{\text{loss}} = m_{\text{pre}} - m_{\text{field}}.$$

The extraction vial with the sample material ($m_{\text{extr-pre}}$, which is the same as m_{pre} if the same container is used for collection and extraction) and the (still empty) collection vial ($m_{\text{coll-pre}}$) are weighed before extraction (or collection) and following the extraction ($m_{\text{extr-post}}$ and $m_{\text{coll-post}}$) to calculate how much water was extracted from the sample (m_{extr}):

$$m_{\text{extr}} = m_{\text{extr-pre}} - m_{\text{extr-post}}.$$

and collected in the collection vial (m_{coll}):

$$m_{\text{coll}} = m_{\text{coll-pre}} - m_{\text{coll-post}}.$$

After the vial with the sample is dried in an oven at 105°C for at least 24 h and weighed again ($m_{\text{extr-dried}}$), the total amount of water that was originally in the sample (m_{total}) can be calculated:

$$m_{\text{total}} = m_{\text{extr-dried}} - m_{\text{field}}.$$

These weights allow us to calculate the extraction, collection, and total extraction efficiency:

$$\text{Eextr} = \frac{m_{\text{extr}}}{m_{\text{total}}} \times 100\%,$$

$$\text{Ecoll} = \frac{m_{\text{coll}}}{m_{\text{extr}}} \times 100\%,$$

$$\text{Etot} = \frac{m_{\text{coll}}}{m_{\text{total}}} \times 100\%.$$

A total extraction efficiency less than 98% indicates incomplete (i.e., failed) extraction and likely isotopic fractionation of the original sample.

isotopic composition of the pore water is calculated from that of the vapor measured with a laser spectrometer using a temperature-dependent equilibrium fractionation value. Importantly, these measurements need to be calibrated with isotopic measurements of water standards measured using the same protocol. Hendry et al. (2015) reported precisions for this method of ±2.1‰ for δ^2H and ±0.4‰ for δ^{18}O values using a Picarro L2120-i laser spectrometer. In contrast, Orlowski, Pratt, et al. (2016) reported lower accuracy for silty sand (SD of 0.9‰–3.6‰ for δ^2H and 0.5‰–0.7‰ for δ^{18}O) and clayey loam (SD of 1.5‰–6‰ for δ^2H and 0.4‰–1.4‰ for δ^{18}O), with varying SWC (8%, 20%, and 30%). Recent studies have investigated the use of different bag types (Gralher et al., 2021; Hendry et al., 2015; Mattei et al., 2019), the effects of equilibration times for different soil types (Vadibeler et al., 2022), the application to plant material (Millar et al., 2018, 2019; Santos Pires et al., 2022), and bias-corrections to account for biogenic gas accumulation or carrier gas changes (Gralher et al., 2016, 2018; Hendry et al., 2011). This method requires manual injections, but it allows for a good daily sample throughput because it takes only ~10 min per sample. The maximum sample storage

time varies between days and weeks (Gralher et al., 2021; Hendry et al., 2015), depending on the type of bag used and the type of sample material. The main strength of this technique, however, is that water is not physically extracted from a solid sample and instead is passively equilibrated with the surrounding headspace. Therefore, liquid water extraction-related fractionation processes are avoided. Fractionation during storage can potentially be corrected, provided that water loss and temperatures are recorded. However, this method requires a minimum volumetric soil moisture of 5% (L. I. Wassenaar et al., 2008) or a water volume of at least 2 mL in the bags (Gralher et al., 2021). The main weaknesses of the technique are (1) lack of a common standard operating procedure (e.g., regarding the required amount of soil/water/plant material, equilibration times, bag types, preparation of standards, Gralher et al., 2021; Vadibeler et al., 2022); and (2) spectral interferences caused by organic contaminants, similar to other extraction techniques (Gralher et al., 2016, 2018; Hendry et al., 2011; Millar et al., 2021). Furthermore, the method may not work as well for soils rich in silica, aluminum and other clay minerals, as Lin and Horita (2016) identified artifacts caused by non-equal equilibrium isotope fractionation for a silica adsorbed soil pore water–water vapor system, and a bulk liquid water–water vapor system.

3.1.3 | Microwave extraction

The protocol for extracting water using microwave ovens has been developed since 2000 (Flórez et al., 2015; Sparr Eskilsson & Björklund, 2000). Munksgaard et al. (2014) were the first to use the method for the analysis of soil, plant, and insect water isotopic composition in combination with IRIS. To extract the water vapor, plant (5 g) and soil (25 g) samples are placed in a sealed glass vessel in a modified domestic microwave oven (see e.g., Munksgaard et al., 2014). The water vapor is extracted into a dry air stream using microwave radiation. The evolving vapor passes through a cooled condensation chamber, which regulates the vapor concentration and flow to the IRIS instrument. A microwave power of 300 W is applied for 15 min (Millar et al., 2018; Munksgaard et al., 2014; Orlowski, Pratt, et al., 2016), which is equivalent to an extraction temperature of ~60–80°C (Millar et al., 2018). The $\delta^{18}O$ and $\delta^{2}H$ values for the extracted water vapor are obtained by integrating the isotopic values over the whole analytical cycle (Munksgaard et al., 2014). Drift corrections and calibrations are based on runs with in-house liquid water standards (Millar et al., 2018; Orlowski, Pratt, et al., 2016). Munksgaard et al. (2014) reported a precision of 2‰ or better for $\delta^{2}H$ and 0.3‰ for $\delta^{18}O$, for sandy soil. However, this precision could not be replicated by Orlowski, Pratt, et al. (2016) for silty sand and clayey loam, nor by Millar et al. (2018) for different parts of spring wheat plants. This variation in precision among studies and sample types highlights the need for users to determine the precision of the method for their own samples.

The advantages of the method are that it involves a relatively simple setup, is rapid (~20 min per sample), and relatively cheap. However, the method is problematic for soils with a low SWC (<8%), as extracted water shows enriched isotopic values. Also, for this method, the co-extraction of volatile organic compounds with the desired water can affect the isotope measurements (Brand et al., 2009; Leen et al., 2012; West et al., 2010).

3.1.4 | High-pressure mechanical squeezing

HPMS has been applied to soil samples and, to a lesser extent, to plant samples since the 1960s (Eichler, 1966; Kelln et al., 2001; Mazurek et al., 2015; Millar et al., 2018; Orlowski, Pratt, et al., 2016). HPMS uses physically constrained high-pressure to compress the sample, mechanically forcing the water out. Typical HPMS systems have the following components: a sample chamber, a baseplate with an outlet port connected to a collection receptacle, a filtration disk, a piston used in sample compression, and a hydraulic press (for schematic examples, see Böttcher, 1997; Mazurek et al. 2015). HPMS is thought to extract mobile and loosely bound water from soils and bulk water from plant samples (Millar et al., 2018; Sprenger et al., 2015). The extraction conditions, amount of sample required, and water recovery rates are dictated by the type of sample and its initial water content. Extraction conditions range between 10 and 70 MPa over 24 h for wet samples (clay, plant material at 15%–65% water content) with recovery rates of 8%–33% (Kelln et al., 2001; Mazurek et al., 2015; Millar et al., 2018).

HPMS is labor-intensive (one sample/per chamber/per extraction period), so it is not practical for large sample sets because it would require several individual HPMS systems (costly) or unacceptably long processing times (Kelln et al., 2001; Millar et al., 2018; Sprenger et al., 2015).

3.1.5 | Centrifugation

Centrifuge extractions of soils for water extraction date back to the 1960s (e.g., Davies & Davies, 1963; Zimmermann et al., 2013). The methodology was originally developed to obtain a solution for the analysis of the chemical composition of the soil water. Peters and Yakir (2008) were the first to use this technique to extract leaf water for isotopic analysis. The soil or plant material is placed within modified centrifuge tubes, with or without filter tips, and placed in a centrifuge (e.g., Adams et al., 2020; Bowers et al., 2020; Geris et al., 2015; Orlowski et al., 2019; Orlowski, Breuer, et al., 2016; Peters & Yakir, 2008; Sánchez-Murillo et al., 2023; Thibault & Sheppard, 1992). Different extraction times, temperatures, and centrifugal forces have been applied depending on the centrifuge type (e.g., rotor size) and soil/plant type (Table A1). The extracted water is usually ready for immediate isotopic analysis but can be filtered if required. The rotational velocity of the centrifuge (calculated from its radii and number of revolutions per minute) is physically related to the energy applied to the soil sample and consequently, the pore size drained (Edmunds & Bath, 1976). Thus, the relative centrifugal force can be converted to soil water matric potential based on soil physics (see Edmunds & Bath, 1976; Figueroa-Johnson et al., 2007).

Centrifuge extraction is moderately time-efficient. Depending on the rotor size, ~8–24 samples can be extracted per round with an extraction time ranging from 10 to 240 min, depending on the water content and sample type. However, similar to other lab-based extraction methods, centrifugation can co-extract organics (depending on the soil and plant sample), which makes the method less suitable for plants (Millar et al., 2018). Centrifugation may also detach small particulate matter from woody tissues and the water sample may therefore require secondary centrifugation or filtration (Millar et al., 2018).

Recently, a flow-rotor centrifuge has been used to extract the water in xylem conduits of woody stems (Barbeta et al., 2022). This "Cavitron-style" centrifugation technique uses a different type of centrifuge than the above-mentioned "standard" centrifugation technique and can only process one sample at a time (Barbeta et al., 2022; Duvert et al., 2022; He et al., 2023). It requires larger intact plant samples, such as (5–10 cm long) intact branches or bundles of grass stems. For the "standard" centrifugation extraction, small branches, leaves, or other herbaceous samples can be collected, and are typically cut into smaller pieces before extraction. An important consideration for the Cavitron extraction is that in-storage-vessel-mixing of the various isotopically unique plant water pools can occur if the samples are stored for extended periods. To avoid this, samples collected for Cavitron extraction should be rapidly transported to the lab and undergo extraction as soon as possible (i.e., on the same day or next day). Second, "Cavitron-style" centrifugation is based on the induction of cavitation in the conduit water column by increasing its matric potential through centrifugation. It allows for sequential extraction of different plant water pools by running the centrifuge multiple times at increasing speeds and collecting the extracts in between the runs. The isotopic composition of extracted water with this technique matched that of the irrigation water but not that of the bulk xylem water extracted via CVD, which had a lower δ^2H (Barbeta et al., 2022). Although further testing of this technique is required, so far, the absence of isotopic offsets between the source and plant stem water is promising. The Cavitron centrifuge efficiency can differ depending on sample water content and the associated xylem matric potential, but centrifugation times should not exceed 10 min to avoid excessive evaporation during spinning (Barbeta et al., 2022). This method also requires approximately 10 min to prepare the sample, including peeling the bark from the stem extremes, sealing the open cuts in the central part of the stem with glue and fitting two collectors at the two extremes of the stem using Parafilm®. The operational cost in terms of consumables should be decidedly lower compared to CVD. The main drawbacks of this methodology are that it is only suitable for relatively long stem or branch samples, that large branches also prevent the use of the common air-tight collection vials, and that it requires a Cavitron within the vicinity of the sample collection sites, which is rarely available.

3.1.6 | Pressure chamber

For woody species, plant water can also be extracted using a Scholander pressure chamber (SPC) (Scholander et al., 1964), an instrument initially developed to determine the water potential in plant tissues. A lignified twig is placed inside the chamber with the cut end exposed to the atmosphere. Then, the pressure inside the chamber is increased by injecting an inert gas (usually N_2) until water is forced out through the cut end, from where the water is collected into a vial using capillary tubes. This process that can take up to 10 min (Zuecco et al., 2022). Some researchers remove the bark and the phloem tissue during sample preparation (Geißler et al., 2019; Magh et al., 2020), while others sample intact twigs, even with leaves attached (Penna et al., 2013, 2021; Zuecco et al., 2022). The advantage of this method is

that the SPC is available in many laboratories around the world and that the SPC can be transported to remote field sites. However, only a limited amount of water can be recovered from stems, which restricts the application of SPC use under water-limiting conditions. Very few studies have compared the isotopic composition of water extracted by CVD and SPC, but those that have done so have found contrasting results. For instance, Geißler et al. (2019) observed no significant differences in the $\delta^{18}O$ for *Acacia mellifera* samples. On the contrary, Zuecco et al. (2022) found marked (and in most cases significant) differences for alder, apple, chestnut, and beech trees. Also Bowers and Williams (2022) found that SPC accessed a significantly distinct isotopic domain compared to CVD, whereby the difference in $\delta^{2}H$ between the two methods was significantly correlated to stem water content as well as the difference in $\delta^{18}O$. Based on these differences and given the smaller volumes of water extracted by SPC than by CVD, Zuecco et al. (2022) argued that the SPC method may extract only the more mobile plant water (i.e., xylem and inter-cellular water), whereas in CVD the bulk plant water is extracted (Millar et al., 2018). Future research based on the SPC method should clarify the exact water pool/s that are extracted, quantify organic contamination, and compare this extraction method with others (e.g., Cavitron-centrifugation, HPMS, water-vapor equilibration, etc.).

3.2 | In situ methods for collecting soil water

Lysimeters, porous cups or plates, and passive capillary samplers (PCSs) allow for the collection of soil water directly in the field. A comprehensive overview of the advantages and disadvantages of the different methods and techniques is presented in Weihermüller et al. (2007). Here we provide a brief description of the techniques and the main aspects to consider when deciding what to use.

Lysimeters are large vessels containing disturbed or undisturbed soil material, of various sizes (Pütz et al., 2018; Reth et al., 2021). Water is collected at the lower boundary of the lysimeter, which is either set to a certain matric potential or a seepage boundary that allows the collection of the outflow when the soil is saturated. Various studies have used lysimeters to investigate flow and transport processes (Asadollahi et al., 2020; Groh et al., 2018; Penna et al., 2021; Stumpp et al., 2012). The benefit of lysimeters is that they can provide additional information about the flow rate. However, depending on the design and size, they can be costly, installation can be labor-intensive, and some require high maintenance because controlling the conditions at the bottom boundary is challenging (Groh et al., 2016).

Suction cups/plates or other porous cups typically consist of a cylindrical, porous cup or plate (often made of ceramic material) sealed to a tube and a sampling bottle (Geris et al., 2017; Weihermüller et al., 2007). The cups can be inserted into the soil vertically, horizontally, or askew, and also function below the water table. When suction cups are installed vertically or askew, protection measures need to be taken to avoid percolation of water along the outer hull of the tube and suction cup, and thus mixing of precipitation with the sample of interest. In all cases, there is a need for a good hydraulic contact between the suction cup and the surrounding soil. To extract soil water, a vacuum pump is connected to the collection system and negative pressure is applied. Sampling can be done by: (1) continuously applying a variable or constant negative pressure over time (e.g., −50 to −1 kPa applied over 1 week, Thomas et al., 2013), or (2) applying stronger negative pressures over a short period (e.g., 10–30 min at −200 kPa, Geris et al., 2015, or 3 h at −60 kPa, Orlowski et al., 2018). The required pressure can also be dynamically controlled and related to data from a tensiometer that measures the actual soil water matric potential at the corresponding depth. There are various factors that determine the amount of extracted water. Longer suction times result in larger quantities of water being extracted, although this is limited by the overall SWC. The applied negative pressure impacts from which pores the water is extracted, with more negative pressures extracting more tightly bound water from smaller pores. Finally, the soil type, through its texture and hydraulic properties, affects how much water can be held in the soil and how tightly it is bound. When installed in soils with very fine textures, the fine soil particles can clog the porous cup that may need to be rewetted (with deionized water) to obtain a sample. Using too much negative pressure during sampling can result in air entry into the porous cup that breaks the water column and impedes water flow.

Suction cups are low cost and the requirement for maintenance is moderate depending on the technical complexity used and soil type. Different versions of suction cups are available on the market, which normally can extract water up to −200 kPa (Geris et al., 2015). This can be a real limitation for isotope-based ecohydrological studies that aim at identifying water sources for plant transpiration (Penna et al., 2018; Sprenger et al., 2018), as suction cups cannot collect water from even moderately dry soils (<200 kPa), and are far from reaching the lower limit of soil water availability (−1500 kPa or lower, depending on the plant species and soil type; Tolk & Evett, 2012).The deepest installation depth depends on the gravitational pressure differences that can be applied using a vacuum pump.

Passive capillary (wick) samplers (PCSs) are simple devices that behave like a hanging water column and are used for sampling soil water by gravitational potential. They were originally developed for the analysis of the hydrochemistry of soil water and contaminant analysis (Brandi-Dohrn et al., 1996; Brown et al., 1989; Maeda et al., 1999), but have been adopted for isotopic studies (Jacobs et al., 2018). A modified version is now also used for sampling snowmelt and does not show any evidence of isotopic fractionation during snowmelt sampling (Frisbee, Phillips, Campbell, & Hendrickx, 2010; Frisbee, Phillips, Campbell, Hendrickx, & Engle, 2010; Penna et al., 2014). PCSs are mostly custom-made and vary in design, but they are typically based on a wick made of an inert material, such as fiberglass or rock wool, connected to a collection bottle or chamber. One end of the wick is in contact with the undisturbed soil from which the water will be collected. This allows water to be drawn from the surrounding soil without the need to actively apply pressure (Frisbee, Phillips, Campbell, & Hendrickx, 2010). As with suction cups, one needs to ensure a good hydraulic connectivity between the soil and the wick.

PCSs have not been used as widely as suction cups, because PCSs can only collect water from larger pores with a much higher, near-saturation, matric potential compared to suction cups (0–6 kPa, see Holder et al., 1991). However, PCSs have several advantages: they do not require maintenance, nor the application of external pressure to extract the water (except for sample collection), and they always work, provided that there is mobile soil water and space in the collection bottle.

3.3 | Additional considerations

3.3.1 | Soil water extraction

The soil matrix is a complex medium in which water is held at different pressures (matric potentials), depending not only on water content but also on the pore sizes and physiochemical interactions at the solid–liquid interface. The different methods extract water from different fractions of the pore space, therefore, it is essential to know beforehand which pool(s) of soil water is(are) of interest. Depending on the soil water matric potential and pore size, the available extraction techniques access soil water held under an overlapping spectrum of matric potentials (Orlowski & Breuer, 2020; Sprenger et al., 2015). Lysimeters, and similar approaches, collect water that is held in the wetter range, with matric potential ranging from 0 to 102 kPa, depending on the boundary conditions applied (i.e., sampling free draining water versus applying a suction with a vacuum pump; Adams et al., 2020; Sprenger et al., 2015). Laboratory-based extraction methods (except for the water-vapor equilibration technique) sample all soil pore water with extraction strength decreasing from CVD to HPMS (Sprenger et al., 2015). The benefit of using HPMS is that it allows the application of increasing extraction pressures to obtain soil water held at different tensions. Furthermore, HPMS is thought to be one of the most accurate extraction approaches for soil pore water based on comparison of the isotopic composition of the extracted water with the known isotopic composition of the soil water (Orlowski, Pratt, et al., 2016). In contrast, particularly large discrepancies in isotopic composition were observed for clay-rich soils extracted using centrifugation (Figueroa-Johnson et al., 2007; Kelln et al., 2001) but centrifugation had the highest proficiency for a silty sand and a clay loam soil type (8%, 20%, and 30% SWC; Orlowski, Breuer, et al., 2016).

Other key aspects to consider when determining the choice of extraction technique are the soil physiochemical properties: pore size distribution, clay minerals, soil organic carbon content, organic matter content, SWC and potential interactions with cations in the soil solution. All of these could influence the isotopic composition of the extracted water, with the effects depending on the extraction method. Thus, it is critical to adapt the extraction conditions (e.g., temperature and duration, applied pressure, sample volume) to the extracted material (Araguás-Araguás et al., 1995; Gaj et al., 2017; Meißner et al., 2014; Orlowski et al., 2013; Orlowski, Pratt, et al., 2016). The effect of some of these aspects have been discussed for the different extraction methods (see Section 3.1 and Table 2). However, the effects of many of these aspects have not been investigated in detail yet, making it difficult to provide solid recommendations for the choice of extraction method and conditions.

3.3.2 | Plant water extraction

Water pools in plant tissues (xylem, phloem, intracellular water, or bulk plant or tissue water) vary in their isotopic composition (Barbeta et al., 2022; Treydte et al., 2021; A. Wang, Siegwolf, et al., 2021). The pool of interest determines

which tissue should be sampled (see Section 2.2.2) and which extraction method is more appropriate. For example, the CVD extraction of leaf water requires a different protocol due to its high spatial isotopic heterogeneity of the water present in the different leaf tissues (see Cernusak et al., 2016; chap. 5.13 in Halbritter et al., 2020). Furthermore, a recent study showed that the (hydrogen and/or oxygen) isotopic composition of bulk water extracted from woody samples via CVD, or other methods that extract bulk water, differs from that of the plant's source water, particularly for δ^2H (Chen et al., 2020). Whether this bias is big enough to invalidate inferences drawn from these data, depends on the context, for example, the magnitude of the bias relative to the signal one uses to draw inferences (Allen & Kirchner, 2022). Still, there is no consensus on how the different pools contribute to the overall isotopic composition of bulk water (Barbeta et al., 2022; Zhao et al., 2016). As mentioned previously, another key consideration is the co-extraction of volatile organic compounds, which may occur with all extraction methods (also in situ), although laboratory-based extraction methods (CVD, HPMS, and centrifugation) appear to be the most impacted (Millar et al., 2018). The water-vapor equilibration technique is also prone to organic contamination-induced errors due to the concentration of organic compounds in the vapor headspace (Millar et al., 2021; Nehemy et al., 2019).

4 | ISOTOPIC ANALYSIS

The determination of the abundance of the hydrogen and oxygen isotopes ($\delta^{18}O$ and δ^2H) in the water extracted from the plant and soil samples in the laboratory may seem like the most straightforward step of the process because there are established protocols, validated instruments, and tools. However, even at this step, the researcher is faced with a series of decisions that can impact the results. According to the most recent assessment of laboratory performance for liquid water stable isotopes (IAEA WICO2020), the analytical performance depends on a combination of data normalization procedures, including robust memory and drift corrections, working reference materials that are potentially compromised, underperforming instruments, and sample preparation templates (L. Wassenaar et al., 2021). These conclusions differ from the previous assessment (IAEA WICO2016), where most errors could be pinned to skill and shortcomings in knowledge (L. I. Wassenaar et al., 2018).

In this section, we describe common analytical procedures step-by-step (determined via an informal, geographically limited survey, see Ceperley & Barbeta, 2023). Because contamination by organic compounds in water samples from plants or organic-rich soils can hinder isotope determination with IRIS because of sensitivity to contaminants which interfere with the spectra (methanol, ethanol, methane), and even IRMS when using certain methods such as pyrolysis, which analyses any compound containing oxygen or hydrogen, or high-temperature conversion (Brand et al., 2009; Martín-Gómez et al., 2015; Schultz et al., 2011), we address risk and mitigation strategies that can be applied both before and after analysis.

4.1 | Run preparation and execution

4.1.1 | Instrument choice: IRMS or IRIS?

More than one approach exists to analyze plant and soil water. The first decision is between the two main technologies for isotope analysis of water samples from plants and soil: IRMS or IRIS, though can both be used in multiple ways. The emergence of IRIS-based isotopic analyzers has increased the number of studies that use isotope techniques to investigate vegetation water use (see de la Casa et al., 2022). For this reason, we discuss more in-depth the use and limitations of IRIS technologies in relation to plant and soil water analysis.

IRIS has become the most popular choice for analysis of water, whether directly or from plants and soil, since the early 2010s for several reasons. IRIS does not require prior chemical equilibration or conversion into elemental constituents, is cheaper (i.e., lower cost for purchase and consumables), and is easier to use (Martín-Gómez et al., 2015; West et al., 2010). Besides, IRMS instruments are more complex and require stable environmental conditions (which limit their use in the field, although it is not impossible, Schnyder et al., 2004), whereas IRIS is portable. Furthermore, IRIS-based instruments can be coupled to automatic samplers for liquid and gaseous water in different compartments of the Critical Zone (e.g., Herbstritt et al., 2012; Munksgaard et al., 2011).

4.1.2 | Target isotopes, run arrangement, and preparation in IRIS

Protocols for run preparation and execution are largely independent of the type of IRIS instrument used. In brief, IRIS analyzers are most often coupled to an autosampler that collects water sequentially from a set of samples. The septum of each vial (water sample) is pierced with a syringe, water is injected and then transferred to a vaporization module connected to the IRIS analyzer that determines the isotopic composition of the water vapor. To avoid memory effects between samples, it is advisable to inject a sample at least six times and to retain the measurements of the last three injections for the calculation of the isotopic composition of that sample (Penna et al., 2012). However, some researchers have suggested that memory effects can be overcome numerically, even for the first three samples (van Geldern & Barth, 2012).

The calculation of the isotopic ratios requires the use of a reference material to normalize data, and to ensure comparability over time and among laboratories (L. Wassenaar et al., 2021). Thus, it is necessary to analyze standards (often 3) of known isotopic composition alongside the samples. Ideally, the standards are distributed as a block throughout the run, and not only at the beginning or the end. The most relevant information regarding the chosen reference materials should be reported: name and provider, isotopic composition, and number of replicates. The isotopic composition of the reference materials should cover the expected range of values for the samples to be analyzed (Gröning, 2004), but the arrangement and number may vary (see sidebar 1). Similarly, a vial with deionized water should be analyzed every 4–10 samples as a quality control to identify potential instrument drift (van Geldern & Barth, 2012).

Manufacturers provide a factory setup for their instruments, but hardware changes or additional adjustments can be necessary. For example, van Geldern and Barth (2012) recommended to modify the hardware from the factory setup to increase the consistency and reliability of the results. Specifically, they recommended the use of different syringes, vials, and septa than those delivered with the instrument, and a specific washing and rinsing protocol.

Filtering of samples is recommended to eliminate particles in suspension that can clog the syringe that is used to inject the samples into the instrument. Besides particle contamination, ethanol and methanol are the primary known organic contaminants because they have a known spectral peak and are easy to experiment with, but many organic molecules (e.g., most C—O—H bonds) will have absorption at similar wavelengths and will influence IRIS analysis (Schultz et al., 2011). It has been suggested to treat the samples with active charcoal can help remove organic compounds, but the results of this procedure have not been fully satisfactory, and it may interfere with post-processing steps (Chang et al., 2016; Schultz et al., 2011; X. Wang, Jansen, et al., 2021; West et al., 2010). Solid-phase extraction with a commercial microcombustion module (which heats samples to ∼200°C to oxidize organic compounds, and is currently only available for Picarro, Inc. instruments, see Chang et al., 2016) can reduce methanol contamination, for example by oxidation. This system will, however, result in altered values in the case that the sample contains a high concentration of organics with oxygen and hydrogen, because they will be included in the resulting values even if they are not influencing the spectra, but it has been shown as an acceptable deviation in the case of samples containing low concentrations of methanol (Martín-Gómez et al., 2015).

4.2 | Post-run processing and analysis

4.2.1 | Normalization and correction of memory effects and drift

Post-run processing includes the normalization to the international isotope standards (Skrzypek, 2013), the check and correction of linearity (Barth et al., 2004), the sample-to-sample memory effect, and the drift (van Geldern & Barth, 2012). The memory effect is relevant for all instruments, except for a dual inlet IRMS, which has a dedicated turbomolecular pump for the changeover valve (Georgiou & Danezis, 2015). The US Geological Survey and the IAEA provide freely available software to post-process isotopic data from laser spectrometers (Coplen & Wassenaar, 2015). The Laboratory Information Management System for Lasers 2015 is a Microsoft Access relational-database application that imports data from instrument templates and executes all the necessary steps for the evaluation and correction of isotopic data.

4.2.2 | Spectral interference by organic compounds in IRIS

Organic compounds that are extracted together with water from soil and plant samples can interfere with the spectral signal absorption in laser-based instruments and result in erroneous isotopic data (West et al., 2006). For contaminated

samples, measurements of the isotopic composition differ between IRMS and IRIS, regardless of the type of IRIS (cavity ring down spectroscopy [CRDS], West et al., 2011 or OA-ICOS, Schultz et al., 2011). However, contamination does not affect all samples equally. For example, changes in the abundance or isotopic ratios can cause a variable contamination signal, creating the illusion or exaggeration of a nonexistent or minor water isotope signal. Zhao et al. (2011) found that among plant and soil samples, leaf samples were the most contaminated, followed by stem and root samples, and then xylem and soil samples. Species and plant functional types, as well as habitat and climate affect the likelihood of contamination (Millar et al., 2018).

Minimizing uncertainties derived from spectral interference caused by organic compounds is possible after implementing a lab-specific protocol. Still, such protocols should be validated from time to time against IRMS systems to ensure their long-standing validity as the variety of organic compounds in water is large. West et al. (2011) proposed a decision-making flow chart to deal with spectral interference during isotopic determination with IRIS. In the past decade, new correction tools have become available, and these have been evaluated by manufacturers and researchers. Here, we provide an updated version of this flow chart by including newly available tools and recent findings (Figure 1).

Currently, there are three solutions to deal with spectral interference caused by organic contamination: first (i), using only IRMS for soil- and plant-water extracts suspected of contamination or running a representative sample subset through both IRMS and IRIS. Second (ii), removing the organic compounds in the water before the analysis via filtration or combustion (see also above). Third, (iii) applying post-run corrections, either self-made or supplied by manufacturers. A common practice to handle spectral interference does not exist, which is why we recommend that each laboratory develops its protocol and protocols are compared.

Analysis with IRMS

Additional analysis with IRMS is not always feasible and the additional storage and transport of samples for reanalysis introduces additional uncertainties (Millar et al., 2022). Besides, IRMS is not a perfect solution for the analysis of highly contaminated samples (such as those from pine trees, desiccated plant samples, or organic rich soils). Specifically, in the case of Thermal Conversion–Elemental Analyzer–IRMS, organic compounds will be combusted and passed into the analysis chamber along with the hydrogen from the plant/soil water. In samples with low (trace) concentrations of organic compounds, the contributions of these organic hydrogen atoms can be considered negligible, but at high concentrations, they can become meaningful when the isotope ratio of the organic contaminant differs markedly from that of the water (Brand et al., 2009; West et al., 2010).

Removing the organic compounds in the water before the analysis

The microcombustion module of CRDS instruments can reduce the concentration of interfering compounds, but it does not always remove them completely (Martín-Gómez et al., 2015). Therefore, regardless of the instrument used and the filtering applied, it is necessary to flag the samples containing organic compounds, either by using the manufacturer's software (e.g., ChemCorrect™ by Picarro Inc.) or by applying custom-made protocols (Leen et al., 2012) according to clear thresholds. These thresholds for detection, even when built-in, can be defined or modified by the user and present an important opportunity for transparency and comparability across the field(s).

Post-run correction

Post-run processing corrections for the interference of organic compounds can have high accuracy for both CRDS (Coplen & Wassenaar, 2015; Martín-Gómez et al., 2015) and OA-ICOS (Leen et al., 2012; Schultz et al., 2011) but are not readily and transparently available from the manufacturers. Instead, these corrections need to be developed for each instrument independently based on empirical relationships between isotopic deviations and proxies of spectral interference. In the case of CRDS, Picarro Inc. provides the software ChemCorrect™ that flags the presence of organic compounds in the samples but the correction for organic compounds needs to be conducted manually by the user by accessing the CRDS software raw output (see the example calculation of calibrated organic compensated isotopic compositions in Hsiao, 2011). From the output of the OA-ICOS instruments, it is possible to compare the baseline offset of the spectra of clean water against those of water samples to identify deviations (see Leen et al., 2012 for details). LGR offers the Spectral Contamination Identifier (LWIA-SCI) software to flag samples affected by spectral interference. Recent advances suggest that values of ^{17}O-excess can be used to flag samples contaminated from organic compounds as well (Millar et al., 2021; Nehemy et al., 2019).

Alternatively, users can follow a method similar to that of Schultz et al. (2011), spiking their own water with ethanol and methanol and testing for the corrections for contamination for to their specific instrument. The isotopic values for flagged samples can be corrected using custom-made calibration curves specific for each instrument (see Leen et al., 2012 for OA-ICOS and Martín-Gómez et al., 2015 for CRDS instruments). Calibration curves can be obtained by measuring the isotopic composition for different samples of clean water of known isotopic composition that are spiked with different concentrations of methanol and ethanol. These relationships between the measured isotopic composition and the concentration must be significant and ideally explain a high proportion of the isotopic deviation. Still, when possible, we recommend analyzing a subset of samples through both IRIS and IRMS (method *i*) to validate the correction method and to ensure the validity of laser-based measurements for each study system (soil type and plant species). The IAEA inter-laboratory comparison does not include plant-extracted water explicitly but includes samples spiked with methanol (L. Wassenaar et al., 2021). We recommend conducting such spiking experiments regardless of the post-run processing tool used to identify thresholds of contamination below which the corrections offer acceptable accuracy.

4.3 | Uncertainty

Any information is accompanied by a level of uncertainty (Zadeh, 2005). For stable isotopes, this means that each individual observation should be accompanied by summary statistics of all potential observations, or in other words error estimates (Beven, 2018). Reporting these limits allows us to determine the certainty of the data, and to make decisions regarding our confidence in them. There is no hard line as to what is acceptable, but an estimation of uncertainty allows comparison and a more nuanced answer. In addition, uncertainty estimates can indicate when sampling and analysis produced reproducible values, helping us to improve our methods. However, as a community, we have not established a convention on how to report or combine multiple sources of uncertainty, nor commonly established thresholds to evaluate whether the results are acceptable.

Uncertainty, or, discrepancies in isotopic determination (Beyer & Penna, 2021), originates from (i) sampling procedures, including sample storage and handling (Section 2); (ii) variation in instrumental determination, including the spectral analysis and curve averaging; (iii) fractionation or stratification within the vial or between vials, which creates memory effects from one vial to the next (Cui et al., 2017; Penna et al., 2012); (iv) drift or systematic change through the course of the run, due to either the instrument itself or the environment (Millar et al., 2022); and (v) the procedure of normalization to international standards (Skrzypek, 2013). The first four discrepancies may manifest themselves differently, depending on the instrument, type of sample, and sampling conditions.

In most laboratories, the overall uncertainty is calculated as the standard deviation of the retained injection values. This accounts for variation from (iii) and is usually reported together with the uncertainty determined by the instrument manufacturer, thus accounting for uncertainty from (ii). Most often, manufacturers calculate uncertainty as the standard deviation from the averaging of the absorption curve. A few laboratories use either a repeated measure of a conditioning vial or a control standard as an additional metric of uncertainty, thereby addressing (iv). Some laboratories collect duplicate or triplicate samples, thus providing an estimate of the repeatability of the collection process (i) and analysis itself. In cases where water is being extracted from samples, it can be divided into vials that can be stored and analyzed separately as an additional control. For the most part, each of these assessments increases analysis cost and time. Uncertainty due to (v) is not commonly reported, but it is necessary to state that normalization was done according to international standards (Gröning, 2011, 2023; Lin et al., 2010; Skrzypek, 2013). All these estimates of uncertainty should be summed up using accepted procedures, such as those provided by the Guide to the Expression of Uncertainty in Measurement (GUM; JCGM, 2008). Gröning (2011) proposed a standard method for uncertainty quantification in water samples called SiCal, which is currently available as a spreadsheet macro. It considers memory and drift effects, calibrates the values to international standards, and calculates the standard uncertainty (Gröning, 2011). Currently, this method is available in Visual Basic and therefore only accessible with a Microsoft© operating system. To allow wider use of this routine, it is necessary to expand it to include uncertainties associated with plant and soil water and to translate it to a language independent from the operating system and the software version, for example, Python or R.

4.4 | Concluding remarks: From vial to isotopic value

Currently, most laboratories yield satisfactory results in terms of precision and accuracy (L. Wassenaar et al., 2021). Underperformance often results from run arrangement and preparation, but also from post-run processing including

drift correction and data normalization (L. Wassenaar et al., 2021). In this sense, we recommend that users of CRDS analyzers follow the protocols proposed by van Geldern and Barth (2012), which should not only improve precision, accuracy, and sample throughput but also reduce the cost per sample. For users of OA-ICOS analyzers, we recommend following Lis et al. (2008). Following these protocols, as well as providing detailed descriptions of all the steps, helps to standardize methods across laboratories (see, e.g., Jones et al., 2017; Millar et al., 2022).

The increasing use of laser-based analyzers has enabled the widespread use of isotopic approaches in ecohydrology. Still, their suitability for plant- and soil-water extracts has been questioned for a long time (West et al., 2010). The errors produced by organic contamination have not been sufficiently addressed by the scientific community and the manufacturers (Millar et al., 2021). There have been some robust assessments of the issue (Leen et al., 2012; Martín-Gómez et al., 2015; Schultz et al., 2011), but a definitive protocol does not exist yet. Software provided by the manufacturers could not only flag spectral interference but also integrate post-run processing tools to evaluate and correct the discrepancies caused, and furthermore, manufacturers could provide clear guidance on how to deal with the presence of organic compounds. We advocate for open access to all these procedures so that the community (and not only the users of a specific instrument) can validate their performance. Moreover, there is a need for a more robust, transparent, and universal, for example, not dependent on instrument manufacturer, protocol for identifying organic contamination and mitigating the consequences.

In the meantime, we propose a simple decision-making flowchart based on that from West et al. (2011) to avoid erroneous isotopic data and ill-founded ecohydrological interpretations. This includes three steps: assessment, correction, and evaluation. A key step of the process is the development of an instrument-based, self-made post-run correction. Currently, the best available procedures are those described in Leen et al. (2012) for OA-ICOS and in Martín-Gómez et al. (2015) for CRDS users, though applicability may depend on model and is not necessarily universally applicable to all models of the same producer. Those procedures should be first tested against IRMS results and with samples covering a range of co-extracted organic compounds representative of the type of samples analyzed in each laboratory (Figure 1). This is important because the precision of the relationship between IRIS-IRMS discrepancies and the amount of methanol, ethanol, or other organic molecules can be too large to result in a reliable correction. We must proceed cautiously with corrections as we can only systematically correct for known uncertainties, there are still uncertainties related to sampling, storage, and extraction, along with other organics contamination which may also affect the isotopic analysis.

5 | CONCLUSION

This present work is meant as a roadmap for users and newcomers to the field of stable isotopic ecohydrology to investigate the sources of plant water uptake. There are many possible paths to obtain a value of isotopic composition of the water in soils or plants, all of which have three steps that should be conceived as a continuum and part of the same process chain: sample collection; water extraction, either in situ or in the laboratory; and analysis of the isotopic composition of the extracted water.

Prior to sample collection, ancillary data including climate, soil and vegetation type should be compiled (summarized in Table 1). The sample frequency will be determined by the climate, precipitation regime mainly, and the phenology of the studied plant species. To determine the spatial extent and soil sampling depth we recommend to account for landscape heterogeneity, soil structure—including rooting depth and groundwater level—and plant species composition. Regarding sample collection, we recommend collecting soil and plant samples directly in the same vials that will be used for water extraction.

Furthermore, we provide guidance on which water extraction method is most appropriate to use for specific research objectives (summarized in Table 2). Selecting an extraction method should be first guided by its compatibility for the given sample as well as by the availability of the water in the sample (e.g., bulk soil water versus mobile soil water). The choice of method is also determined by the number of samples, the samples' physicochemical properties, the type of laboratory equipment accessible, and the availability of resources (money, time, and labor). The reader should note that extraction artifacts have been detected, particularly during CVD. Novel methodologies developed recently, such as the Cavitron method or the SPC technique, appear to bypass some of these artifacts, but their implementation is still challenging, and CVD still remains as the most broadly accessible method. Besides, we still view CVD as the most plausible methodology for extracting water from small shrubs or nonwoody plant species or from soil samples well above the permanent wilting point and with low clay and organic matter content.

Finally, analysis of the extracted water, regardless of the instrument, should follow established protocols regarding run arrangement and preparation with particular attention to how samples are assessed for uncertainty and contamination. A basis for navigating the spectral interference caused by contamination by organics has been established but the future will certainly hold more widespread, transparent, and widely available methods.

Considering the three steps interdependently should allow for obtaining temporally and spatially representative soil and plant samples, from which fractionation-free water samples are obtained and contamination-free isotopic analyses are produced. This sets the prerequisite to take the next and final step, outside of the focus of this work, that is, the modeling of plant water uptake patterns based on isotopic information.

AUTHOR CONTRIBUTIONS

Natalie Ceperley: Conceptualization (lead); writing – original draft (lead); writing – review and editing (lead). **Teresa E. Gimeno:** Conceptualization (lead); writing – original draft (lead); writing – review and editing (lead). **Suzanne R. Jacobs:** Conceptualization (lead); writing – original draft (lead); writing – review and editing (lead). **Matthias Beyer:** Writing – original draft (equal). **Maren Dubbert:** Writing – original draft (equal). **Benjamin Fischer:** Writing – original draft (equal). **Josie Geris:** Writing – original draft (equal); writing – review and editing (equal). **Ladislav Holko:** Writing – original draft (equal). **Angelika Kübert:** Writing – original draft (equal). **Samuel Le Gall:** Writing – original draft (equal). **Marco M. Lehmann:** Writing – original draft (equal). **Pilar Llorens:** Writing – original draft (equal). **Cody Millar:** Writing – original draft (equal); writing – review and editing (equal). **Daniele Penna:** Funding acquisition (equal); writing – original draft (equal); writing – review and editing (equal). **Iván Prieto:** Writing – original draft (equal). **Jesse Radolinski:** Writing – original draft (equal). **Francesca Scandellari:** Writing – original draft (equal); writing – review and editing (equal). **Michael Stockinger:** Writing – original draft (equal). **Christine Stumpp:** Writing – original draft (equal); writing – review and editing (equal). **Dörthe Tetzlaff:** Writing – original draft (equal); writing – review and editing (equal). **Ilja van Meerveld:** Funding acquisition (equal); writing – original draft (equal); writing – review and editing (equal). **Christiane Werner:** Writing – original draft (equal); writing – review and editing (equal). **Oktay Yildiz:** Writing – original draft (equal). **Giulia Zuecco:** Writing – original draft (equal). **Adrià Barbeta:** Conceptualization (lead); writing – original draft (lead); writing – review and editing (lead). **Natalie Orlowski:** Conceptualization (lead); writing – original draft (lead); writing – review and editing (lead). **Youri Rothfuss:** Conceptualization (lead); writing – original draft (lead); writing – review and editing (lead).

AFFILIATIONS

[1]Institute of Geography (GIUB) and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland
[2]CREAF, Bellaterra, Catalonia, Spain
[3]Centre for International Development and Environmental Research, Justus Liebig University Giessen, Giessen, Germany
[4]Institute of Geoecology, Technical University Braunschweig, Braunschweig, Germany
[5]Isotope Biogeochemistry and Gas Fluxes, Leibniz Centre for Agricultural and Landscape Research, Müncheberg, Germany
[6]Department of Earth Sciences, Uppsala University, Uppsala, Sweden
[7]School of Geosciences, University of Aberdeen, Aberdeen, United Kingdom
[8]Institute of Hydrology, Slovak Academy of Sciences, Bratislava, Slovak Republic
[9]Institute for Atmospheric and Earth System Research (INAR), University of Helsinki, Helsinki, Finland
[10]Institute of Bio- and Geosciences - Agrosphere (IBG-3), Forschungszentrum Jülich, Jülich, Germany
[11]Swiss Federal Institute for Forest, Snow & Landscape Research (WSL), Birmensdorf, Switzerland
[12]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain
[13]Global Institute for Water Security, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
[14]Department of Agriculture, Food, Environment and Forestry, University of Florence, Florence, Italy
[15]Forest Engineering Resources and Management Department, Oregon State University, Corvallis, Oregon, USA
[16]Departamento de Biodiversidad y Gestión Ambiental, Facultad de Ciencias Biológicas y Ambientales, Universidad de León, León, España, Spain
[17]Department of Ecology, University of Innsbruck, Innsbruck, Austria
[18]Department of Environmental Science and Technology, University of Maryland, College Park, Maryland, USA

[19]U-Series Srl, Bologna, Italy
[20]Department of Water, Atmosphere and Environment, Institute of Soil Physics and Rural Water Management, University of Natural Resources and Life Sciences, Vienna, Vienna, Austria
[21]Department of Geography, Humboldt-Universität zu Berlin, Berlin, Germany
[22]Leibniz Institute of Freshwater Ecology and Inland Fisheries, Berlin, Germany
[23]Department of Geography, University of Zurich, Zurich, Switzerland
[24]Chair of Ecosystem Physiology, Faculty of Environment and Natural Resources, University of Freiburg, Freiburg, Germany
[25]Forestry Faculty, Duzce University, Konuralp, Turkey
[26]Department of Land, Environment, Agriculture and Forestry, University of Padova, Legnaro, Italy
[27]Department of Chemical Sciences, University of Padova, Padua, Italy
[28]BEECA-UB, Department of Evolutionary Biology, Ecology and Environmental Sciences, University of Barcelona, Barcelona, Catalonia, Spain
[29]Chair of Hydrology, Faculty of Environment and Natural Resources, University of Freiburg, Freiburg, Germany
[30]Chair of Site Ecology and Plant Nutrition, Institute of Soil Science and Site Ecology, Technical University Dresden, Tharandt, Germany

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CONFLICT OF INTEREST STATEMENT

The authors have declared no conflicts of interest for this article.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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ORCID

Natalie Ceperley https://orcid.org/0000-0002-2260-8426
Teresa E. Gimeno https://orcid.org/0000-0002-1707-9291
Suzanne R. Jacobs https://orcid.org/0000-0003-2223-6973
Matthias Beyer https://orcid.org/0000-0002-1618-6036
Maren Dubbert https://orcid.org/0000-0002-2352-8516
Benjamin Fischer https://orcid.org/0000-0003-2530-6084
Josie Geris https://orcid.org/0000-0003-0159-0543
Ladislav Holko https://orcid.org/0000-0002-4589-7478
Angelika Kübert https://orcid.org/0000-0003-3985-9261
Marco M. Lehmann https://orcid.org/0000-0003-2962-3351
Pilar Llorens https://orcid.org/0000-0003-4591-5303
Cody Millar https://orcid.org/0000-0002-2171-581X

Daniele Penna https://orcid.org/0000-0001-6915-0697
Iván Prieto https://orcid.org/0000-0001-5549-1132
Jesse Radolinski https://orcid.org/0000-0003-4341-4046
Francesca Scandellari https://orcid.org/0000-0002-2242-2656
Michael Stockinger https://orcid.org/0000-0002-7715-8100
Christine Stumpp https://orcid.org/0000-0001-9041-2735
Dörthe Tetzlaff https://orcid.org/0000-0002-7183-8674
Ilja van Meerveld https://orcid.org/0000-0002-7547-3270
Christiane Werner https://orcid.org/0000-0002-7676-9057
Oktay Yildiz https://orcid.org/0000-0002-8058-4506
Giulia Zuecco https://orcid.org/0000-0002-2125-0717
Adrià Barbeta https://orcid.org/0000-0002-8357-1719
Natalie Orlowski https://orcid.org/0000-0003-4368-4580
Youri Rothfuss https://orcid.org/0000-0002-8874-5036

FURTHER READING

For current perspectives regarding in situ *and online techniques, see* Beyer, M., Kühnhammer, K., & Dubbert, M. (2020). In situ measurements of soil and plant water isotopes: A review of approaches, practical considerations and a vision for the future. *Hydrology and Earth System Sciences*, *24*(9), 4413–4440. https://doi.org/10.5194/hess-24-4413-2020

To explore discussion around isotopic notation and terminology (*a must-read for students and newcomers*), *see* Coplen, T. B. (2011). Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results: Guidelines and recommended terms for expressing stable isotope results. *Rapid Communications in Mass Spectrometry*, *25*(17), 2538–2560. https://doi.org/10.1002/rcm.5129

To further explore dimensions of uncertainty, see Millar, C., Janzen, K., Nehemy, M. F., Koehler, G., Hervé-Fernández, P., Wang, H., Orlowski, N., Barbeta, A., & McDonnell, J. J. (2022). On the urgent need for standardization in isotope-based ecohydrological investigations. *Hydrological Processes*, *36*(10), e14698. https://doi.org/10.1002/hyp.14698

To explore community perspectives, see Orlowski, N., Rinderer, M., Dubbert, M., Ceperley, N., Hrachowitz, M., Gessler, A., Rothfuss, Y., Sprenger, M., Heidbüchel, I., Kübert, A., Beyer, M., Zuecco, G., & McCarter, C. (2023). Challenges in studying water fluxes within the soil–plant-atmosphere continuum: A tracer-based perspective on pathways to progress. *Science of the Total Environment*, *881*, 163510. https://doi.org/10.1016/j.scitotenv.2023.163510

For further insights on hydrological process in the Critical Zone assessed with water isotopes, see Sprenger, M., Leistert, H., Gimbel, K., & Weiler, M. (2016). Illuminating hydrological processes at the soil-vegetation atmosphere interface with water stable isotopes. *Reviews of Geophysics*, *54*(3), 674–704. https://doi.org/10.1002/2015RG000515

REFERENCES

Adams, R. E., Hyodo, A., SantaMaria, T., Wright, C. L., Boutton, T. W., & West, J. B. (2020). Bound and mobile soil water isotope ratios are affected by soil texture and mineralogy, whereas extraction method influences their measurement. *Hydrological Processes*, *34*(4), 991–1003. https://doi.org/10.1002/hyp.13633

Allen, S. T., & Kirchner, J. W. (2022). Potential effects of cryogenic extraction biases on plant water source partitioning inferred from xylem-water isotope ratios. *Hydrological Processes*, *36*(2), e14483. https://doi.org/10.1002/hyp.14483

Allen, S. T., Kirchner, J. W., Braun, S., Siegwolf, R. T. W., & Goldsmith, G. R. (2019). Seasonal origins of soil water used by trees. *Hydrology and Earth System Sciences*, *23*(2), 1199–1210. https://doi.org/10.5194/hess-23-1199-2019

Amin, A., Zuecco, G., Geris, J., Schwendenmann, L., McDonnell, J. J., Borga, M., & Penna, D. (2020). Depth distribution of soil water sourced by plants at the global scale: A new direct inference approach. *Ecohydrology*, *13*(2), e2177. https://doi.org/10.1002/eco.2177

Amin, A., Zuecco, G., Marchina, C., Engel, M., Penna, D., McDonnell, J. J., & Borga, M. (2021). No evidence of isotopic fractionation in olive trees (*Olea europaea*): A stable isotope tracing experiment. *Hydrological Sciences Journal*, *66*(16), 2415–2430. https://doi.org/10.1080/02626667.2021.1987440

Araguás-Araguás, L., Rozanski, K., Gonfiantini, R., & Louvat, 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

Asadollahi, M., Stumpp, C., Rinaldo, A., & Benettin, P. (2020). Transport and water age dynamics in soils: A comparative study of spatially integrated and spatially explicit models. *Water Resources Research*, *56*(3), e2019WR025539. https://doi.org/10.1029/2019WR025539

Barbeta, A., Burlett, R., Martín-Gómez, P., Fréjaville, B., Devert, N., Wingate, L., Domec, J., & Ogée, J. (2022). Evidence for distinct isotopic compositions of sap and tissue water in tree stems: Consequences for plant water source identification. *New Phytologist*, *233*(3), 1121–1132. https://doi.org/10.1111/nph.17857

Barbeta, A., Gimeno, T. E., Clavé, L., Fréjaville, B., Jones, S. P., Delvigne, C., Wingate, L., & Ogée, J. (2020). An explanation for the isotopic offset between soil and stem water in a temperate tree species. *New Phytologist*, *227*(3), 766–779. https://doi.org/10.1111/nph.16564

Barbeta, A., Jones, S. P., Clavé, L., Wingate, L., Gimeno, T. E., Fréjaville, B., Wohl, S., & Ogée, J. (2019). Unexplained hydrogen isotope offsets complicate the identification and quantification of tree water sources in a riparian forest. *Hydrology and Earth System Sciences*, *23*(4), 2129–2146. https://doi.org/10.5194/hess-23-2129-2019

Barbeta, A., & Peñuelas, J. (2017). Relative contribution of groundwater to plant transpiration estimated with stable isotopes. *Scientific Reports*, *7*(1), 10580. https://doi.org/10.1038/s41598-017-09643-x

Barnard, R. L., de Bello, F., Gilgen, A. K., & Buchmann, N. (2006). The $\delta^{18}O$ of root crown water best reflects source water $\delta^{18}O$ in different types of herbaceous species. *Rapid Communications in Mass Spectrometry*, *20*(24), 3799–3802. https://doi.org/10.1002/rcm.2778

Barnes, C. J., & Allison, G. B. (1983). The distribution of deuterium and ^{18}O in dry soils: 1. Theory. *Journal of Hydrology*, *60*, 141–156. https://doi.org/10.1016/0022-1694(83)90018-5

Barth, J. A. C., Tait, A., & Bolshaw, M. (2004). Automated analyses of $^{18}O/^{16}O$ ratios in dissolved oxygen from 12-mL water samples: Automated O_2(aq) isotope analysis. *Limnology and Oceanography: Methods*, *2*(2), 35–41. https://doi.org/10.4319/lom.2004.2.35

Benettin, P., Nehemy, M. F., Cernusak, L. A., Kahmen, A., & McDonnell, J. J. (2021). On the use of leaf water to determine plant water source: A proof of concept. *Hydrological Processes*, *35*(3), e14073. https://doi.org/10.1002/hyp.14073

Beven, K. J. (2018). On hypothesis testing in hydrology: Why falsification of models is still a really good idea. *Wiley Interdisciplinary Reviews: Water*, *5*(3), e1278. https://doi.org/10.1002/wat2.1278

Beyer, M., Kühnhammer, K., & Dubbert, M. (2020). In situ measurements of soil and plant water isotopes: A review of approaches, practical considerations and a vision for the future. *Hydrology and Earth System Sciences*, *24*(9), 4413–4440. https://doi.org/10.5194/hess-24-4413-2020

Beyer, M., & Penna, D. (2021). On the Spatio-temporal under-representation of isotopic data in ecohydrological studies. *Frontiers in Water*, *3*, 643013. https://doi.org/10.3389/frwa.2021.643013

Böttcher, G. (1997). A new high-pressure squeezing technique for pore fluid extraction from terrestrial soils. *Water, Air, and Soil Pollution*, *94*(3/4), 289–296. https://doi.org/10.1023/A:1026499319006

Bowen, G. J., Putman, A., Brooks, J. R., Oerter, E. J., & Good, S. P. (2018). Inferring the source of evaporated waters using stable H and O isotopes. *Oecologia*, *187*(4), 1025–1039. https://doi.org/10.1007/s00442-018-4192-5

Bowers, W. H., Mercer, J. J., Pleasants, M. S., & Williams, D. G. (2020). A combination of soil water extraction methods quantifies the isotopic mixing of waters held at separate tensions in soil. *Hydrology and Earth System Sciences*, *24*(8), 4045–4060. https://doi.org/10.5194/hess-24-4045-2020

Bowers, W. H., & Williams, D. G. (2022). Isotopic heterogeneity of stem water in conifers is correlated to xylem hydraulic traits and supports multiple residence times. *Frontiers in Water*, *4*, 861590. https://doi.org/10.3389/frwa-04-861590

Brand, W. A., Geilmann, H., Crosson, E. R., & Rella, C. W. (2009). Cavity ring-down spectroscopy versus high-temperature conversion isotope ratio mass spectrometry; a case study on δ^2H and $\delta^{18}O$ of pure water samples and alcohol/water mixtures: Letter to the editor. *Rapid Communications in Mass Spectrometry*, *23*(12), 1879–1884. https://doi.org/10.1002/rcm.4083

Brandi-Dohrn, F. M., Hess, M., Selker, J. S., & Dick, R. P. (1996). Field evaluation of passive capillary samplers. *Soil Science Society of America Journal*, *60*(6), 1705–1713. https://doi.org/10.2136/sssaj1996.03615995006000060014x

Brooks, P. D., Chorover, J., Fan, Y., Godsey, S. E., Maxwell, R. M., McNamara, J. P., & Tague, C. (2015). Hydrological partitioning in the critical zone: Recent advances and opportunities for developing transferable understanding of water cycle dynamics. *Water Resource Research*, *51*, 6973–6987. https://doi.org/10.1002/2015WR017039

Brown, K. W., Thomas, J. C., & Holder, M. W. (1989). *Development of a capillary wick unsaturated zone pore water sampler (No. EPA/600/S4-88/001)*. United States Environmental Protection Agency.

Cabon, A., Martínez-Vilalta, J., de Aragón, J. M., Poyatos, R., & De Cáceres, M. (2018). Applying the eco-hydrological equilibrium hypothesis to model root distribution in water-limited forests. *Ecohydrology*, *11*(7), e2015. https://doi.org/10.1002/eco.2015

Canadell, J., Jackson, R. B., Ehleringer, J. R., Mooney, H. A., Sala, O. E., & Schulze, E. D. (1996). Maximum rooting depth of vegetation types at the global scale. *Oecologia*, *108*(4), 583–595. https://doi.org/10.1007/BF00329030

Ceperley, N., & Barbeta, A. (2023). Isotopic analysis: How our community analyzes soil and plant water samples for their isotopic composition [data set]. *Zenodo*. https://doi.org/10.5281/zenodo.10125128

Cernusak, L. A., Barbour, M. M., Arndt, S. K., Cheesman, A. W., English, N. B., Feild, T. S., Helliker, B. R., Holloway-Phillips, M. M., Holtum, J. A. M., Kahmen, A., McInerney, F. A., Munksgaard, N. C., Simonin, K. A., Song, X., Stuart-Williams, H., West, J. B., & Farquhar, G. D. (2016). Stable isotopes in leaf water of terrestrial plants: Stable isotopes in leaf water. *Plant, Cell & Environment*, *39*(5), 1087–1102. https://doi.org/10.1111/pce.12703

Chang, E., Wolf, A., Gerlein-Safdi, C., & Caylor, K. K. (2016). Improved removal of volatile organic compounds for laser-based spectroscopy of water isotopes: Removal of VOCs in water samples for infrared spectroscopy. *Rapid Communications in Mass Spectrometry*, *30*(6), 784–790. https://doi.org/10.1002/rcm.7497

Chen, Y., Helliker, B. R., Tang, X., Li, F., Zhou, Y., & Song, X. (2020). Stem water cryogenic extraction biases estimation in deuterium isotope composition of plant source water. *Proceedings of the National Academy of Sciences of the United States of America*, *117*(52), 33345–33350. https://doi.org/10.1073/pnas.2014422117

Coplen, T. B., & Wassenaar, L. I. (2015). LIMS for lasers 2015 for achieving long-term accuracy and precision of δ^2H, $\delta^{17}O$, and $\delta^{18}O$ of waters using laser absorption spectrometry: LIMS for lasers 2015. *Rapid Communications in Mass Spectrometry*, *29*(22), 2122–2130. https://doi.org/10.1002/rcm.7372

Couvreur, V., Rothfuss, Y., Meunier, F., Bariac, T., Biron, P., Durand, J. L., Richard, P., & Javaux, M. (2020). Disentangling temporal and population variability in plant root water uptake from stable isotopic analysis: When rooting depth matters in labeling studies. *Hydrology and Earth System Sciences*, *24*, 3057–3075. https://doi.org/10.5194/hess-24-3057-2020

Craig, H., & Gordon, L. (1965). *Deuterium and oxygen 18 variations in the ocean and marine atmosphere* (pp. 9–130). Stable Isotopes in Oceanographic Studies and Paleotemperatures.

Cramer, V. A., Thorburn, P. J., & Fraser, G. W. (1999). Transpiration and groundwater uptake from farm forest plots of *Casuarina glauca* and *Eucalyptus camaldulensis* in saline areas of southeast Queensland, Australia. *Agricultural Water Management*, *39*(2–3), 189–204. https://doi.org/10.1016/S0378-3774(98)00078-X

Cui, J., Tian, L., Gerlein-Safdi, C., & Qu, D. (2017). The influence of memory, sample size effects, and filter paper material on online laser-based plant and soil water isotope measurements: Memory and sample size effect corrections for IM-CRDS. *Rapid Communications in Mass Spectrometry*, *31*(6), 509–522. https://doi.org/10.1002/rcm.7824

Davies, B. E., & Davies, R. I. (1963). A simple centrifugation method for obtaining small samples of soil solution. *Nature*, *198*(4876), 216–217. https://doi.org/10.1038/198216a0

Dawson, T. E. (1993). Hydraulic lift and water use by plants: Implications for water balance, performance and plant-plant interactions. *Oecologia*, *95*, 565–574. https://doi.org/10.1007/BF00317442

Dawson, T. E., & Ehleringer, J. R. (1991). Streamside trees that do not use stream water. *Nature*, *350*(6316), 335–337. https://doi.org/10.1038/350335a0

Dawson, T. E., & Ehleringer, J. R. (1993). Isotopic enrichment of water in the "woody" tissues of plants: Implications for plant water source, water uptake, and other studies which use the stable isotopic composition of cellulose. *Geochimica et Cosmochimica Acta*, *57*(14), 3487–3492. https://doi.org/10.1016/0016-7037(93)90554-A

De Deurwaerder, H. P. T., Visser, M. D., Detto, M., Boeckx, P., Meunier, F., Kuehnhammer, K., Magh, R.-K., Marshall, J. D., Wang, L., Zhao, L., & Verbeeck, H. (2020). Causes and consequences of pronounced variation in the isotope composition of plant xylem water. *Biogeosciences*, *17*, 4853–4870. https://doi.org/10.5194/bg-17-4853-2020

de la Casa, J., Barbeta, A., Rodríguez-Uña, A., Wingate, L., Ogée, J., & Gimeno, T. E. (2022). Isotopic offsets between bulk plant water and its sources are larger in cool and wet environments. *Hydrology and Earth System Sciences*, *26*(15), 4125–4146. https://doi.org/10.5194/hess-26-4125-2022

Delzon, S., Sartore, M., Granier, A., & Loustau, D. (2004). Radial profiles of sap flow with increasing tree size in maritime pine. *Tree Physiology*, *24*(11), 1285–1293. https://doi.org/10.1093/treephys/24.11.1285

Deseano Diaz, P. A., Van Dusschoten, D., Kübert, A., Brüggemann, N., Javaux, M., Merz, S., Vanderborght, J., Vereecken, H., Dubbert, M., & Rothfuss, Y. (2023). Response of a grassland species to dry environmental conditions from water stable isotopic monitoring: No evident shift in root water uptake to wetter soil layers. *Plant and Soil*, *482*(1–2), 491–512. https://doi.org/10.1007/s11104-022-05703-y

Diao, H., Schuler, P., Goldsmith, G. R., Siegwolf, R. T. W., Saurer, M., & Lehmann, M. M. (2022). Technical note: On uncertainties in plant water isotopic composition following extraction by cryogenic vacuum distillation. *Hydrology and Earth System Sciences*, *26*(22), 5835–5847. https://doi.org/10.5194/hess-26-5835-2022

Diongue, D. M. L., Stumpp, C., Roupsard, O., Orange, D., Do, F. C., & Faye, S. (2023). Estimating water fluxes in the critical zone using water stable isotope approaches in the groundnut and Ferlo basins of Senegal. *Hydrological Processes*, *37*(1), e14787. https://doi.org/10.1002/hyp.14787

Dubbert, M., Couvreur, V., Kübert, A., & Werner, C. (2023). Plant water uptake modelling: Added value of cross-disciplinary approaches. *Plant Biology*, *25*, 32–42. https://doi.org/10.1111/plb.13478

Duvert, C., Canham, C. A., Barbeta, A., Cortes, D. A., Chandler, L., Harford, A. J., Leggett, A., Setterfield, S. A., Humphrey, C. L., & Hutley, L. B. (2022). Deuterium depletion in xylem water and soil isotopic effects complicate the assessment of riparian tree water sources in the seasonal tropics. *Ecohydrology*, *2022*(15), e2383. https://doi.org/10.1002/eco.2383

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

Ehleringer, J. R., & Dawson, T. E. (1992). Water uptake by plants: Perspectives from stable isotope composition. *Plant, Cell and Environment*, *15*(9), 1073–1082. https://doi.org/10.1111/j.1365-3040.1992.tb01657.x

Eichler, R. (1966). Deuterium-Isotopengeochemie des Grund- und Oberflächenwassers. *Geologische Rundschau*, *55*(1), 144–159. https://doi.org/10.1007/BF01982963

Ellsworth, P. Z., & Williams, D. G. (2007). Hydrogen isotope fractionation during water uptake by woody xerophytes. *Plant and Soil*, *291*(1–2), 93–107. https://doi.org/10.1007/s11104-006-9177-1

Espino, S., & Schenk, H. J. (2009). Hydraulically integrated or modular? Comparing whole-plant-level hydraulic systems between two desert shrub species with different growth forms. *New Phytologist*, *183*(1), 142–152. https://doi.org/10.1111/j.1469-8137.2009.02828.x

Evaristo, J., & McDonnell, J. J. (2017). Prevalence and magnitude of groundwater use by vegetation: A global stable isotope meta-analysis. *Scientific Reports*, *7*(1), 44110. https://doi.org/10.1038/srep44110

Fan, Y. (2015). Groundwater in the Earth's critical zone: Relevance to large-scale patterns and processes: Groundwater at large scales. *Water Resources Research*, *51*(5), 3052–3069. https://doi.org/10.1002/2015WR017037

Fan, Y., Miguez-Macho, G., Jobbágy, E. G., Jackson, R. B., & Otero-Casal, C. (2017). Hydrologic regulation of plant rooting depth. *Proceedings of the National Academy of Sciences of the United States of America*, *114*, 10572–10577. https://doi.org/10.1073/pnas.171238111

Fernández, M. E., Gyenge, J., Licata, J., Schlichter, T., & Bond, B. J. (2008). Belowground interactions for water between trees and grasses in a temperate semiarid agroforestry system. *Agroforestry Systems*, *74*(2), 185–197. https://doi.org/10.1007/s10457-008-9119-4

Figueroa-Johnson, M. A., Tindall, J. A., & Friedel, M. (2007). A comparison of $\delta^{18}O$ 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

Fischer, B. M. C., Frentress, J., Manzoni, S., Cousins, S. A. O., Hugelius, G., Greger, M., Smittenberg, R. H., & Lyon, S. W. (2019). Mojito, anyone? An exploration of low-tech plant water extraction methods for isotopic analysis using locally-sourced materials. *Frontiers in Earth Science*, *7*, 150. https://doi.org/10.3389/feart.2019.00150

Flórez, N., Conde, E., & Domínguez, H. (2015). Microwave assisted water extraction of plant compounds: Microwave assisted water extraction of plant compounds. *Journal of Chemical Technology & Biotechnology*, *90*(4), 590–607. https://doi.org/10.1002/jctb.4519

Frisbee, M. D., Phillips, F. M., Campbell, A. R., & Hendrickx, J. M. H. (2010). Modified passive capillary samplers for collecting samples of snowmelt infiltration for stable isotope analysis in remote, seasonally inaccessible watersheds 1: Laboratory evaluation. *Hydrological Processes*, *24*(7), 825–833. https://doi.org/10.1002/hyp.7523

Frisbee, M. D., Phillips, F. M., Campbell, A. R., Hendrickx, J. M. H., & Engle, E. M. (2010). Modified passive capillary samplers for collecting samples of snowmelt infiltration for stable isotope analysis in remote, seasonally inaccessible watersheds 2: Field evaluation. *Hydrological Processes*, *24*(7), 834–849. https://doi.org/10.1002/hyp.7524

Gaj, M., Kaufhold, S., Koeniger, P., Beyer, M., Weiler, M., & Himmelsbach, T. (2017). Mineral mediated isotope fractionation of soil water. *Rapid Communications in Mass Spectrometry*, *31*(3), 269–280. https://doi.org/10.1002/rcm.7787

Geißler, K., Heblack, J., Uugulu, S., Wanke, H., & Blaum, N. (2019). Partitioning of water between differently sized shrubs and potential groundwater recharge in a semiarid savanna in Namibia. *Frontiers in Plant Science*, *10*, 1411. https://doi.org/10.3389/fpls.2019.01411

Georgiou, C. A., & Danezis, G. P. (2015). Elemental and isotopic mass spectrometry. In *Comprehensive analytical chemistry* (Vol. 68, pp. 131–243). Elsevier. https://doi.org/10.1016/B978-0-444-63340-8.00003-0

Geris, J., Tetzlaff, D., McDonnell, J., Anderson, J., Paton, G., & Soulsby, C. (2015). Ecohydrological separation in wet, low energy northern environments? A preliminary assessment using different soil water extraction techniques: Ecohydrological separation in northern environments. *Hydrological Processes*, *29*(25), 5139–5152. https://doi.org/10.1002/hyp.10603

Geris, J., Tetzlaff, D., McDonnell, J. J., & Soulsby, C. (2017). Spatial and temporal patterns of soil water storage and vegetation water use in humid northern catchments. *Science of the Total Environment*, *595*(C), 486–493. https://doi.org/10.1016/j.scitotenv.2017.03.275

Goldsmith, G. R., Allen, S. T., Braun, S., Engbersen, N., González-Quijano, C. R., Kirchner, J. W., & Siegwolf, R. T. W. (2018). Spatial variation in throughfall, soil, and plant water isotopes in a temperate forest. *Ecohydrology*, *e2059*. https://doi.org/10.1002/eco.2059

Goldsmith, G. R., Lehmann, M. M., Cernusak, L. A., Arend, M., & Siegwolf, R. T. W. (2017). Inferring foliar water uptake using stable isotopes of water. *Oecologia*, *184*, 763–766. https://doi.org/10.1007/s00442-017-3917-1

Gómez-Navarro, C., Pataki, D. E., Bowen, G. J., & Oerter, E. J. (2019). Spatiotemporal variability in water sources of urban soils and trees in the semiarid, irrigated Salt Lake Valley. *Ecohydrology*, *12*(8), e2154. https://doi.org/10.1002/eco.2154

Gralher, B., Herbstritt, B., & Weiler, M. (2021). Technical note: Unresolved aspects of the direct vapor equilibration method for stable isotope analysis ($\delta^{18}O$, $\delta^{2}H$) of matrix-bound water: Unifying protocols through empirical and mathematical scrutiny. *Hydrology and Earth System Sciences*, *25*(9), 5219–5235. https://doi.org/10.5194/hess-25-5219-2021

Gralher, B., Herbstritt, B., Weiler, M., Wassenaar, L. I., & Stumpp, C. (2016). Correcting laser-based water stable isotope readings biased by carrier gas changes. *Environmental Science & Technology*, *50*(13), 7074–7081. https://doi.org/10.1021/acs.est.6b01124

Gralher, B., Herbstritt, B., Weiler, M., Wassenaar, L. I., & Stumpp, C. (2018). Correcting for biogenic gas matrix effects on laser-based pore water-vapor stable isotope measurements. *Vadose Zone Journal*, *17*(1), 1–10. https://doi.org/10.2136/vzj2017.08.0157

Groh, J., Stumpp, C., Lücke, A., Pütz, T., Vanderborght, J., & Vereecken, H. (2018). Inverse estimation of soil hydraulic and transport parameters of layered soils from water stable isotope and lysimeter data. *Vadose Zone Journal*, *17*(1), 170168. https://doi.org/10.2136/vzj2017.09.0168

Groh, J., Vanderborght, J., Pütz, T., & Vereecken, H. (2016). How to control the lysimeter bottom boundary to investigate the effect of climate change on soil processes? *Vadose Zone Journal*, *15*(7), 1–15. https://doi.org/10.2136/vzj2015.08.0113

Gröning, M. (2004). International stable isotope reference materials. In *Handbook of stable isotope analytical techniques* (pp. 874–906). Elsevier. https://doi.org/10.1016/B978-044451114-0/50042-9

Gröning, M. (2011). Improved water $\delta^{2}H$ and $\delta^{18}O$ calibration and calculation of measurement uncertainty using a simple software tool: Spreadsheet calibration strategy for water stable isotopes. *Rapid Communications in Mass Spectrometry*, *25*(19), 2711–2720. https://doi.org/10.1002/rcm.5074

Gröning, M. (2023). Some pitfalls in the uncertainty evaluation of isotope delta reference materials. *Accreditation and Quality Assurance*, *28*, 101–114. https://doi.org/10.1007/s00769-022-01527-6

Hahm, W. J., Rempe, D. M., Dralle, D. N., Dawson, T. E., & Dietrich, W. E. (2020). Oak transpiration drawn from the weathered bedrock vadose zone in the summer dry season. *Water Resources Research*, *56*, e2020WR027419. https://doi.org/10.1029/2020WR027419

Halbritter, A. H., De Boeck, H. J., Eycott, A. E., Reinsch, S., Robinson, D. A., Vicca, S., Berauer, B., Christiansen, C. T., Estiarte, M., Grunzweig, J. M., Gya, R., Hansen, K., Jentsch, A., Lee, H., Linder, S., Marshall, J., Penuelas, J., Schmidt, I. K., Stuart-Haentjens, E., … the ClimMani Working Group. (2020). The handbook for standardized field and laboratory measurements in terrestrial climate change experiments and observational studies (ClimEx). *Methods in Ecology and Evolution*, *11*(1), 22–37. https://doi.org/10.1111/2041-210X.13331

He, D., Wen, M. Y., Wang, Y. B., Dub, G., Zhang, C. C., He, H. L., Jin, J. J., Li, M., & Si, B. C. (2023). Xylem water cryogenic vacuum extraction: Testing correction methods with CaviTron-based apple twig sampling, *Journal of Hydrology*, *621*, ARTN 129572, https://doi.org/10.1016/j.jhydrol.2023.129572

Hendry, M. J., Richman, B., & Wassenaar, L. I. (2011). Correcting for methane interferences on $\delta^{2}H$ and $\delta^{18}O$ measurements in pore water using $H_2O_{(liquid)}$–$H_2O_{(vapor)}$ equilibration laser spectroscopy. *Analytical Chemistry*, *83*(14), 5789–5796. https://doi.org/10.1021/ac201341p

Hendry, M. J., Schmeling, E., Wassenaar, L. I., Barbour, S. L., & Pratt, D. (2015). Determining the stable isotope composition of pore water from saturated and unsaturated zone core: Improvements to the direct vapour equilibration laser spectrometry method. *Hydrology and Earth System Sciences*, *19*(11), 4427–4440. https://doi.org/10.5194/hess-19-4427-2015

Herbstritt, B., Gralher, B., & Weiler, M. (2012). Continuous in situ measurements of stable isotopes in liquid water: Technical Note. *Water Resources Research*, *48*(3), W03601. https://doi.org/10.1029/2011WR011369

Hirl, R. T., Schnyder, H., Ostler, U., Schäufele, R., Schleip, I., Vetter, S. H., Auerswald, K., Baca Cabrera, J. C., Wingate, L., Barbour, M. M., & Ogée, J. (2019). The ^{18}O ecohydrology of a grassland ecosystem—Predictions and observations. *Hydrology and Earth System Sciences*, *23*(6), 2581–2600. https://doi.org/10.5194/hess-23-2581-2019

Holder, M., Brown, K. W., Thomas, J. C., Zabcik, D., & Murray, H. E. (1991). Capillary-Wick unsaturated zone soil pore water sampler. *Soil Science Society of America Journal*, *55*(5), 1195–1202. https://doi.org/10.2136/sssaj1991.03615995005500050001x

Hsiao, G. (2011). *Applying corrections to contaminated water isotope measurement: Example calculation of calibrated organic compensated isotope ratios*. Picarro Community Forum. https://www.picarro.com/support/community/applying-corrections-contaminated-water-isotope-measurements-using-chemcorrect

Illuminati, A., Querejeta, J. I., Pías, B., Escudero, A., & Matesanz, S. (2022). Coordination between water uptake depth and the leaf economic spectrum in a Mediterranean shrubland. *Journal of Ecology*, *110*(8), 1844–1856. https://doi.org/10.1111/1365-2745.13909

International Atomic Energy Agency (IAEA). (2007). *Introduction to water sampling and analysis for isotope hydrology*. Non-serial Publications, IAEA.

Jacobs, S. R., Timbe, E., Weeser, B., Rufino, M. C., Butterbach-Bahl, K., & Breuer, L. (2018). Assessment of hydrological pathways in East African montane catchments under different land use. *Hydrology and Earth System Sciences*, *22*(9), 4981–5000. https://doi.org/10.5194/hess-22-4981-2018

JCGM. (2008). 100: 2008 (GUM 1995 with minor corrections) evaluation of measurement data-guide to the expression of uncertainty in measurement. *Joint Committee for Guides in Meteorology*, *19*, 120.

Jones, T. R., White, J. W. C., Steig, E. J., Vaughn, B. H., Morris, V., Gkinis, V., Markle, B. R., & Schoenemann, S. W. (2017). Improved methodologies for continuous-flow analysis of stable water isotopes in ice cores. *Atmospheric Measurement Techniques*, *10*(2), 617–632. https://doi.org/10.5194/amt-10-617-2017

Kelln, C. J., Wassenaar, L. I., & Hendry, M. J. (2001). Stable isotopes ($\delta^{18}O$, $\delta^{2}H$) of pore waters in clay-rich aquitards: A comparison and evaluation of measurement techniques. *Groundwater Monitoring & Remediation*, *21*(2), 108–116. https://doi.org/10.1111/j.1745-6592.2001.tb00306.x

Koeniger, P., Marshall, J. D., Link, T., & Mulch, A. (2011). An inexpensive, fast, and reliable method for vacuum extraction of soil and plant water for stable isotope analyses by mass spectrometry: Vacuum extraction of soil and plant water for stable isotope analyses. *Rapid Communications in Mass Spectrometry*, *25*(20), 3041–3048. https://doi.org/10.1002/rcm.5198

Kübert, A., Paulus, S., Dahlmann, A., Werner, C., Rothfuss, Y., Orlowski, N., & Dubbert, M. (2020). Water stable isotopes in ecohydrological field research: Comparison between in situ and destructive monitoring methods to determine soil water isotopic signatures. *Frontiers in Plant Science*, *11*, 387. https://doi.org/10.3389/fpls.2020.00387

Kühnhammer, K., Dahlmann, A., Iraheta, A., Gerchow, M., Birkel, C., Marshall, J. D., & Beyer, M. (2022). Continuous in situ measurements of water stable isotopes in soils, tree trunk and root xylem: Field approval. *Rapid Communications in Mass Spectrometry*, *36*(5), e9232. https://doi.org/10.1002/rcm.9232

Kulmatiski, A., Beard, K. H., Verweij, R. J. T., & February, E. C. (2010). A depth-controlled tracer technique measures vertical, horizontal and temporal patterns of water use by trees and grasses in a subtropical savanna. *New Phytologist*, *188*(1), 199–209. https://doi.org/10.1111/j.1469-8137.2010.03338.x

Landgraf, J., Tetzlaff, D., Dubbert, M., Dubbert, D., Smith, A., & Soulsby, C. (2022). Xylem water in riparian willow trees (*Salix alba*) reveals shallow sources of root water uptake by in situ monitoring of stable water isotopes. *Hydrology and Earth System Sciences*, *26*(8), 2073–2092. https://doi.org/10.5194/hess-26-2073-2022

Leen, B. J., Berman, E. S. F., Liebson, L., & Gupta, M. (2012). Spectral contaminant identifier for off-axis integrated cavity output spectroscopy measurements of liquid water isotopes. *Review of Scientific Instruments*, *83*(4), 044305. https://doi.org/10.1063/1.4704843

Liebhard, G., Klik, A., Stumpp, C., & Nolz, R. (2022). Partitioning evapotranspiration using water stable isotopes and information from lysimeter experiments. *Hydrological Sciences Journal*, *67*(4), 646–661. https://doi.org/10.1080/02626667.2022.2030866

Lin, Y., Clayton, R. N., & Gröning, M. (2010). Calibration of $\delta^{17}O$ and $\delta^{18}O$ of international measurement standards—VSMOW, VSMOW2, SLAP, and SLAP2: Calibration of VSMOW, VSMOW2, SLAP, and SLAP2. *Rapid Communications in Mass Spectrometry*, *24*(6), 773–776. https://doi.org/10.1002/rcm.4449

Lin, Y., & Horita, J. (2016). An experimental study on isotope fractionation in a mesoporous silica-water system with implications for vadose-zone hydrology. *Geochimica et Cosmochimica Acta*, *184*, 257–271. https://doi.org/10.1016/j.gca.2016.04.029

Lis, G., Wassenaar, L. I., & Hendry, M. J. (2008). High-precision laser spectroscopy D/H and $^{18}/^{16}O$ measurements of microliter natural water samples. *Analytical Chemistry*, *80*(1), 287–293. https://doi.org/10.1021/ac701716q

Liu, H. T., Schäufele, R., Gong, X. Y., & Schnyder, H. (2017). The $\delta^{18}O$ and $\delta^{2}H$ of water in the leaf growth-and-differentiation zone of grasses is close to source water in both humid and dry atmospheres. *New Phytologist*, *214*(4), 1423–1431. https://doi.org/10.1111/nph.14549

Maeda, M., Liyanage, B. C., & Ozaki, Y. (1999). Water collection efficiency of wick samplers under steady state flow conditions. *Soil Science and Plant Nutrition*, *45*(2), 485–492. https://doi.org/10.1080/00380768.1999.10409363

Magh, R.-K., Eiferle, C., Burzlaff, T., Dannenmann, M., Rennenberg, H., & Dubbert, M. (2020). Competition for water rather than facilitation in mixed beech-fir forests after drying-wetting cycle. *Journal of Hydrology*, *587*, 124944. https://doi.org/10.1016/j.jhydrol.2020.124944

Mahindawansha, A., Orlowski, N., Kraft, P., Rothfuss, Y., Racela, H., & Breuer, L. (2018). Quantification of plant water uptake by water stable isotopes in rice paddy systems. *Plant and Soil*, *429*(1–2), 281–302. https://doi.org/10.1007/s11104-018-3693-7

Marshall, J. D., Cuntz, M., Beyer, M., Dubbert, M., & Kuehnhammer, K. (2020). Borehole equilibration: Testing a new method to monitor the isotopic composition of tree xylem water in situ. *Frontiers in Plant Science*, *11*, 358. https://doi.org/10.3389/fpls.2020.00358

Martín-Gómez, P., Barbeta, A., Voltas, J., Peñuelas, J., Dennis, K., Palacio, S., Dawson, T. E., & Ferrio, J. P. (2015). Isotope-ratio infrared spectroscopy: A reliable tool for the investigation of plant-water sources? *New Phytologist*, *207*(3), 914–927. https://doi.org/10.1111/nph.13376

Martín-Gómez, P., Serrano, L., & Ferrio, J. P. (2017). Short-term dynamics of evaporative enrichment of xylem water in woody stems: Implications for ecohydrology. *Tree Physiology*, *37*(4), 511–522. https://doi.org/10.1093/treephys/tpw115

Matesanz, S., Escudero, A., & Valladares, F. (2009). Impact of three global change drivers on a Mediterranean shrub. *Ecology*, *90*(9), 2609–2621. https://doi.org/10.1890/08-1558.1

Matheny, A. M., Mirfedneresgi, G., & Bohrer, G. (2017). Trait-based representation of hydrological functional properties of plants in weather and ecosystem models. *Plant Diversity*. *39*(1), 1–12, https://doi.org/10.1016/j.pld.2016.10.001

Mattei, A., Barbecot, F., Guillon, S., Goblet, P., Hélie, J., & Meyzonnat, G. (2019). Improved accuracy and precision of water stable isotope measurements using the direct vapour equilibration method. *Rapid Communications in Mass Spectrometry*, *33*(20), 1613–1622. https://doi.org/10.1002/rcm.8494

Mazurek, M., Oyama, T., Wersin, P., & Alt-Epping, P. (2015). Pore-water squeezing from indurated shales. *Chemical Geology*, *400*, 106–121. https://doi.org/10.1016/j.chemgeo.2015.02.008

Meißner, M., Koehler, M., Schwendenmann, L., Hoelscher, D., & Dyckmans, J. (2014). Soil water uptake by trees using water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$)-a method test regarding soil moisture, texture and carbonate. *Plant and Soil*, *376*(1–2), 327–335. https://doi.org/10.1007/s11104-013-1970-z

Merchant, A., Callister, A., Arndt, S., Tausz, M., & Adams, M. (2007). Contrasting physiological responses of six eucalyptus species to water deficit. *Annals of Botany*, *100*(7), 1507–1515. https://doi.org/10.1093/aob/mcm234

Miguez-Macho, G., & Fan, Y. (2021). Spatiotemporal origin of soil water taken up by vegetation. *Nature*, *598*(7882), 624–628. https://doi.org/10.1038/s41586-021-03958-6

Millar, C., Janzen, K., Nehemy, M. F., Koehler, G., Hervé-Fernández, P., & McDonnell, J. J. (2021). Organic contamination detection for isotopic analysis of water by laser spectroscopy. *Rapid Communications in Mass Spectrometry*, *35*(15), e9118. https://doi.org/10.1002/rcm.9118

Millar, C., Janzen, K., Nehemy, M. F., Koehler, G., Hervé-Fernández, P., Wang, H., Orlowski, N., Barbeta, A., & McDonnell, J. J. (2022). On the urgent need for standardization in isotope-based ecohydrological investigations. *Hydrological Processes*, *36*(10), e14698. https://doi.org/10.1002/hyp.14698

Millar, C., Pratt, D., Schneider, D. J., Koehler, G., & McDonnell, J. J. (2019). Further experiments comparing direct vapor equilibration and cryogenic vacuum distillation for plant water stable isotope analysis. *Rapid Communications in Mass Spectrometry*, *33*(23), 1850–1854. https://doi.org/10.1002/rcm.8530

Millar, C., Pratt, D., Schneider, D. J., & McDonnell, J. J. (2018). A comparison of extraction systems for plant water stable isotope analysis. *Rapid Communications in Mass Spectrometry*, *32*(13), 1031–1044. https://doi.org/10.1002/rcm.8136

Moreno-Gutiérrez, C., Dawson, T. E., Nicolás, E., & Querejeta, J. I. (2012). Isotopes reveal contrasting water use strategies among coexisting plant species in a Mediterranean ecosystem. *New Phytologist*, *196*(2), 489–496. https://doi.org/10.1111/j.1469-8137.2012.04276.x

Munksgaard, N. C., Cheesman, A. W., Wurster, C. M., Cernusak, L. A., & Bird, M. I. (2014). Microwave extraction-isotope ratio infrared spectroscopy (ME-IRIS): A novel technique for rapid extraction and in-line analysis of $\delta^{18}O$ and $\delta^{2}H$ values of water in plants, soils and insects: Rapid extraction and isotope analysis of plant, soil and insect water. *Rapid Communications in Mass Spectrometry*, *28*(20), 2151–2161. https://doi.org/10.1002/rcm.7005

Munksgaard, N. C., Wurster, C. M., & Bird, M. I. (2011). Continuous analysis of $\delta^{18}O$ and δD values of water by diffusion sampling cavity ring-down spectrometry: A novel sampling device for unattended field monitoring of precipitation, ground and surface waters: Continuous analysis of $\delta^{18}O$ and δD values of water. *Rapid Communications in Mass Spectrometry*, *25*(24), 3706–3712. https://doi.org/10.1002/rcm.5282

Muñoz-Villers, L., Holwerda, F., Alvarado-Barrientos, M. S., Geissert, D. R., & Dawson, T. E. (2018). Reduced dry season transpiration is coupled with shallow soil water use in tropical montane forest trees. *Oecologia*, *118*(1), 303–317. https://doi.org/10.1007/s00442-018-4209-0

Nehemy, M. F., Benettin, P., Asadollahi, M., Pratt, D., Rinaldo, A., & McDonnell, J. J. (2021). Tree water deficit and dynamic source water partitioning. *Hydrological Processes*, *35*, e14004. https://doi.org/10.1002/hyp.14004

Nehemy, M. F., Maillet, J., Perron, N., Pappas, C., Sonnentag, O., Baltzer, J. L., Laroque, C. P., & McDonnell, J. J. (2022). Snowmelt water use at transpiration onset: Phenology, isotope tracing, and tree water transit time. *Water Resources Research*, *58*(9), e14004. https://doi.org/10.1029/2022WR032344

Nehemy, M. F., Millar, C., Janzen, K., Gaj, M., Pratt, D. L., Laroque, C. P., & McDonnell, J. J. (2019). ^{17}O-excess as a detector for co-extracted organics in vapor analyses of plant isotope signatures. *Rapid Communications in Mass Spectrometry*, *33*(16), 1301–1310. https://doi.org/10.1002/rcm.8470

Orlowski, N., & Breuer, L. (2020). Sampling soil water along the pF curve for δ^{2} H and $\delta^{18}O$ analysis. *Hydrological Processes*, *34*(25), 4959–4972. https://doi.org/10.1002/hyp.13916

Orlowski, N., Breuer, L., Angeli, N., Boeckx, P., Brumbt, C., Cook, C. S., Dubbert, M., Dyckmans, J., Gallagher, B., Gralher, B., Herbstritt, B., Herve-Fernandez, P., Hissler, C., Koeniger, P., Legout, A., Macdonald, C. J., Oyarzun, C., Redelstein, R., Seidler, C., ... McDonnell, J. J. (2018). Inter-laboratory comparison of cryogenic water extraction systems for stable isotope analysis of soil water. *Hydrology and Earth System Sciences*, *22*(7), 3619–3637. https://doi.org/10.5194/hess-22-3619-2018

Orlowski, N., Breuer, L., & McDonnell, J. J. (2016). Critical issues with cryogenic extraction of soil water for stable isotope analysis. *Ecohydrology*, *9*(1), 1–5. https://doi.org/10.1002/eco.1722

Orlowski, N., Frede, H., Bruggemann, N., & Breuer, L. (2013). Validation and application of a cryogenic vacuum extraction system for soil and plant water extraction for isotope analysis. *Journal of Sensors and Sensor Systems*, *2*(2), 179–193. https://doi.org/10.5194/jsss-2-179-2013

Orlowski, N., Pratt, D. L., & McDonnell, J. J. (2016). Intercomparison of soil pore water extraction methods for stable isotope analysis. *Hydrological Processes*, *30*(19), 3434–3449. https://doi.org/10.1002/hyp.10870

Orlowski, N., Pratt, D. L., & McDonnell, J. J. (2019). Intercomparison of soil pore water extraction methods for stable isotope analysis and interpretation of hillslope runoff sources. *Hydrological Processes*, *33*(22), 2939–2954. https://doi.org/10.1002/hyp.13539

Orlowski, N., Rinderer, M., Dubbert, M., Ceperley, N., Hrachowitz, M., Gessler, A., Rothfuss, Y., Sprenger, M., Heidbüchel, I., Kübert, A., Beyer, M., Zuecco, G., & McCarter, C. (2023). Challenges in studying water fluxes within the soil-plant-atmosphere continuum: A tracer-based perspective on pathways to progress. *Science of the Total Environment*, *881*, 163510. https://doi.org/10.1016/j.scitotenv.2023.163510

Palacio, S., Azorín, J., Montserrat-Martí, G., & Ferrio, J. P. (2014). The crystallization water of gypsum rocks is a relevant water source for plants. *Nature Communications*, *5*(1), 4660. https://doi.org/10.1038/ncomms5660

Palacio, S., Montserrat-Martí, G., & Ferrio, J. P. (2017). Water use segregation among plants with contrasting root depth and distribution along gypsum hills. *Journal of Vegetation Science*, *28*(6), 1107–1117. https://doi.org/10.1111/jvs.12570

Penna, D., Ahmad, M., Birks, S. J., Bouchaou, L., Brenčič, M., Butt, S., Holko, L., Jeelani, G., Martínez, D. E., Melikadze, G., Shanley, J. B., Sokratov, S. A., Stadnyk, T., Sugimoto, A., & Vreča, P. (2014). A new method of snowmelt sampling for water stable isotopes. *Hydrological Processes*, *28*(22), 5637–5644. https://doi.org/10.1002/hyp.10273

Penna, D., Hopp, L., Scandellari, F., Allen, S. T., Benettin, P., Beyer, M., Geris, J., Klaus, J., Marshall, J. D., Schwendenmann, L., Volkmann, T. H. M., von Freyberg, J., Amin, A., Ceperley, N., Engel, M., Frentress, J., Giambastiani, Y., McDonnell, J. J., Zuecco, G., … Kirchner, J. W. (2018). Ideas and perspectives: Tracing terrestrial ecosystem water fluxes using hydrogen and oxygen stable isotopes—Challenges and opportunities from an interdisciplinary perspective. *Biogeosciences*, *15*(21), 6399–6415. https://doi.org/10.5194/bg-15-6399-2018

Penna, D., Oliviero, O., Assendelft, R., Zuecco, G., van Meerveld, I., Anfodillo, T., Carraro, V., Borga, M., & Fontana, G. D. (2013). Tracing the water sources of trees and streams: Isotopic analysis in a small pre-alpine catchment. *Procedia Environmental Sciences*, *19*, 106–112. https://doi.org/10.1016/j.proenv.2013.06.012

Penna, D., Stenni, B., Sanda, M., Wrede, S., Bogaard, T. A., Michelini, M., Fischer, B. M. C., Gobbi, A., Mantese, N., Zuecco, G., Borga, M., Bonazza, M., Sobotkova, M., Cejkova, B., & Wassenaar, L. I. (2012). Technical note: Evaluation of between-sample memory effects in the analysis of DH and O-18 of water samples measured by laser spectroscopes. *Hydrology and Earth System Sciences*, *16*, 3925–3933. https://doi.org/10.5194/hess-16-3925-2012

Penna, D., & van Meerveld, H. J. (Ilja). (2019). Spatial variability in the isotopic composition of water in small catchments and its effect on hydrograph separation. *WIREs Water*, *6*(5), e1367. https://doi.org/10.1002/wat2.1367

Penna, D., Zanotelli, D., Scandellari, F., Aguzzoni, A., Engel, M., Tagliavini, M., & Comiti, F. (2021). Water uptake of apple trees in the Alps: Where does irrigation water go? *Ecohydrology*, *14*, 107572. https://doi.org/10.1002/eco.2306

Peters, L. I., & Yakir, D. (2008). A direct and rapid leaf water extraction method for isotopic analysis. *Rapid Communications in Mass Spectrometry*, *22*(18), 2929–2936. https://doi.org/10.1002/rcm.3692

Pinos, J., Flury, M., Latron, J., & Llorens, P. (2022). Routing stemflow water through the soil: A dual labelling approach with artificial tracers. *Hydrology and Earth System Sciences*, *27*, 2865–2881. https://doi.org/10.5194/hess-2022-382

Poyatos, R., Martínez-Vilalta, J., Čermák, J., Ceulemans, R., Granier, A., Irvine, J., Köstner, B., Lagergren, F., Meiresonne, L., Nadezhdina, N., Zimmermann, R., Llorens, P., & Mencuccini, M. (2007). Plasticity in hydraulic architecture of Scots pine across Eurasia. *Oecologia*, *153*, 245–259. https://doi.org/10.1007/s00442-007-0740-0

Pütz, T., Fank, J., & Flury, M. (2018). Lysimeters in vadose zone research. *Vadose Zone Journal*, *17*(1), 1–4. https://doi.org/10.2136/vzj2018.02.0035

Querejeta, J. I., Ren, W., & Prieto, I. (2021). Vertical decoupling of soil nutrients and water under climate warming reduces plant cumulative nutrient uptake, water-use efficiency and productivity. *New Phytologist*, *230*(4), 1378–1393. https://doi.org/10.1111/nph.17258

Reth, S., Perez-Priego, O., Coners, H., & Nolz, R. (2021). Lysimeter. In T. Foken (Ed.), *Springer handbook of atmospheric measurements* (pp. 1569–1584). Springer International Publishing. https://doi.org/10.1007/978-3-030-52171-4_58

Richards, L. A. (1931). Capillary conduction of liquids through porous mediums. *Physics*, *1*(5), 318–333. https://doi.org/10.1063/1.1745010

Rodriguez-Dominguez, C. M., Forner, A., Martorell, S., Choat, B., Lopez, R., Peters, J. M. R., Pfautsch, S., Mayr, S., Carins-Murphy, M. R., McAdam, S. A. M., Richardson, F., Diaz-Espejo, A., Hernandez-Santana, V., Menezes-Silva, P. E., Torres-Ruiz, J. M., Batz, T. A., & Sack, L. (2022). Leaf water potential measurements using the pressure chamber: Synthetic testing of assumptions towards best practices for precision and accuracy. *Plant, Cell & Environment*, *45*(7), 2037–2061. https://doi.org/10.1111/pce.14330

Rosas, T., Mencuccini, M., Barba, J., Cochard, H., Saura-Mas, S., & Martínez-Vilalta, J. (2019). Adjustments and coordination of hydraulic, leaf and stem traits along a water availability gradient. *New Phytologist*, *223*(2), 632–646. https://doi.org/10.1111/nph.15684

Rothfuss, Y., & Javaux, M. (2017). Reviews and syntheses: Isotopic approaches to quantify root water uptake: A review and comparison of methods. *Biogeosciences*, *14*(8), 2199–2224. https://doi.org/10.5194/bg-14-2199-2017

Rothfuss, Y., Vereecken, H., & Brüggemann, N. (2013). Monitoring water stable isotopic composition in soils using gas-permeable tubing and infrared laser absorption spectroscopy. *Water Resources Research*, *49*(6), 3747–3755. https://doi.org/10.1002/wrcr.20311

Sánchez-Murillo, R., Todini-Zicavo, D., Poca, M., Birkel, C., Esquivel-Hernández, G., Chavarría, M. M., Zuecco, G., & Penna, D. (2023). Dry season plant water sourcing in contrasting tropical ecosystems of Costa Rica. *Ecohydrology*, *16*, e2541. https://doi.org/10.1002/eco.2541

Santos Pires, S., Herbstritt, B., Stumpp, C., Weiler, M., & Stockinger, M. P. (2022). Influence of sample preparation procedures on water stable isotopes in plant organs using the water-vapour equilibrium method. *Ecohydrology*, *15*(4), e2444. https://doi.org/10.1002/eco.2444

Savage, M. J., Ritchie, J. T., Bland, W. L., & Dugas, W. A. (1996). Lower limit of soil water availability. *Agronomy Journal*, *88*(4), 644–651. https://doi.org/10.2134/agronj1996.00021962008800040024x

Schenk, H. J., Espino, S., Goedhart, C. M., Nordenstahl, M., Cabrera, H. I. M., & Jones, C. S. (2008). Hydraulic integration and shrub growth form linked across continental aridity gradients. *Proceedings of the National Academy of Sciences of the United States of America*, *105*(32), 11248–11253. https://doi.org/10.1073/pnas.0804294105

Schnyder, H., Schäufele, R., & Wenzel, R. (2004). Mobile, outdoor continuous-flow isotope-ratio mass spectrometer system for automated high-frequency ^{13} C- and ^{18} O-CO_2 analysis for keeling plot applications: Outdoor IMRS for automated ^{13}C and ^{18}O analysis of air CO_2. *Rapid Communications in Mass Spectrometry*, *18*(24), 3068–3074. https://doi.org/10.1002/rcm.1731

Schultz, N. M., Griffis, T. J., Lee, X., & Baker, J. M. (2011). Identification and correction of spectral contamination in $^{2}H/^{1}H$ and $^{18}O/^{16}O$ measured in leaf, stem, and soil water: Correction of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ in plant and soil water using IRIS. *Rapid Communications in Mass Spectrometry*, *25*(21), 3360–3368. https://doi.org/10.1002/rcm.5236

Scholander, P. F., Hemmingsen, E. A., Hammel, H. T., & Bradstreet, E. D. P. (1964). *Hydrostatic Pressure + Osmotic Potential in Leaves of Mangroves + Some Other Plants*, Proceedings of the National Academy of Sciences of the United States of America, *52*, 119–125, https://doi.org/10.1073/pnas.52.1.119

Skrzypek, G. (2013). Normalization procedures and reference material selection in stable HCNOS isotope analyses: An overview. *Analytical and Bioanalytical Chemistry*, *405*(9), 2815–2823. https://doi.org/10.1007/s00216-012-6517-2

Smith, A., Tetzlaff, D., Landgraf, J., Dubbert, M., & Soulsby, C. (2022). Modelling temporal variability of in situ soil water and vegetation isotopes reveals ecohydrological couplings in a riparian willow plot. *Biogeosciences*, *19*(9), 2465–2485. https://doi.org/10.5194/bg-19-2465-2022

Sparr Eskilsson, C., & Björklund, E. (2000). Analytical-scale microwave-assisted extraction. *Journal of Chromatography A*, *902*(1), 227–250. https://doi.org/10.1016/S0021-9673(00)00921-3

Sprenger, M., Herbstritt, B., & Weiler, M. (2015). Established methods and new opportunities for pore water stable isotope analysis. *Hydrological processes*, *29*(25), 5174–5192. https://doi.org/10.1002/hyp.10643

Sprenger, M., Leistert, H., Gimbel, K., & Weiler, M. (2016). Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. *Reviews of Geophysics*, *54*(3), 674–704. https://doi.org/10.1002/2015RG000515

Sprenger, M., Llorens, P., Cayuela, C., Gallart, F., & Latron, J. (2019). Mechanisms of consistently disjunct soil water pools over (pore) space and time. *Hydrological Earth Systems Sciences*, *23*, 2751–2762. https://doi.org/10.5194/hess-23-2751-2019

Sprenger, M., Tetzlaff, D., Buttle, J., Laudon, H., Leistert, H., Mitchell, C. P. J., Snelgrove, J., Weiler, M., & Soulsby, C. (2018). Measuring and modeling stable isotopes of mobile and bulk soil water. *Vadose Zone Journal*, *17*(1), 1–18. https://doi.org/10.2136/vzj2017.08.0149

Stocker, B. D., Tumber-Dávila, S. J., Konings, A. G., Anderson, M. C., Hain, C., & Jackson, R. B. (2023). Global patterns of water storage in the rooting zones of vegetation. *Nature Geoscience*, *16*, 250–256. https://doi.org/10.1038/s41561-023-01125-2

Stumpp, C., Stichler, W., Kandolf, M., & Šimůnek, J. (2012). Effects of land cover and fertilization method on water flow and solute transport in five lysimeters: A long-term study using stable water isotopes. *Vadose Zone Journal*, *11*(1). https://doi.org/10.2136/vzj2011.0075

Tetzlaff, D., Buttle, J., Carey, S. K., McGuire, K., Laudon, H., & Soulsby, C. (2014). Tracer-based assessment of flow paths, storage and runoff generation in northern catchments: A review. *Hydrological Processes*, *29*(16), 3475–3490. https://doi.org/10.1002/hyp.10412

Thibault, D. H., & Sheppard, M. I. (1992). A disposable system for soil pore-water extraction by centrifugation. *Communications in Soil Science and Plant Analysis*, *23*(13–14), 1629–1641. https://doi.org/10.1080/00103629209368692

Thomas, E. M., Lin, H., Duffy, C. J., Sullivan, P. L., Holmes, G. H., Brantley, S. L., & Jin, L. (2013). Spatiotemporal patterns of water stable isotope compositions at the Shale Hills Critical Zone Observatory: Linkages to subsurface hydrologic processes. *Vadose Zone Journal*, *12*(4), 1–16. https://doi.org/10.2136/vzj2013.01.0029

Tolk, J. A., & Evett, S. R. (2012). Lower limits of crop water use in three soil textural classes. *Soil & Water Management & Conservation*, *76*(2), 607–616. https://doi.org/10.2136/sssaj2011.0248

Treydte, K., Lehmann, M. M., Wyczesany, T., & Pfautsch, S. (2021). Radial and axial water movement in adult trees recorded by stable isotope tracing. *Tree Physiology*, tpab080, *41*, 2248–2261. https://doi.org/10.1093/treephys/tpab080

Vadibeler, D., Stockinger, M. P., Wassenaar, L. I., & Stumpp, C. (2022). Influence of equilibration time, soil texture, and saturation on the accuracy of porewater water isotope assays using the direct $H_2O_{(liquid)}$–$H_2O_{(vapor)}$ equilibration method. *Journal of Hydrology*, *607*, 127560. https://doi.org/10.1016/j.jhydrol.2022.127560

van Geldern, R., & Barth, A. C. (2012). Optimization of instrument setup and postrun corrections for oxygen and hydrogen stable isotope measurements of water by isotope ratio infrared spectroscopy (IRIS). *Limnology and Oceonography: Methods*, *10*, 1024–1036. https://doi.org/10.4319/lom.2012.10.1024

Van Looy, K., Bouma, J., Herbst, M., Koestel, J., Minasny, B., Mishra, U., Montzka, C., Nemes, A., Pachepsky, Y. A., Padarian, J., Schaap, M. G., Tóth, B., Verhoef, A., Vanderborght, J., Ploeg, M. J., Weihermüller, L., Zacharias, S., Zhang, Y., & Vereecken, H. (2017). Pedotransfer functions in earth system science: Challenges and perspectives. *Reviews of Geophysics*, *55*(4), 1199–1256. https://doi.org/10.1002/2017RG000581

Vandegehuchte, M. W., & Steppe, K. (2013). Sap-flux density measurement methods: Working principles and applicability. *Functional Plant Biology*, *40*(3), 213–223. https://doi.org/10.1071/FP12233

Volkmann, T. H. M., & Weiler, M. (2014). Continual in situ monitoring of pore water stable isotopes in the subsurface. *Hydrology and Earth System Sciences*, *18*(5), 1819–1833. https://doi.org/10.5194/hess-18-1819-2014

Wang, A., Siegwolf, R. T. W., Joseph, J., Thomas, F. M., Werner, W., Gessler, A., Rigling, A., Schaub, M., Saurer, M., Li, M.-H., & Lehmann, M. M. (2021). Effects of soil moisture, needle age and leaf morphology on carbon and oxygen uptake, incorporation and allocation: A dual labeling approach with $^{13}CO_2$ and $H_2{}^{18}O$ in foliage of a coniferous forest. *Tree Physiology*, *41*(1), 50–62. https://doi.org/10.1093/treephys/tpaa114

Wang, S. F., Gao, X. D., Yang, M., Huo, G. P., Song, X. L., Siddique, K. H. M., Wu, P. T., & Zhao, X. N. (2023). The natural abundance of stable water isotopes method may overestimatedeep-layer soil water use by trees. *Hydrology and Earth System Sciences*, *27*, 123–137. https://doi.org/10.5194/hess-27-123-2023

Wang, X., Jansen, H. G., Duin, H., & Meijer, H. A. J. (2021). Measurement of $\delta^{18}O$ and $\delta^{2}H$ of water and ethanol in wine by off-axis integrated cavity output spectroscopy and isotope ratio mass spectrometry. *European Food Research and Technology*, *247*(8), 1899–1912. https://doi.org/10.1007/s00217-021-03758-2

Wassenaar, L., Terzer-Wassmuth, S., & Douence, C. (2021). Progress and challenges in dual- and triple-isotope ($\delta^{18}O$, δ^{2} H, $\Delta^{17}O$) analyses of environmental waters: An international assessment of laboratory performance. *Rapid Communications in Mass Spectrometry*, *35*(24), e9193. https://doi.org/10.1002/rcm.9193

Wassenaar, L. I., Hendry, M. J., Chostner, V. L., & Lis, G. P. (2008). High resolution pore water $\delta^{2}H$ and $\delta^{18}O$ measurements by $H_2O_{(liquid)}-H_2O_{(vapor)}$ equilibration laser spectroscopy. *Environmental Science & Technology*, *42*(24), 9262–9267. https://doi.org/10.1021/es802065s

Wassenaar, L. I., Terzer-Wassmuth, S., Douence, C., Araguas-Araguas, L., Aggarwal, P. K., & Coplen, T. B. (2018). Seeking excellence: An evaluation of 235 international laboratories conducting water isotope analyses by isotope-ratio and laser-absorption spectrometry. *Rapid Communications in Mass Spectrometry*, *32*(5), 393–406. https://doi.org/10.1002/rcm.8052

Weihermüller, L., Siemens, J., Deurer, M., Knoblauch, S., Rupp, H., Göttlein, A., & Pütz, T. (2007). In situ soil water extraction: A review. *Journal of Environmental Quality*, *36*(6), 1735–1748. https://doi.org/10.2134/jeq2007.0218

Werner, C., Meredith, L. K., Ladd, S. N., Ingrisch, J., Kübert, A., van Haren, J., Bahn, M., Bailey, K., Bamberger, I., Beyer, M., Blomdahl, D., Byron, J., Daber, E., Deleeuw, J., Dippold, M. A., Fudyma, J., Gil-Loaiza, J., Honeker, L. K., Hu, J., … Williams, J. (2021). Ecosystem fluxes during drought and recovery in an experimental forest. *Science*, *374*(6574), 1514–1518. https://doi.org/10.1126/science.abj6789

West, A. G., Goldsmith, G. R., Brooks, P. D., & Dawson, T. E. (2010). Discrepancies between isotope ratio infrared spectroscopy and isotope ratio mass spectrometry for the stable isotope analysis of plant and soil waters: Discrepancies between IRIS and IRMS analysis of plant and soil waters. *Rapid Communications in Mass Spectrometry*, *24*(14), 1948–1954. https://doi.org/10.1002/rcm.4597

West, A. G., Goldsmith, G. R., Matimati, I., & Dawson, T. E. (2011). Spectral analysis software improves confidence in plant and soil water stable isotope analyses performed by isotope ratio infrared spectroscopy (IRIS): Plant and soil water stable isotope analyses performed by IRIS. *Rapid Communications in Mass Spectrometry*, *25*(16), 2268–2274. https://doi.org/10.1002/rcm.5126

West, A. G., Patrickson, S. J., & Ehleringer, J. R. (2006). Water extraction times for plant and soil materials used in stable isotope analysis. *Rapid Communications in Mass Spectrometry*, *20*(8), 1317–1321. https://doi.org/10.1002/rcm.2456

Xiang, W., Si, B. C., Li, M., Li, H., Lu, Y. W., Zhao, M. H., & Feng, H. (2021). Stable isotopes of deep soil water retain long-term evaporation loss on China's Loess Plateau. *Science of the Total Environment*, *784*, 147153. https://doi.org/10.1016/j.scitotenv.2021.147153

Yang, B., Wen, X., & Sun, X. (2015). Seasonal variations in depth of water uptake for a subtropical coniferous plantation subjected to drought in an East Asian monsoon region. *Agricultural and Forest Meteorology*, *201*, 218–228. https://doi.org/10.1016/j.agrformet.2014.11.020

Zadeh, L. A. (2005). Toward a generalized theory of uncertainty (GTU)—An outline. *Information Sciences*, *172*(1–2), 1–40. https://doi.org/10.1016/j.ins.2005.01.017

Zhao, L., Wang, L., Cernusak, L. A., Liu, X., Xiao, H., Zhou, M., & Zhang, S. (2016). Significant difference in hydrogen isotope composition between xylem and tissue water in *Populus euphratica*. *Plant, Cell & Environment*, *39*(8), 1848–1857. https://doi.org/10.1111/pce.12753

Zhao, L., Xiao, H., Zhou, J., Wang, L., Cheng, G., Zhou, M., Yin, L., & McCabe, M. F. (2011). Detailed assessment of isotope ratio infrared spectroscopy and isotope ratio mass spectrometry for the stable isotope analysis of plant and soil waters: Comparison of IRIS and IRMS analysis. *Rapid Communications in Mass Spectrometry*, *25*(20), 3071–3082. https://doi.org/10.1002/rcm.5204

Zimmermann, U., Münnich, K. O., & Roether, W. (2013). Downward movement of soil moisture traced by means of hydrogen isotopes. In G. E. Stout (Ed.), *Geophysical monograph series* (pp. 28–36). American Geophysical Union. https://doi.org/10.1029/GM011p0028

Zuecco, G., Amin, A., Frentress, J., Engel, M., Marchina, C., Anfodillo, T., Borga, M., Carraro, V., Scandellari, F., Tagliavini, M., Zanotelli, D., Comiti, F., & Penna, D. (2022). A comparative study of plant water extraction methods for isotopic analyses: Scholander-type pressure chamber vs. cryogenic vacuum distillation. *Hydrology and Earth System Sciences*, *26*(13), 3673–3689. https://doi.org/10.5194/hess-26-3673-2022

Zweifel, R., Haeni, M., Buchmann, N., & Eugster, W. (2016). Are trees able to grow in periods of stem shrinkage? *New Phytologist*, *211*(3), 839–849. https://doi.org/10.1111/nph.13995

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APPENDIX

TABLE A1 Overview of centrifugation applications for isotope analysis and applied settings.

Centrifuge type	Sample type	Sample amount (g)	Extraction time (min)	Extraction temperature (°C)	Force (rpm)	Reference
Sorvall Legend RT+ (Thermo Fisher Scientific, Waltham, MA; USA)	Loamy sands, sand	11, 18	3 × 15	20	5000	Adams et al., 2020
Sorvall RC 5B Plus centrifuge fitted with a Sorvall aluminum rotor with four stainless-steel sleeves designed for 50-mL Falcon tubes (Sorvall, Newton, CT, USA)	Sandy loam	18–30 (soil wetted to near saturation)	"Low" matric potential (≈0.016 MPa): 180; "mid" potential (≈1.14 MPa): 240	All <25	"Low" matric potential 950; "mid" potential: 8000	Bowers et al., 2020
Thermo Scientific Multifuge 1S (Thermo Scientific, Waltham, MA; USA)	Different grass species and a melon plant	5 (grounded plant material)	30	21	5000	Fischer et al., 2019
Fresco 21 Microcentrifuge (Thermo Scientific, Waltham, MA; USA)	Two histosols, two podzols (Bruntland Burn catchment, UK)	0.12–0.2 (organic soils); 1.5–2.5 (mineral soils)	60	5	6300, 11,700, and 14,700	Geris et al., 2015
High-speed centrifuge[a]	Clay-rich till soils from the Battleford Formation and the Upper Floral Formation (Saskatchewan, CA)	50 mm × 60 mm cores[a]	1.440–2.880	21	4000–10,000	Kelln et al., 2001
Eppendorf centrifuge model 5804 (Eppendorf Corp., Hamburg, DE)	Heads, leaves, stems and roots from spring wheat	9 (head), 7 (leaf), 9 (stem), 14 (root)	30; second step to remove particulate matter: 60	Both 4	10,000; second step to remove particulate matter: 11,000	Millar et al., 2018
Eppendorf centrifuge model 5804 (Eppendorf Corp., Hamburg, DE)	Clayey loam, silty sand	40 (8, 20, 30% vol. water content)	15	4	5000	Orlowski, Breuer, et al., 2016
Beckman Coulter centrifuge (Avanti JXN-26, Beckman Coulter Inc., DE)	Ground basaltic tephra with a loamy sand	50	30	4	5000	Orlowski et al., 2019
Sorvall Superspeed RC2-B centrifuge, (Thermo Scientific, Waltham, MA, USA)	Different species' leaf samples	1.5–2.5 (dependent on succulence)	10	4	10,000	Peters & Yakir, 2008

[a]No further information is available.