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Insights into tension-mediated and antecedent water effects on soil water isotopic composition

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Abstract

Using isotopic spike experiments, we investigated the existence and magnitude of soil-mediated isotopic effects and of the interaction between isotopically distinct soil water pools, both associated in isotopic mismatches between water extracted from soil and soil water taken up by the roots. For this, we applied and compared four established techniques commonly used for the extraction of water (vapor) from soil, three of them relying on destructive soil sampling (cryogenic vacuum distillation, centrifugation, and direct water vapor equilibration), and one being a nondestructive in situ online technique. We observed an almost complete mixing of sequentially added, isotopically distinct water samples to a pure quartz sand (memory effect). The isotopic composition of water held at high soil tension in the pure quartz sand (pF = 2) as well as in a sandy soil (pF = 1.8 and 3) deviated considerably from that of the added water (tension effect). However, we could attribute this deviation not exclusively to a soil-mediated effect but also to methodological shortcomings during our experiments. Finally, we found the following decreasing trend in precision as well as in accuracy of the used water extraction methods: in situ online > centrifugation > direct water vapor equilibration > cryogenic vacuum distillation. The investigation of isotopic fractionation of soil water due to physicochemical processes in soil can be facilitated if the experimental techniques used do not involve isotopic fractionation. In addition, methodological uncertainties and inaccuracies can be minimized by method standardization, increasing the potential of water stable isotopic monitoring in ecohydrological studies.

Abbreviations: CF, centrifugation; CRDS, cavity ring-down spectrometer; CVD, cryogenic vacuum distillation; DVE, direct water vapor equilibration; IS, in situ online method; MFC, mass flow controller; PC, pressure controller; PPE, pressure plate extractor; PVC, polyvinyl chloride; RC, repeatability coefficient; SV, soil-filled vessels; WV, water-filled vessels.

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1 | INTRODUCTION

Using the hydrogen and oxygen isotopic composition (δ^2H and δ^{18}O) of soil water to determine the spatial distribution of vegetation water use relies on a series of important assumptions (Rothfuss & Javaux, 2017) and is affected by non-negligible uncertainties (Millar et al., 2022). One of the main sources of uncertainties when quantifying spatio-temporal patterns of water use by comparing the isotopic composition of soil and xylem water is associated with the step of water extraction. This is typically done retrospectively in the laboratory using a range of methods including cryogenic vacuum extraction (Orlowski et al., 2013), centrifugation (Walker et al., 1994), or direct water vapor equilibration (Wassenaar et al., 2008). The isotopic composition of soil water may not be conserved during extraction because of, for example, an incomplete water recovery or occurrence of the disequilibrium phase change (evaporation). One of the most popular experiments to identify and quantify the uncertainty associated with one particular water extraction method is so-called "spike experiments." These experiments consist of adding water of known isotopic composition (i.e., spike water) to a dry soil sample, extract water from the sample using one of the aforementioned methods, and analyze its isotopic composition to determine if it is conserved, that is, if it is equal to that of the spike water.

In the majority of the methodologically diverse spike experiments—the study of Goebel and Lascano (2012) being an exception—the isotopic composition of extracted soil water differs from the isotopic composition of the spike water (e.g., Bowers et al., 2020; Figueroa-Johnson et al., 2007; Newberry, Nelson, et al., 2017; Orlowski et al., 2013; Orlowski, Pratt, et al., 2016; Thielemann et al., 2019; Walker et al., 1994). Even a small amount of residual soil water—very difficult to eliminate, likely heavily fractionated and therefore isotopically different from the spike water—was potentially mixed with the newly added water, resulting in an observed isotopic mismatch (e.g., Thielemann et al., 2019; Wen et al., 2021), or as Newberry, Prechsi, et al. (2017) called it, an "isotopic memory effect."

Partly as a result of this observation, some have investigated the mixing of and equilibrium time between isotopically distinct soil water pools that may co-occur in the soil (e.g., Sprenger et al., 2018) held at different tension values (e.g., Gaj & McDonnell, 2019; Orlowski & Breuer, 2020). In structured soil, it has been shown that water fluxes could be conceptualized as flow in and between two fractions of water: an immobile one located in finer pores within aggregates, having a significantly lower velocity than the other, and the mobile pool in larger pores between aggregates (De Smedt & Wierenga, 1979; Gaudet et al., 1977; Gerke & van Genuchten, 1993). More recently, researchers using water stable isotopes have proposed this concept as a mechanism for preferential

Core Ideas

- There was almost complete mixing of pre-existing and newly added water in quartz sand.
- The isotopic composition of soil water in a sandy soil changed as a function of modeled soil water potential.
- There were considerable measurement differences between four isotopic methods.

flow at larger scales (at the watershed and global scale, e.g., Bowling et al., 2017; Brooks et al., 2010; Evaristo et al., 2015). The spatially heterogeneous distribution of soil water isotopic composition has been explicitly linked to the "moisture history" (Newberry, Prechsi, et al., 2017), that is, the contribution of "new" and "old" water (i.e., antecedent) to the mobile and immobile water pools. In addition to the effect of an incomplete mixing of water within the soil pore space, the nature of soil particles and the chemical properties of the liquid phase may result in isotopic fractionation and lead to a heterogeneous distribution of the isotopic composition of soil water (e.g., Meißner et al., 2014; Orlowski, Breuer, et al., 2016 ; Richard et al., 2007).

Describing mixing or fractionating processes in the soil is a prerequisite for the quantification of root water uptake using water stable isotopic monitoring. Nevertheless, the abovementioned methodological uncertainties make the interpretation of the results of experiments, aiming at determining soil-related fractionating effects, challenging. If water isotopic fractionation is observed, is it a result of the extraction technique or can it undoubtedly be traced to soil physicochemical properties and processes that should be considered in root water uptake quantification studies?

Our research questions were as follows: (i) How well does antecedent and newly added water mix within a soil sample? (ii) Excluding soil-chemistry-related processes, is the isotopic composition of soil water mainly a function of soil water tension? (iii) Does the isotopic composition of extracted soil water match that of spike water? Our null hypotheses were as follows: (a) two isotopically distinct water sources successively added to an isotopically inert soil (i.e., a soil, the properties of which do not lead to any quantifiable isotopic effect on pore space water) mix completely; (b) the isotopic composition of extracted soil water is independent from soil water tension in that same inert soil and equals that of the added (spike) water; and (c) the isotopic composition of water extracted using a range of techniques is comparable (i.e., the differences observed are <1‰ in δ^2H and <0.5‰ in δ^{18}O).

To test null hypothesis (a), we compared the measured isotopic composition of soil water in a pure quartz sand

after two successive saturation-desaturation cycles (one with deionized tap water and one with isotopically enriched water) with the theoretical value of perfectly mixed soil water. To test null hypothesis (b), we compared the isotopic composition of soil water in a standard soil classified as a sand near saturation, at pF = 1.8, and near residual water content (pF = 3) with the isotopic composition of the added water. Finally, to test null hypothesis (c), we compared the isotopic composition of soil water recovered with four methods: cryogenic vacuum distillation (CVD), centrifugation (CF), direct water vapor equilibration (DVE), and a nondestructive in situ online method (IS; Rothfuss et al., 2013), which is similar in its prerequisites and assumptions to the DVE method.

2 | MATERIALS AND METHODS

The experiments were conducted in custom-made acrylic glass vessels (Figure 1a) (301.6 cm^3 inner volume), each consisting of one upper and one lower part attached together. The upper part, in which the soil was placed, was equipped with two 1/8 in. openings, one inlet and one outlet, both connected to a 19-cm-long piece of gas-permeable polypropylene tubing (0.155 cm wall thickness, 0.55 cm inner diameter, 0.86 cm outer diameter, 0.2 μm pore size; Katmaj Filtration) for the sampling of the soil water vapor. The lower part of the vessel included a membrane of regenerated cellulose (diameter = 33.02 cm; pore size = 24 Å; Soilmoisture Equipment Corp.) supported by a stainless steel mesh. Underneath the steel mesh, a hollow space connected to one stainless steel outlet was designed to collect liquid soil water. In the center of the vessel lid, a 1/8 in. opening allowed the soil pore air to exit the vessel during the saturation with water through the membrane (Figure 1a).

2.1 | Continuous isotopic monitoring: Pressure-extraction of water

With this method (Figure 1c), soil water from the vessels was pushed through the membrane by applying pressure inside the extractor with dry synthetic air (20.5% O$_2$ in N$_2$ with ∼20–30 ppmv water vapor; Air Liquide). The method is based on the principle that at equilibrium, the soil water tension reaches a value equal to the opposite of the pressure set inside the extractor and water collection ends. For this, two types of pressure plate extractors were used: two 5-bar maximum pressure and two 15-bar maximum pressure (Soilmoisture Equipment Corp.). Custom-designed polypropylene pierced screws were used to seal the three vessel openings (center of the lid, inlet, and outlet of the permeable tubing, Figure 1a) during pressure-mediated extraction. These pierced screws

allowed the pressure inside the vessel to equilibrate with that outside the vessel (i.e., inside the pressure plate extractor), while minimizing soil water evaporation. The stainless steel tubing connecting the hollow space underneath the membrane with the outside of the vessel was attached inside the extractor with one of the outlets of the extractor (the 5-bar extractors had two and the 15-bar extractors had four). The extractor outlet, through which the extracted water was transferred, was equipped with a 1/16 in. diameter needle, which perforated a piece of Parafilm covering a glass beaker, in which extracted soil water was collected.

2.2 | Discrete isotopic measurements

The hydrogen and oxygen isotopic compositions (δ^2H and δ^{18}O) of soil water extracted under pressure (Section 2.1) were compared to those determined with in situ online (i.e., nondestructively) and with the following destructive techniques: CVD, CF, and DVE.

2.2.1 | In situ online isotopic analysis

Prior to the in situ isotopic measurement, the vessel with soil and added moisture was placed in a water bath at a constant temperature of 19°C for 4 days to ensure thermodynamic equilibrium between soil water and its vapor (Figure 1b). The in situ isotopic measurement was then conducted three times on three different days. Each time, the water vapor inside the gas-permeable tubing in each vessel was flushed at a low flow rate (100 mL min^{-1}) with synthetic dry air (20.5% O$_2$ in N$_2$ with 20–30 ppmv water vapor; Air Liquide) and directed to a cavity ring-down spectrometer (CRDS, L2130-i; Picarro). The soil water vapor was sampled until constant δ^2H and δ^{18}O readings were observed (standard deviations <0.7% and <0.2% for δ^2H and δ^{18}O, respectively; Rothfuss et al., 2013), which was usually the case after ∼30 min. The δ-value of soil liquid water in the vessel was calculated from the δ-value of the soil water vapor averaged over the last 5.5 min of online measurements (yielding exactly 330 measurements with the abovementioned standard deviation) and the soil temperature (assumed to be 19°C, i.e., that of the water bath) considering thermodynamic equilibrium between the liquid and gas phase. Then, it was calibrated against measurements of two soil water vapor standards. These standards consisted of acrylic glass vessels, different in design from those used in the water extraction (see Rothfuss et al., 2013), also incorporating the gas-permeable tubing, and filled with the same soil type as the vessels. One standard was saturated with isotopically depleted water (i.e., melted ice; δ^2H = −78.8 ± 0.4‰ and δ^{18}O = −18.9 ± 0.1‰), and the other with isotopically enriched water (i.e., evaporated water; δ^2H = 7.7 ± 0.6‰ and
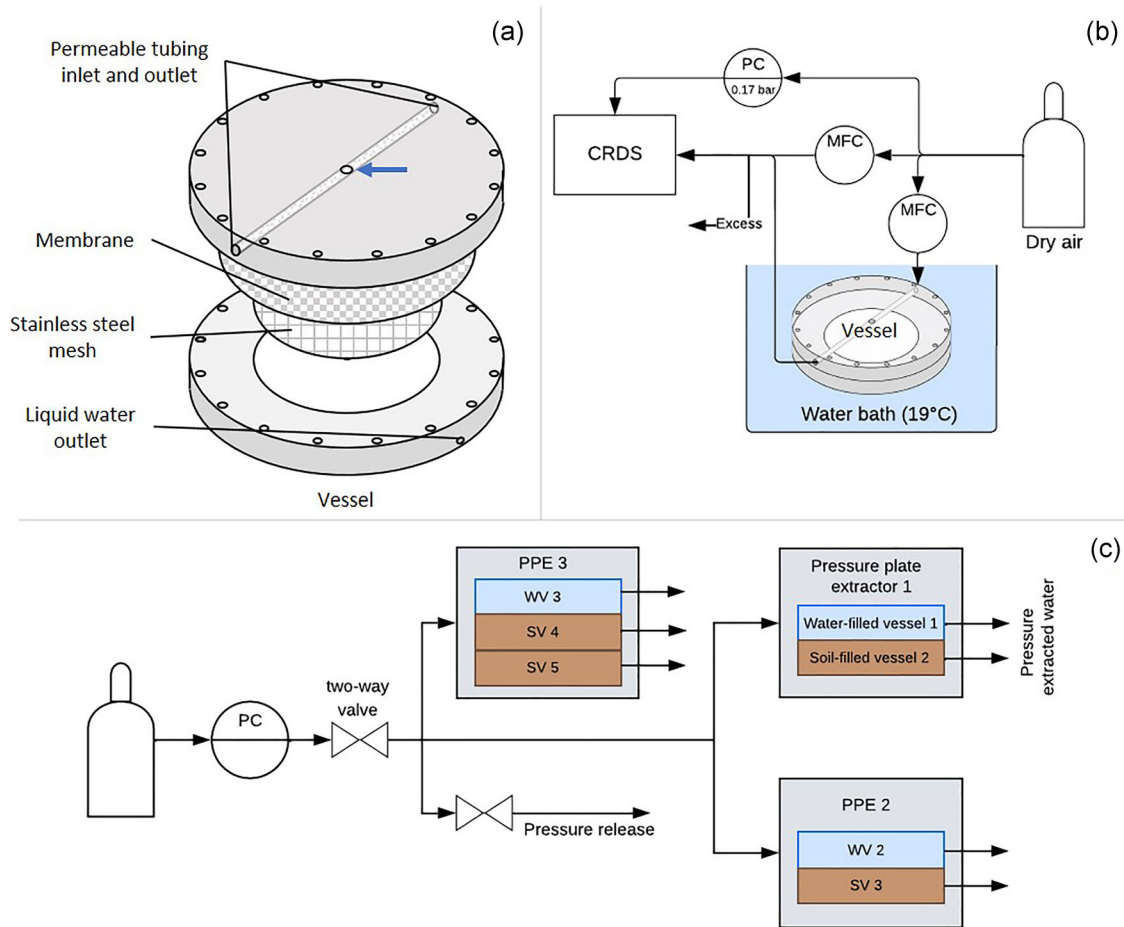
FIGURE 1 (a) Elements of the custom-made acrylic glass vessel, (b) principle of the in situ online method, and (c) scheme of the system to extract soil water by increasing the soil water tension (ψ, pF) inside the vessels with two types of pressure plate extractors. A blue arrow in (a) indicates the opening in the upper part of the vessels, allowing increasing the soil tension. The two-way valve marked as pressure release in (c) was closed during the water extraction and was opened once equilibrium between the pressure applied and soil water tension was reached to release the dry air inside the extractors and be able to open them. CRDS, cavity ring-down spectrometer; MFC, mass flow controller; PC, pressure controller (pressure range during the experiments: 0.01–0.1 MPa); PPE, pressure plate extractor; SV and WV, soil-filled (brown) and water-filled (blue) vessels.

$\delta^{18}O = 10.4 \pm 0.1‰$). The soil water vapor in the standards was sampled and measured twice before and twice after the vapor in the vessels.

2.2.2 | Cryogenic vacuum distillation

Soil samples (20 g each) were processed in two locations, namely, the Chair of Ecosystem Physiology at University of Freiburg (extraction temperature = 95–98˚C; duration = 1.5 h) and the Institute for Landscape Ecology and Resources Management at the Justus Liebig University Giessen, according to Orlowski et al. (2013) (extraction temperature > 90˚C; duration = 4 h). The isotopic composition of the extracted water was determined offline via CRDS (L2120-*i*, Picarro; long-term precision = 1‰ and 0.5‰ for δ^2H and $\delta^{18}O$, respectively) at the Insti-

tute for Bio- and Geosciences, Agrosphere (IBG-3) at Forschungszentrum Jülich. The extraction efficiency in all but three samples was above 98% (Araguás-Araguás et al., 1995).

2.2.3 | Centrifugation

Soil samples (40 g each) were placed in custom-made polyvinyl chloride (PVC) centrifuge tubes, sealed with plastic plugs to avoid soil water evaporation, placed in a centrifuge (6K15; Sigma Laborzentrifugen GmbH) and spun at 10,000 *g* forces (equivalent to a soil tension of ∼2.1 MPa) for 20 min at 20˚C together with water-filled tubes used as controls. The isotopic composition of the water used for the controls was measured before and after centrifugation to ensure that no isotopic fractionation occurred during the handling and

centrifugation of the samples. Isotopic analyses were performed via CRDS (L2120-*i*, Picarro).

2.2.4 | Direct water vapor equilibration

Soil samples (100 g each) were placed in stand-up pouches (i.e., sample pouches) with zip-seal locks (152 × 98 × 229 mm; WEBER Packaging GmbH). Additionally, six pouches were filled each with 10 mL of deionized local tap water ($\delta^2H = -51.8 \pm 0.4‰$ and $\delta^{18}O = -7.8 \pm 0.1‰$) and six with 10 mL of evaporated water ($\delta^2H = 7.7 \pm 0.6‰$ and $\delta^{18}O = 10.4 \pm 0.1‰$) and were used as isotopic standards (i.e., standard pouches). Sample and standard pouches were inflated with dry air, and their tops were sealed with hot pliers (WEBER Packaging GmbH). A small amount of silicon (transparent sanitary silicon; OBI, Germany) was placed on an upper section of each sample and standard pouch to serve as septum. All pouches were then stored for 4 days so that isotopic equilibrium between (soil) water and the headspace water vapor was reached. On the day of measurement, the pouches were pierced through the silicon septum with a needle attached to a piece of 1/8 in. polytetrafluoroethylene tubing connected to a CRDS (L2130-*i*, Picarro) for online isotopic analysis for ~15 min. The δ-value of the soil water in the sample pouches was calculated using the last 2 min of recorded raw soil water vapor δ-data considering thermodynamic equilibrium at the observed laboratory temperature (Sprenger et al., 2015; Wassenaar et al., 2008) and calibrated against the δ-values of the standard pouches. The mean standard deviation of the water vapor measurements in the standard pouches was $0.4 \pm 0.2‰$ for δ^2H and $0.1 \pm 0.0‰$ for $\delta^{18}O$. In the sample pouches, these values were $0.5 \pm 0.1‰$ for δ^2H and $0.1 \pm 0.0‰$ for $\delta^{18}O$.

2.3 | Experimental protocols: "Memory effect" and "tension effect" experiments

2.3.1 | Memory effect experiment

The memory effect experiment consisted of two consecutive saturation/pressure-extraction stages (stages A and B, left panel in Figure 2). In stage A step I, five custom-made vessels (numbered 1 to 5) were filled and packed with quartz sand (grain size distribution between 0.72 and 0.18 mm; Quarzwerke Frechen; mean dry bulk density = 1.67 ± 0.01 g cm^{-3}) and saturated from the bottom through the membrane with deionized local tap water ($\delta^2H = -51.8 \pm 0.4‰$ and $\delta^{18}O = -7.8 \pm 0.1‰$) to a mean volumetric soil water content (θ) of 0.35 ± 0.01 cm^3 cm^{-3}. Following saturation, the isotopic composition of soil water in vessels 1–5 was determined with the in situ online method (IS, step II), and a total of

nine samples intended for the destructive water recovery techniques (i.e., three for CVD, three for CF, and three for DVE) were taken from vessel 1. Subsequently, the four remaining vessels (2–5) were placed in pressure plate extractors with three vessels containing 100 mL of tap water each (step III). These water-filled vessels served as controls to verify that water was extracted free of fractionation. An air pressure of 0.01 MPa (corresponding to a soil water tension pF value of 2) was applied to extract (soil) liquid water. At this pressure, almost all soil water should have been extracted (discontinuous line in Figure 3). After 47 days, equilibrium was reached, and no more water was collected from the vessels. After this first extraction, mean θ across vessels was 0.04 ± 0.01 cm^3 cm^{-3} (determined gravimetrically). In step IV, the soil water isotopic composition in vessels 2–5 was measured with IS. Soil from vessel 2 was then sampled for destructive isotopic determinations.

In stage B of the experiment, vessels 3–5 were re-saturated (mean θ = 0.33 ± 0.01 cm^3 cm^{-3}) with isotopically enriched water (step V; $\delta^2H = 29.0 \pm 0.5‰$ and $\delta^{18}O = 15.7 \pm 0.0‰$). After 4 days, the isotopic composition of the soil water in these vessels was determined with IS, and the soil in vessel 3 was destructively sampled (step VI). Vessels 4 and 5 were then placed again in the extractors with two control vessels, one containing 100 mL and the other 180 mL of the isotopically enriched water (step VII). The same air pressure (i.e., 0.01 MPa, pF = 2) was applied, and the time to reach equilibrium and the final mean θ were 35 days and 0.04 ± 0.00 cm^3 cm^{-3}, respectively. Finally, the isotopic composition of soil water in vessels 4–5 was measured with IS, and the soil in vessel 4 was destructively sampled (step VIII).

2.3.2 | Tension effect experiment

Possible tension-mediated isotopic effects were investigated using a two-step pressure extraction process (stages A and B, right panel in Figure 2), but in contrast to the memory effect experiment without re-saturation at the end of stage A. The experiment was conducted using a soil classified as a sand (standard soil 2.1, particle size distribution = 84.7% 2–0.063 mm, 11.4% 0.063–0.002 mm, 3.9% <0.002 mm; LUFA Speyer). In step I, nine custom-made vessels (numbered 1–9) were filled and packed with air-dried and homogenized sand (dry bulk density = 1.53 ± 0.02 g cm^{-3}) and saturated with deionized local tap water (θ = 0.39 ± 0.03 cm^3 cm^{-3}, δ^2H = $-51.0 \pm 0.4‰$ and $\delta^{18}O = -7.7 \pm 0.1‰$). The isotopic composition of the soil water in vessels 1–9 was measured with IS and the soil in vessel 1 was sampled for the different water recovery techniques in triplicates (step II), similar to the memory effect experiment. The remaining eight vessels (2–9) were placed in pressure plate extractors, and 0.006 MPa pressure was applied (step III). This pressure corresponded to a
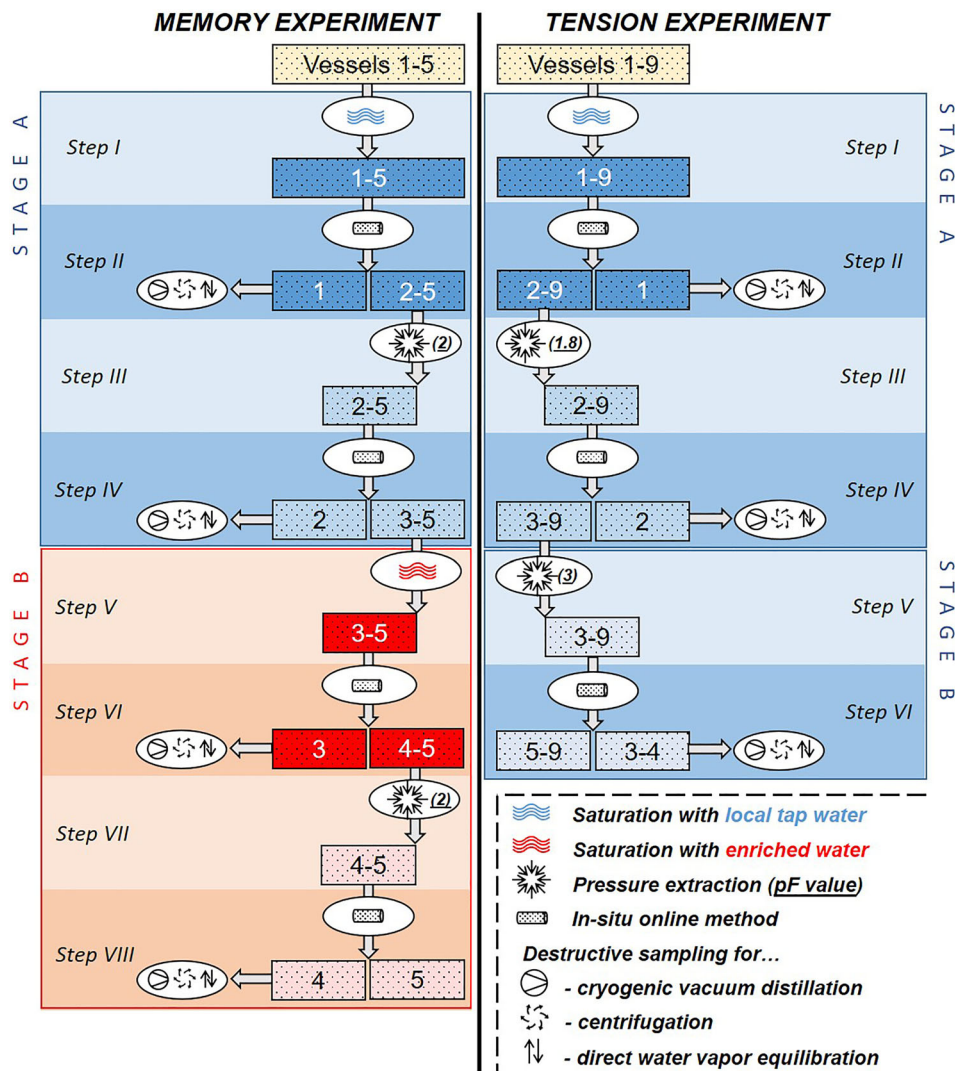
FIGURE 2 Stages and steps of the memory effect and tension effect experiments. Numbers in boxes refer to the vessels, while symbols in circles refer to the action performed (i.e., water saturation, pressure-extraction of water, in situ online isotopic analysis, and sampling for destructive water recovery techniques). The background color refers to the isotopic composition of the water in the vessels: blue shades for tap water and orange shades for isotopically enriched water.

soil tension pF of ∼1.8 and was necessary to extract 50% of the soil water inside the vessels (continuous line in Figure 3). Two control vessels containing 100 mL of deionized tap water ($\delta^2H = -51.0 \pm 0.4‰$ and $\delta^{18}O = -7.7 \pm 0.1‰$) were also placed in the extractors. Equilibrium was reached after 30 days of extraction with a final mean θ of 0.29 ± 0.03 cm^3 cm^{-3}. The isotopic composition of the soil water in vessels 2–9 was determined with IS, and the soil in vessel 2 was destructively sampled (step IV). In stage B, vessels 3–9 were placed again in the pressure plate extractors with two control vessels containing 200 mL of deionized tap water, and a pressure of 0.1 MPa (pF = 3) was applied (step V). Since more water was extracted from the control vessels at a higher pressure, more water had to be added to these so that the extraction

period of the controls was as long as that of the soil vessels. After 14 days, equilibrium was reached ($\theta = 0.09 \pm 0.08$ m^3 m^{-3}), the isotopic composition of soil water in vessels 3–9 was determined with IS, and the soil in vessels 3 and 4 was destructively sampled (step VI).

For stages A and B of the memory effect experiment and for stage A of the tension effect experiment (soil saturated or partly filled with local tap water of isotopic composition $\delta_{tap\,water}$), we express the isotopic composition of the water extracted ($\delta_{extracted\,water}$, determined either nondestructively with the pressure plate extractors and IS or destructively) relative to $\delta_{tap\,water}$ using the Δ notation (Equation 1a):

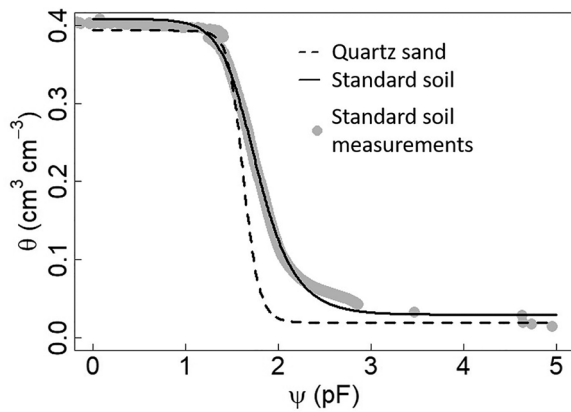$$\Delta = \delta_{extracted\,water} - \delta_{tap\,water}. \quad (1a)$$

FIGURE 3 Water retention curve for quartz sand (discontinuous line), fitted water retention curve for the standard soil classified as a sand (continuous line), and measurements with the standard soil (gray filled circles).

For stage B in the memory effect experiment (i.e., re-saturation with isotopically enriched water, steps V–VIII), the measured $\delta_{\text{extracted water}}$ value was compared to the result of a two-end-member mixing equation (δ_{mix}), considering perfect mixing between tap water remaining after stage A extraction (step III) and the added isotopically enriched water ($\delta_{\text{enriched water}}$) in stage B, step V (Equation 1b):

$$\Delta = \delta_{\text{extracted water}} - \delta_{\text{mix}}, \tag{1b}$$

with δ_{mix} defined as:

$$\delta_{\text{mix}} = \delta_{\text{tap water}} x_{\text{tap water}} + \delta_{\text{enriched water}} \left(1 - x_{\text{tap water}}\right), \tag{2}$$

where $x_{\text{tap water}}$ (-) is the fraction of tap water in the soil water mixture after re-saturation:

$$x = \frac{w_{\text{tap water}}}{w_{\text{mix}}}, \tag{3}$$

where $w_{\text{tap water}}$ (g) is the amount of deionized tap water remaining in the vessels after the extraction in stage A, and w_{mix} (g) is the sum of remaining tap water and added isotopically enriched water amounts.

2.4 | Intercomparison of discrete isotopic measurements

We compared in pairs the different discrete isotopic determinations with so-called Bland–Altman plots (Altman & Bland, 1983). This statistical approach was proposed for comparing the measurements obtained using an "established" method A with those of a "new" method B to ultimately decide whether

method B rendered reliable results, as method A was assumed to do. First, the repeatability of IS and of the three destructive methods (i.e., CVD, CF, and DVE) was assessed for the two soil types to rule out a dependency between the within-subject standard deviation (s_w) and the magnitude of the measurement (mean δ-value) that could produce misleading results. The significance of the correlation between the mean δ-values and s_w associated with the mean of each method was tested by calculating Kendall's rank correlation coefficient (Bland & Altman, 1996).

Then, a repeatability coefficient (RC, ‰) was calculated using Equation (4) (Bland & Altman, 1996):

$$\text{RC} = 1.96 \left(\sqrt{2} \right) s_w. \tag{4}$$

The RC value is the expected difference between two measurements done with a certain method for the same subject (vessel in our study) for 95% of subjects. In other words, the lower the RC, the better the repeatability of the method.

Afterward, the difference between the δ-values of the soil water extracted from vessel j measured with method A and method B ($\delta_{(A-B)j}$), and the mean of the δ-values obtained with both methods A and B ($\bar{\delta}_{A,Bj}$) were calculated using Equations (5a) and (5b), respectively, for the method pairs IS/CF, IS/DVE, IS/CVD, CF/DVE, CF/CVD, and DVE/CVD (Altman & Bland, 1983):

$$\delta_{(A-B)j} = \delta_{Aj} - \delta_{Bj}, \tag{5a}$$

$$\bar{\delta}_{A,Bj} = \frac{\delta_{Aj} + \delta_{Bj}}{2}. \tag{5b}$$

In each Bland–Altman plot (or method pair), $\bar{\delta}_{A,Bj}$ is expressed as a function of $\delta_{(A-B)j}$, and the dependency between these two variables was assessed by calculating a Kendall's rank correlation coefficient (as done for the measurements of each method). Then, the lower (LL) and upper limits of agreement (UL), between which we expect to find 95% of the differences, were calculated using Equations (6a) and (6b), respectively:

$$\text{LL} = \bar{\bar{\delta}}_{A-B} - 1.96 \hat{s}_{\text{diff}}, \tag{6a}$$

$$\text{UL} = \bar{\bar{\delta}}_{A-B} = 1.96 \hat{s}_{\text{diff}}, \tag{6b}$$

where $\bar{\bar{\delta}}_{A-B}$ is the mean of the δ-value differences between methods A and B, and $\hat{s}_{\text{diff}}$ is a corrected standard deviation for these differences. This corrected standard deviation is employed when repeated measurements of the same subject for each method were performed ($n = 3$ in our study;

Bland & Altman, 1999).

$$\widehat{s}_{\text{diff}} = s_{\text{diff}} + \left(1 - \frac{1}{n_A}\right) s_{wA} + \left(1 - \frac{1}{n_B}\right) s_{wB}, \quad (7)$$

where s_{diff} is the standard deviation of the δ-value differences between methods A and B, n_A and n_B are the numbers of observations of each subject in methods A and B, respectively, and s_{wA} and s_{wB} are the within-subject standard deviations in methods A and B, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Time-evolution in isotopic composition and evaporative enrichment during pressure-extraction of water

A continuous increase in the Δ-values (up to 13.3 and 3.8‰ in Δ^2H and Δ^{18}O, respectively) of the water extracted under pressure from the soil and water-filled (i.e., control) vessels was observed during stage A of the memory effect experiment (step III, Figure 4). Such increase was strongest in the last 15 days of the extraction (day of the experiment: 30–45). This was also reflected in the higher Δ-values determined with the destructive and in situ methods before (up to 3.8 and 1.2‰ in Δ^2H and Δ^{18}O, respectively) and after (up to 11.0 and 3.0‰ in Δ^2H and Δ^{18}O, respectively) stage A pressure extraction (steps II and IV, Figure 4). Noticeably, such a Δ-increase was not observed during stage B extraction (i.e., after re-saturation of the soil vessels with isotopically enriched water; step VII, Figure 4). The maximum Δ-values determined destructively and in situ before and after stage B pressure extraction (steps VI and VIII, Figure 4) did not differ as greatly as they did in stage A (2.5 against 4.0‰ in Δ^2H and 1.3 against 1.5‰ in Δ^{18}O). It is important to note that stage B extraction was shorter than stage A extraction and that the results from CF and CVD after the extractions were not included in our analysis. It was not possible to collect soil water via CF after each pressure extraction (steps IV and VIII) due to very low θ in the soil samples, and the extraction of water via CVD in the same steps was incomplete (i.e., extraction efficiency below 98%; Araguás-Araguás et al., 1995).

The Δ-values calculated based on isotopic results of the destructive and in situ methods and the variation among methods seemed to be higher in vessels with lower θ compared to the Δ-values in vessels close to water saturation. The average absolute Δ^2H (Δ^{18}O) value in the vessel sampled in step II (θ = 0.34 cm³ cm⁻³, Figure 4) and step VI (θ = 0.33 cm³ cm⁻³) was 2.7 and 0.9‰ (0.6 and 0.5‰), respectively, whereas in the vessel sampled in step IV (θ = 0.05 cm³ cm⁻³) and step VIII (θ = 0.04 cm³ cm⁻³) was 9.2 and 3.5‰ (2.8 and 0.8‰).
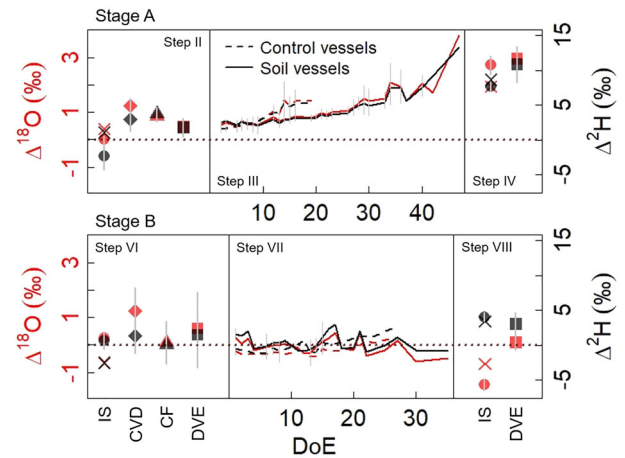

FIGURE 4 Time series (days of experiment [DoE]) of Δ (‰) recorded during the memory effect experiment. Δ is the mean difference between the δ-value of the water measured destructively or in situ and the δ-value of the spike water (stage A) or the theoretical δ-value of a perfect mix between remaining tap water and added enriched water (stage B). Continuous and discontinuous lines refer to soil-filled and water-filled (used as controls) vessels, respectively. The Δ-values from in situ online determinations (circle, IS) or following destructive sampling via cryogenic vacuum distillation (diamond, CVD), centrifugation (triangle, CF), or direct water vapor equilibration (square, DVE) before and after the pressure-extraction in stage A (step III) are presented in the panels labeled steps II and IV, respectively. Likewise, the Δ-values of soil water measured destructively or in situ before and after the pressure-extraction in stage B (step VII) are presented in the panels labeled steps VI and VIII, respectively. In steps II, IV, VI, and VIII, the mean Δ-value measured with IS in all vessels (not only in the vessel destructively sampled) is indicated with the symbol "x".

As for the tension effect experiment, a smaller (compared to the memory effect experiment) increase in Δ-value (up to 7.7‰ in Δ^2H and 1.8‰ in Δ^{18}O) was observed in the soil vessels and controls during stage A pressure-extraction (step III, Figure 5), but not during stage B extraction (step V, Figure 5). Like in the memory effect experiment, the second extraction step was considerably shorter. The Δ-values calculated based on results of the in situ and destructive techniques after stage A pressure-extraction (up to 9.5‰ in Δ^2H and 2.3‰ in Δ^{18}O; step IV, Figure 5) were greater than those calculated before stage A pressure-extraction (up to 3.7‰ in Δ^2H and 0.9‰ in Δ^{18}O; step II, Figure 5).

Again, the increase in Δ-values and the variation among methods seemed to be higher in the vessel with the driest soil. The average absolute Δ^2H (Δ^{18}O)-value in the vessels destructively sampled in steps II and IV (θ = 0.42 and 0.27 cm³ cm⁻³, respectively) and one of the vessels sampled in step VI (θ = 0.24 cm³ cm⁻³, empty symbols) was below 4.4‰ (1.3‰), whereas in the other vessel sampled in step VI (θ = 0.01 cm³ cm⁻³, filled symbols in Figure 5), the average absolute Δ^2H (Δ^{18}O)-value was 63.9‰ (5.7‰).
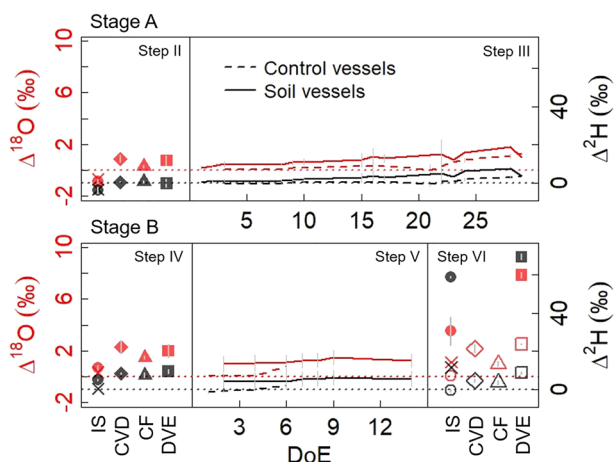
FIGURE 5 Time series (days of experiment [DoE]) of Δ (‰) recorded during the tension effect experiment. Δ is the mean difference between the δ-value of the water measured destructively or in situ and the δ-value of the spike water. Continuous and discontinuous lines refer to soil-filled and water-filled (used as controls) vessels, respectively. The Δ-values from in situ online determinations (circle, IS) or following destructive sampling via cryogenic vacuum distillation (diamond, CVD), centrifugation (triangle, CF), or direct water vapor equilibration (square, DVE) before the pressure-extraction in stage A (step III) are presented in the panel labeled step II. Likewise, the Δ-values of soil water measured destructively or in situ before and after the pressure-extraction in stage B (step V) are presented in the panels labeled steps IV and VI, respectively. Empty and full symbols in step VI refer to two different vessels, one with wet soil (empty symbols) and one with dry soil (full symbols). In steps II, IV, and VI, the mean Δ-value measured with IS in all vessels (not only in the vessel destructively sampled) is indicated with the symbol "x".

Based on the small difference between the δ-values of the pressure-extracted water in stage B in the memory effect experiment and the reference, we could accept our null hypothesis (a): complete mixing between the remaining local tap water after step III and added isotopically enriched water in step V. Nevertheless, we cannot definitely assert this at this point, since the zigzagging pattern in the time series of the extraction and the bigger Δ-values observed in the destructive and in situ measurements in step VI point toward spatial heterogeneities (see Section 3.2). In Section 3.2, we also discuss in more detail the results of the tension effect experiment to either accept or reject null hypothesis (b) dependency of the soil water isotopic composition on soil tension.

The increase in Δ described in the previous paragraphs in the extractions in both the memory and tension effect experiments was very likely the consequence of water having evaporated from the soil vessels and controls inside the pressure plate extractors. In the memory effect experiment, the conditions (air temperature and relative humidity) prevailing in the extractors and driving the isotopic enrichment seemed to have been comparable during the extractions in stages A

and B as seen from similar values of the slopes of the δ^2H-δ^{18}O linear models fitted separately (3.7 vs. 3.5, $p < 0.05$; light blue vs. dark blue continuous lines in Figure 6). Furthermore, regardless of the stage, the isotopic enrichments observed in water extracted under pressure from the soil vessels and controls were comparable, which points toward no soil-texture-related isotopic fractionation of soil water.

The δ-values measured with the discrete isotopic techniques (i.e., IS, CVD, CF, and DVE) deviated more from those obtained continuously under pressure and from the δ-values of the reference water during stage B than during stage A. This is most likely because there were differences across soil vessels in the amount of tap water remaining after the extraction in stage A and in the amount of isotopically enriched water added in the re-saturation.

In the tension effect experiment, the slope of the correlation between the δ^{18}O- and δ^2H-values of the nondestructive and destructive water samples during the extraction stages A and B was 7.9 ($p < 0.05$, continuous black line in Figure 7). This value was 4.1 ($p < 0.05$, discontinuous black line) when the paired δ-values associated with an extremely high standard deviation or that deviated considerably from the cluster of points shown in the lower left side of Figure 7 were excluded from the analysis. These data points, indicated by a red arrow, are those of soil water in the vessel with dry soil after extraction stage B measured via DVE (square) and IS (circle).

Alternatively, the increase in Δ could have been related to the amount of pressure-extracted water. To explore this possibility, we expressed Δ as a function of the amount of water (w, g) collected daily from the pressure plate extractors from each control and soil vessel in the memory and tension effect experiments (Figure 8). Δ^2H and Δ^{18}O in the memory effect experiment during stage A extraction in the soil vessels (yellow triangles, left panels in Figure 8) and controls (light blue inverted triangles) seemed to be higher the lower the amount of pressure-extracted water was. This trend is also observed in the tension effect experiment in both extraction steps (right panels in Figure 8). However, no clear trend was observed between Δ^2H and Δ^{18}O and the amount of pressure-extracted water (pink triangles and dark blue inverted triangles) in stage B extraction in the memory effect experiment (bottom left panel).

The parameters of a fitted exponential model (Equation S1) for the data points of stage A extraction in the memory and in the tension effect experiment were very similar (Table S1), and they were both statistically significant (i.e., $p < 0.05$), albeit with a low r^2 (<0.21). Likewise, the parameters of the models fitted to the data of both extractions (stages A and B) in the memory and tension effect experiment were very similar (Table S1) and statistically significant. However, the r^2 in these cases was below 0.15. The results presented in Figures 6–8 led us to conclude that the isotopic effect of water
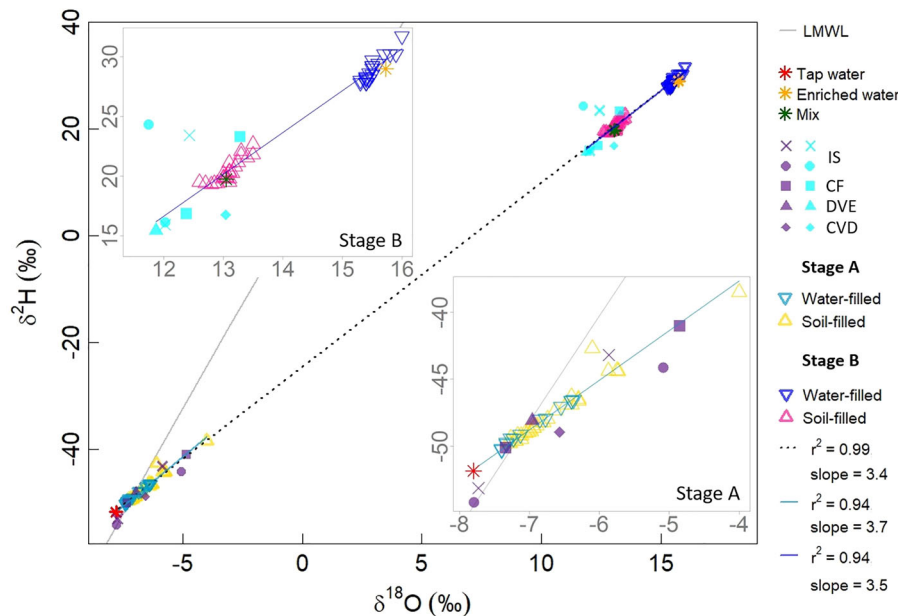
FIGURE 6　Dual isotope plot of the water extracted under pressure from the soil vessels (empty triangles) and the (water-filled) control vessels (empty inverted triangles) in stages A and B during the memory effect experiment. Soil water δ-values obtained before and after stage A extraction using the in situ online method (circles, IS), via centrifugation (filled triangles, CF), direct water vapor equilibration (squares, DVE), and cryogenic vacuum distillation (diamonds, CVD) are presented as purple symbols. The results determined before and after stage B extraction are presented as cyan symbols. The mean δ-values measured with IS in all vessels (not only in the destructively sampled vessel) are indicated with an "x". The δ-values of the water used to saturate the soil vessels and to fill the controls are presented as asterisks in red (stage A) and orange (stage B). The calculated mean δ-value of the soil water inside the re-saturated vessels is shown as a green asterisk. Linear regression models of $\delta^{18}O$ versus δ^2H were fitted to the data obtained during both extraction steps (black dotted line) and separately for each extraction step (light and dark blue continuous lines). All correlations were significant ($p < 0.05$). The local meteoric water line (i.e., LMWL—gray line, $\delta^2H = 7.9 \times \delta^{18}O + 6.9$) is included as a reference.

evaporation in both memory and tension effect experiments was comparable and that this evaporation could have happened both inside and outside of the pressure plate extractors. Furthermore, the fact that the parameters of the model fitted to the data in the memory and in the tension effect experiment were similar and that the trend for the Δ in the controls was the same as that of Δ in the soil vessels was an indication of no soil-texture-related isotopic effect on soil water.

3.2 | Analysis of the memory and tension effects

Regarding our research question (i), we observed the so-called "memory effect" (Newberry, Prechsi, et al., 2017) in the isotopic composition of soil water after two isotopically distinct water sources were sequentially added to the same soil sample in the memory effect experiment. Like in the study of Newberry, Prechsi, et al. (2017), the isotopic composition of extracted water after re-saturation differed from (in our case, was lower than) that of the reference water (in our study, isotopically enriched water, Figure 6). Thus, the extracted water was a mixture of isotopically enriched water and remaining

tap water from the previous wetting event. Thielemann et al. (2019) reported that this memory effect could still be observed even after several re-wetting events (three in their case).

Interestingly, there seemed to be spatial heterogeneity in the degree of mixing in the soil-filled vessels, since we recorded a zigzagging trend of the difference to reference water (i.e., Δ) during stage B extraction in the memory effect experiment (i.e., step VII, Figure 4). The mean δ-value of soil water measured across vessels with the IS method before the extraction (i.e., step VI, Figure 4) was lower than that of the reference water (i.e., δ-value of a perfect mixture), which may support the previous statement. Of course, this could also have a methodological explanation: the perfectly mixed soil water had not yet completely replaced the depleted tap water around the permeable tubing (Rothfuss et al., 2013). However, we do not believe this was the case, since no significant differences were observed between the IS measurements performed on three different days after a four-day equilibration time. Bowers et al. (2020) reported a mixing and equilibration time for isotopically distinct and sequentially added water of little more than 4 days. We believe our results support the conclusion of Gaj et al. (2016) that the well-documented spatial heterogeneity of soil water content and differences in the
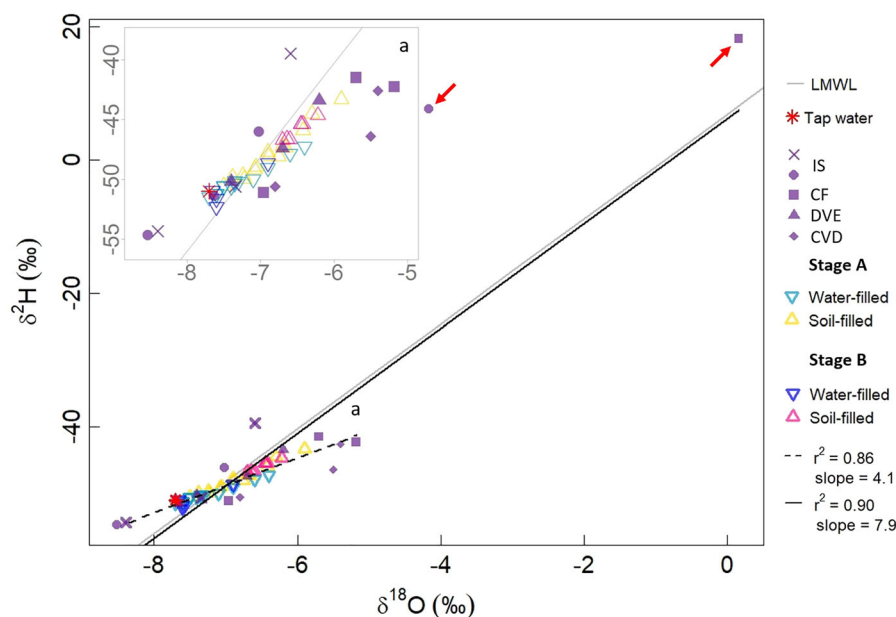
FIGURE 7 Dual isotope plot of the water extracted under pressure from the soil vessels (empty triangles) and the (water-filled) control vessels (empty inverted triangles) in stages A and B during the tension effect experiment. Results for soil water sampled destructively (filled triangle for centrifugation [CF], square for direct water vapor equilibration [DVE], and diamond for cryogenic vacuum distillation [CVD]) and in situ online (circle, IS) are presented as purple symbols. The mean δ-values measured with IS in all vessels (not only in the destructively sampled vessel) are indicated with an "x". The δ-values of the water used to saturate the soil vessels and to fill the controls are presented as a red asterisk. Linear regression models of $\delta^{18}O$ versus δ^2H were fitted to the data obtained during both extraction steps (black continuous line) and excluding the data points measured in the vessel with dry soil (marked with red arrows; discontinuous black line). Both relationships were significant ($p < 0.05$). The local meteoric water line (i.e., LMWL—gray line, $\delta^2H = 7.9 \times \delta^{18}O + 6.9$) is included as a reference.

degree of equilibration between different water pools (Hsieh et al., 1998) in the unsaturated zone naturally leads to spatial differences in the distribution of soil water stable isotopes.

To draw a conclusion to our research question (ii), we fitted a linear and exponential model to the function between Δ and soil water potential (ψ, pF) (Equation S2). The linear correlation was positive and significant ($p < 0.05$) for both tension (left panels in Figure 9, Table S1) and the memory effect experiments (right panels in Figure 9, Table S1) for the data points measured in both extractions. However, all calculated correlations had very low r^2 values (≤0.15, Table S1). The r^2 of the correlation of the data in the tension effect experiment following an exponential trend was slightly higher than that of the linear correlation, but it was still low (≤0.20). An exponential correlation for the data points in the memory effect experiment was not statistically significant. The slope of the linear correlations in the tension effect experiment was lower (up to ∼60%) than those obtained in the memory effect experiment.

It seemed that the isotopic fractionation of soil water in the memory effect experiment was stronger than in the tension effect experiment as shown by a lower evaporation line slope in the former (Figure 6) than in the latter (Figure 7). This result is contrary to the conclusions of Gaj and McDonnell (2019), who found that the slope of the evaporation line is lower for soils with a finer structure. Although this effect might have also been related with the higher clay content in their soil samples with a finer structure. The low r^2 of the correlations between Δ and the amount of pressure-extracted water and between Δ and soil tension, as well as the observed evaporative enrichment of the pressure-extracted water in both memory and tension effect experiments, hindered a more conclusive and quantitative assessment of a soil tension fractionating effect (e.g., calibration equations like the ones presented by Oerter et al., 2017 or Newberry, Prechsi, et al., 2017). However, we observed a higher standard deviation associated with isotopic measurements (e.g., Gaj et al., 2016; Meißner et al., 2014; Oerter & Bowen, 2017), greater differences between the results of the different methods (e.g., Tsuruta et al., 2019; Walker et al., 1994) and between the extracted soil water and the reference water (e.g., Orlowski, Pratt et al., 2016; Sprenger et al., 2015), when soil tension was high (i.e., at low soil water content). In our study, the highest mean isotopic differences to the reference water not attributable to methodological issues (e.g., incomplete water extraction via CVD) were 9.5 ± 1.2‰ in δ^2H and 2.5 ± 0.0‰ in $\delta^{18}O$ measured via DVE in the tension effect experiment. In the memory effect experiment, the highest mean differences were 10.8 ± 2.5‰ in δ^2H and 3.0 ± 5.0‰ in $\delta^{18}O$ determined via DVE in a vessel sampled in step VIII (θ < 4%). For
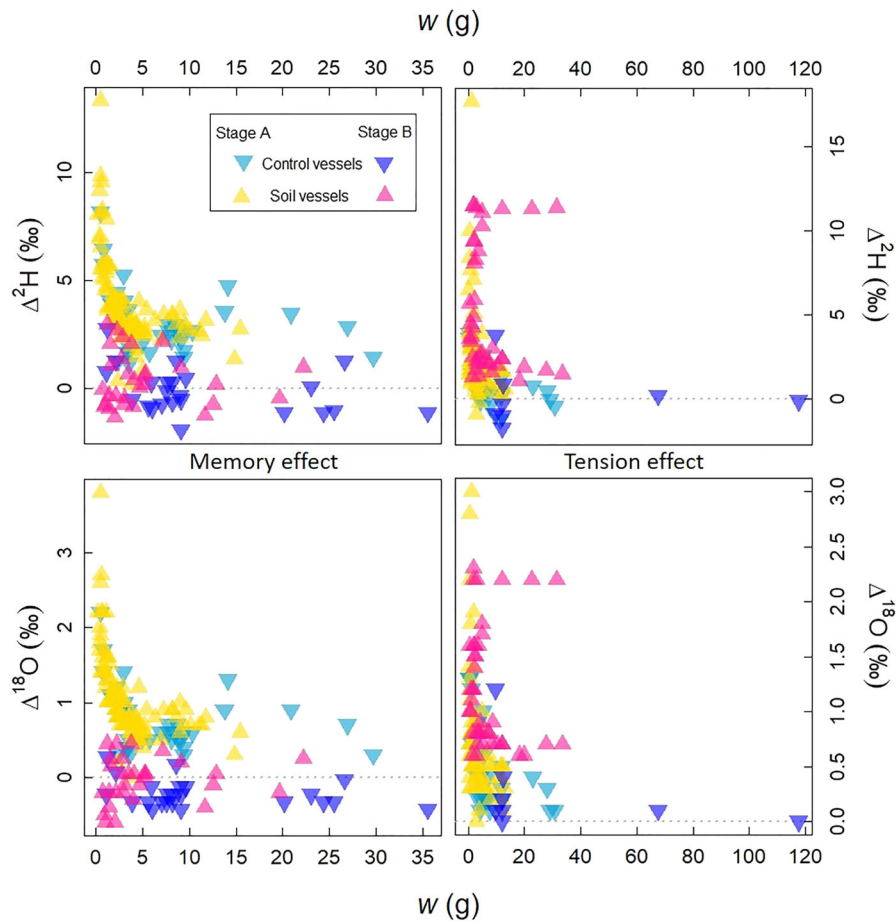
FIGURE 8 The difference between the δ-value of the water extracted daily from the pressure plate extractors and the δ-value of the reference water (i.e., Δ, ‰) in the soil vessels (triangles) and (water-filled) control vessels (inverted triangles) during stage A (yellow and light blue, respectively) and stage B extraction (pink and dark blue, respectively) in the memory (left panels) and tension (right panels) effect experiment as a function of the amount of water extracted under pressure (w, g). The δ-value of the reference water in stage A in the memory effect experiment and in stages A and B in the tension effect experiment was that of tap water. For stage B extraction in the memory effect experiment, the reference water δ-value was that of a perfect mixture between remaining tap water in the soil vessels after stage A extraction and the isotopically enriched water added in the second saturation (i.e., step V). A gray dotted line at Δ = 0 (no difference between extracted and reference water) is included as reference.

comparison, Sprenger et al. (2015) summarized the discrepancies between the isotopic composition of soil water extracted via CVD and the reference water in several studies: up to ~15‰ in δ^2H (clay; Walker et al., 1994) and ~2‰ in $\delta^{18}O$ (clayey silt; Orlowski et al., 2013).

We could not explain the observed isotopic differences only by methodological artifacts or shortcomings. We reject then our null hypothesis (ii): we observed isotopic differences in the soil water when the soil was close to saturation, at a pF of 1.8 and close to residual water content. However, we could not establish a clear relationship between soil tension and isotopic changes, since these changes could also have been caused exclusively or simultaneously by evaporation of soil water during the extraction process. Furthermore, we believe that our experimental set-up with some improvements (aiming at quantifying evaporation) could be used to further test soil-texture-related isotopic fractionation because there is already

numerous studies that have found such an effect (e.g., Gaj et al., 2019; Koeniger et al., 2011; Meißner et al., 2014; Orlowski & Breuer, 2020).

3.3 | Intercomparison of discrete isotopic measurements

The mean soil water δ-values and standard deviation obtained with the discrete methods are summarized in Table 1. The IS and CF methods showed to be the most reproducible, with a mean standard deviation of 1.0‰ (0.3‰) and 1.3‰ (0.3‰) for δ^2H ($\delta^{18}O$), respectively, compared to the DVE (1.9‰ [0.4‰]) and CVD (2.3‰ [0.9‰]).

No dependency between the within-subject standard deviation measured with the IS or destructive methods and the magnitude of the measurement was found in the memory or

TABLE 1 Mean δ^2H and $\delta^{18}O$ ($\bar{\delta}^2H$ and $\bar{\delta}^{18}O$, ‰) and standard deviation (s_w) in soil water measured in four vessels filled with quartz sand in steps II, IV, VI, and VIII of the memory effect experiment and four vessels filled with standard soil in steps II, IV, and VI of the tension effect experiment with the discrete isotopic measurement methods: in situ online (IS), cryogenic vacuum distillation (CVD), centrifugation (CF), and direct water vapor equilibration (DVE).

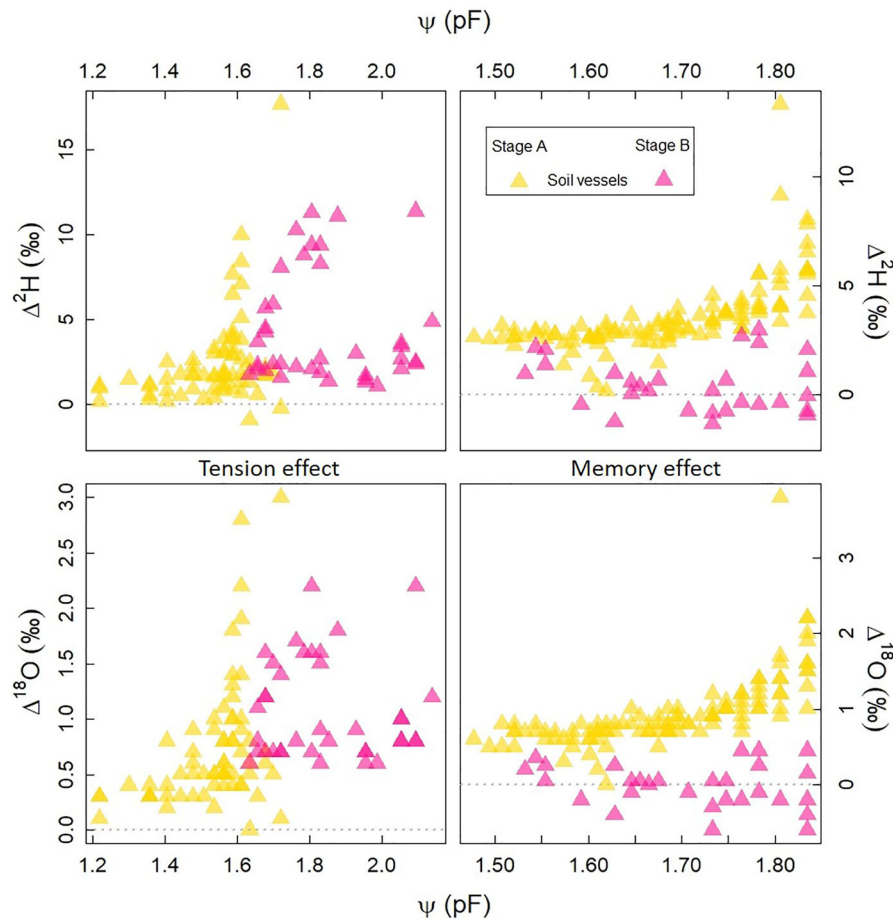|	Description	IS (‰) $\bar{\delta}^2H \pm s_w, \bar{\delta}^{18}O \pm s_w$	CVD (‰)	CF (‰)	DVE (‰)
Memory effect experiment	Stage A/step II	−54.2 ± 1.9 −7.8 ± 0.1	−49.0 ± 1.7 −6.6 ± 0.3	−48.1 ± 0.9 −7.0 ± 0.2	−50.1 ± 1.3 −7.3 ± 0.2
	Stage A/step IV	−44.2 ± 0.7 −5.1 ± 0.3	NA NA	NA NA	−41.0 ± 2.5 −4.9 ± 0.5
	Stage B/step VI	16.1 ± 1.3 12.0 ± 0.2	16.8 ± 2.6 13.0 ± 0.8	15.5 ± 2.8 11.9 ± 0.8	16.9 ± 4.7 12.4 ± 1.3
	Stage B/step VIII	24.3 ± 0.7 11.8 ± 0.2	NA NA	NA NA	23.3 ± 1.7 13.3 ± 0.3
Tension effect experiment	Stage A/step II	−54.7 ± 1.7 −8.5 ± 0.2	−50.6 ± 0.4 −6.8 ± 0.3	−50.2 ± 0.6 −7.4 ± 0.1	−51.1 ± 2.1 −7.0 ± 0.4
	Stage A/step IV	−46.0 ± 0.4 −7.0 ± 0.2	−42.6 ± 0.4 −5.4 ± 0.5	−43.4 ± 1.1 −6.2 ± 0.1	−41.5 ± 1.2 −5.7 ± 0.5
	Stage B/step VI (wet soil)	−51.4 ± 0.8 −7.6 ± 0.0	−46.4 ± 0.7 −5.5 ± 0.3	−47.4 ± 1.0 −6.7 ± 0.2	−42.3 ± 0.6 −5.2 ± 0.0
	Stage B/step VI (dry soil)	7.7 ± 0.23 −4.2 ± 1.1	NA NA	NA NA	18.2 ± 1.4 0.2 ± 0.2

Abbreviation: NA, not available.

FIGURE 9 The difference between the δ-value of the water extracted daily from the pressure plate extractors and the δ-value of the reference water (i.e., Δ; ‰) in the soil vessels during stage A extraction (yellow) and stage B extraction (pink) in the tension (left panels) and memory (right panels) effect experiment as a function of the soil water potential (ψ, pF). The δ-value of the reference water in stage A extraction in the memory effect experiment and in both extractions in the tension effect experiment was that of tap water. For stage B extraction in the memory effect experiment, the reference water δ-value was that of a perfect mixture between remaining tap water in the soil vessels after stage A extraction and the isotopically enriched water added in the second saturation (i.e., step V). A gray dotted line at Δ = 0 (no difference between extracted and reference water) is included as reference.

tension effect experiments ($p > 0.05$ of the Kendall's rank correlation coefficient). This meant that no data transformation of the isotopic determinations from the discrete methods was necessary to analyze visually the agreement of the isotopic determinations in the Bland–Altman plots.

With a few exceptions, the RCs (Table 2) of all methods at the different experimental stages were higher than the long-term precision of the CRDS: 1‰ and 0.5% in δ^2H and δ^{18}O, respectively. Only for IS, it was possible to calculate RC values considering isotopic determinations in several vessels (values in parenthesis in Table 2) and not only in the destructively sampled ones. These values were in some cases smaller than the ones calculated with only the isotopic determinations in the destructively sampled vessels.

The IS method had a lower mean RC (2.7 ± 1.0‰ and 0.6 ± 0.2‰) compared to the destructive methods (6.0 ± 1.6‰ and 1.5 ± 1.1‰ for CVD; 4.7 ± 5.6‰ and 1.4 ± 1.7‰ for CF; and 7 ± 4.2‰ and 1.6 ± 1.5‰ for DVE) in δ^2H and δ^{18}O, respectively. In other words, the expected difference in δ-values between two measurements of the same soil water sample in 95% of all soil water samples was smaller using IS. The RC of CF was very close to that of IS and even smaller in some vessels.

The mean upper and lower limits in the method pairs including CF (±7.5 and ±1.8‰ in δ^2H and δ^{18}O, respectively, Figure 10) and IS (±8.5 and ±1.8‰ in δ^2H and δ^{18}O, respectively) were slightly higher than the mean values in the pairs including CVD (±6.9 and ±1.8‰ in δ^2H and δ^{18}O, respectively). The highest values were in the pairs including DVE (±9.5 and ±2.3‰ in δ^2H and δ^{18}O, respectively). We highlight here the fact that for the pairs including CF and CVD, less data points were included, due to zero or incomplete water extraction in dry soil samples.

TABLE 2 Repeatability coefficient (RC, ‰) for the in situ online (IS), cryogenic vacuum distillation (CVD), centrifugation (CF), and direct water vapor equilibration (DVE) methods in each of the vessels where the isotopic composition (i.e., δ^2H and $\delta^{18}O$) of soil water was measured: steps II, IV, VI, and VIII in the memory effect experiment and steps II, IV, and VI in the tension effect experiment. For IS, RC values (in parenthesis) considering the isotopic determinations in all vessel and not only in those destructively sampled could be calculated.

	Description	IS (‰) RC δ^2H RC $\delta^{18}O$	CVD (‰)	CF (‰)	DVE (‰)
Memory effect experiment	Stage A/step II	5.4 (4.0) 0.3 (0.5)	4.8 0.7	0.7 0.2	3.6 0.6
	Stage A/step IV	1.9 (1.7) 0.9 (0.8)	NA NA	NA NA	7.0 1.2
	Stage B/step VI	3.5 (2.7) 0.7 (0.4)	7.1 2.3	8.6 2.6	12.9 3.7
	Stage B/step VIII	1.8 (2.5) 0.6 (0.8)	NA NA	NA NA	4.6 0.7
Tension effect experiment	Stage A/step II	4.7 (3.0) 0.4 (0.3)	1.1 0.9	1.7 0.3	5.8 1.0
	Stage A/step IV	1.0 (1.7) 0.5 (0.5)	5.4 1.3	1.7 0.3	3.4 1.4
	Stage B/step VI (wet soil)	2.2 (2.5) 0.0 (1.1)	1.9 0.9	2.4 0.7	1.6 0.1
	Stage B/step VI (dry soil)	0.7 3.0	NA NA	NA NA	3.9 0.7

Abbreviation: NA, not available.

In general, the agreement between measurements with the different methods shown in Figure 10 was not good, since the observed differences were higher than the long-term precision of the CRDS (1‰ and 0.5‰ in δ^2H and $\delta^{18}O$).

3.4 | Different water pools sampled with different extraction methods?

Since the differences we observed between the isotopic determinations from the discrete methods were greater than 1‰ in δ^2H and 0.5‰ in $\delta^{18}O$, we reject our null hypothesis (c): the isotopic composition of soil water measured or extracted using IS, CF, CVD, and DVE was not comparable. Considerable isotopic differences between methods, like the ones we present here, have been reported. Tsuruta et al. (2019) reported differences of up to 17.5‰ and 1.8‰ in δ^2H and in $\delta^{18}O$, respectively, between CF and CVD determinations. Kübert et al. (2020) reported isotopic differences between IS and CVD of up to 152.2‰ in δ^2H and 14.2‰ in $\delta^{18}O$ rooted mainly in spatial heterogeneity in the field following isotopic labeling. Oerter and Bowen (2017) reported a difference of up to 30‰ in δ^2H and 4‰ in $\delta^{18}O$ between IS and CVD in natural samples. Here, spatial heterogeneity could have contributed greatly to the observed differences. In our controlled laboratory study, the highest absolute difference in δ^2H and $\delta^{18}O$ was 15.4‰ and 4.1‰, respectively, between IS and CVD.

In both memory and tension effect experiments, the following trend of the Δ-values was observed: IS < CF < DVE < CVD. It could be hypothesized that we determined the isotopic composition of different soil water pools with different degrees of mixing (e.g., Adams et al., 2020; Geris et al., 2015; Landon et al., 1999; Oerter & Bowen, 2017) or equilibration (e.g., Hsieh et al., 1998) with each method, a conclusion presented in several studies. For example, Figueroa-Johnson et al. (2007) explained that there was a concentration gradient of the water stable isotopes around the soil particles after extracting isotopically enriched water with CF (water held at low soil water tension or "mobile water") and depleted water with azeotropic distillation (water held at high soil water tension or "immobile water"). Likewise, Adams et al. (2020) concluded that soil water extracted via CF was biased (i.e., isotopically more similar) toward the mobile pool, whereas soil water extracted via CVD was biased more toward the immobile pool. Moreover, Orlowski et al. (2018) call CVD a "brute force technique" through which water held at a wide range of soil tensions can be extracted. Geris et al. (2015) found the following trend in the isotopic composition of extracted soil water in the field: porous rhizon samplers > CF > CVD, matching the decreasing ability of the methods to extract water at increasing soil tensions.

The two main water pools in the soil in our study would be tap water and enriched water in the memory effect experiment, and residual water in the dry soil and tap water in the tension effect experiment. The isotopic composition of the mobile
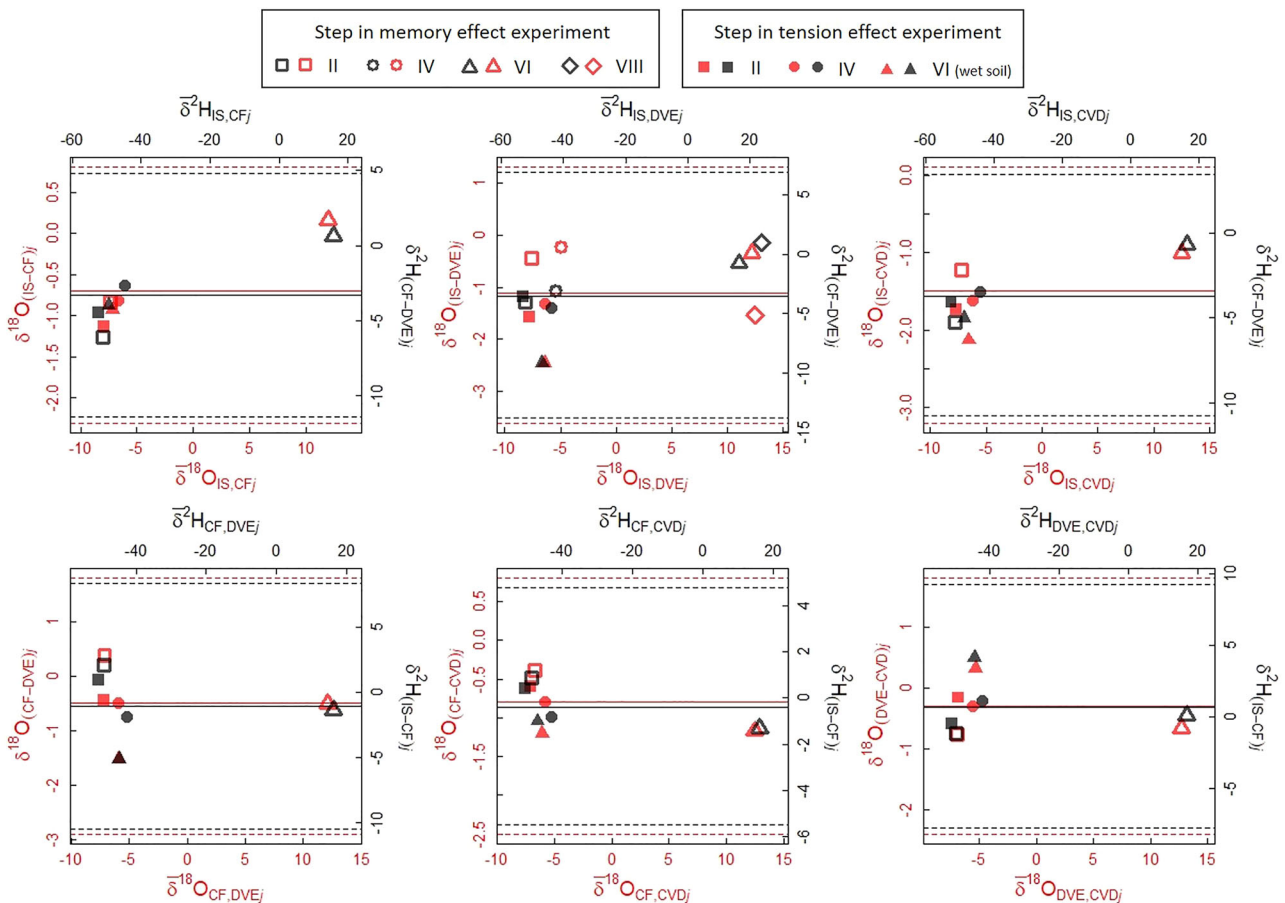
FIGURE 10 Bland–Altman plots for the comparison in pairs of the four discrete isotopic methods (in situ online, IS; cryogenic vacuum distillation, CVD; centrifugation, CF; and direct water vapor equilibration, DVE) used to measure the δ-value (‰) of water at different steps (II, IV, VI, and VIII) during the memory effect experiment and during the tension effect experiment (steps II, IV, and VI). In each plot, the difference between the δ-value calculated with methods A and B (i.e., $\delta_{(A-B)j}$, ‰) is displayed as a function of the mean δ-value calculated with methods A and B (i.e., $\bar{\delta}_{A,Bj}$, ‰). The continuous horizontal line represents the mean $\delta_{(A-B)j}$ (i.e., $\bar{\delta}_{(A-B)j}$, ‰). The discontinuous horizontal lines are the upper (UL, above $\bar{\delta}_{(A-B)j}$, ‰) and lower (LL, below $\bar{\delta}_{(A-B)j}$, ‰) limits calculated with the corrected standard deviation of $\bar{\delta}_{(A-B)j}$ (i.e., $\hat{s}_{\text{diff}}$, ‰).

water (theoretically sampled via CF) in stage A extraction in the memory effect experiment and in the tension effect experiment would be close to that of tap water, whereas in stage B extraction in the memory effect experiment, it would be closer to that of enriched water. This means that Δ measured via CF before stage B extraction in the memory effect experiment (step VI, Figure 4) would have been higher (i.e., closer to the isotopic composition of recently added enriched water) than that measured via DVE or CVD. Likewise, the isotopic composition of soil water (mobile and immobile) measured via DVE and CVD would be closer to the mixture of depleted and enriched water. However, this is not what we observed. Additionally, we did not observe comparable results from the IS method and DVE, even though both methods are based on measurements of the isotopic composition of soil water vapor.

The presence of isotopically distinct soil water pools that incompletely mix (Sprenger et al., 2018; Thielemann et al., 2019), spatial heterogeneity (both in soil water content and soil water isotopes) and methodological issues (that led to soil water evaporation) together, allow us to explain the

"disagreement" among the isotopic measurements from the different methods. This disagreement is clearly reflected in the important span between the upper and lower limits in the Bland–Altman plots (Figure 10). Regarding spatial heterogeneity, isotopic measurements of all discrete methods might have been similarly representative at near-saturation conditions. Quade et al. (2019) reported representative soil volumes between CVD and IS of the same order of magnitude. However, Quade et al. (2019) also reported a 10-fold increase of the representative soil volume for IS in dry conditions while the representative soil volume for CVD decreased. Regarding the methodological issues, the preponderance of isotopic fractionation during collection and handling of the soil samples followed the same trend as the isotopic measurements (IS < CF < DVE < CVD).

We believe that the above-presented order of the methods in the observed trend in the isotopic measurements might not have changed if we had used a soil with a higher clay content. However, the differences between methods and with the spike water might have been higher. Additionally, water extraction

with certain methods might have been more challenging: no water extracted via CF or incomplete water extraction via CVD at relatively higher soil water contents.

As explained in several studies, there are isotopic exchanges happening among the different water pools in the soil. We observed this during stage B extraction in the memory effect experiment, in the overall match between the isotopic composition of the pressure-extracted water and the theoretical δ-value of a perfect mix between remaining tap water and added enriched water. Sprenger et al. (2018) compared experimental data with a two-pore domain model and found a better match when using a conceptualization of co-existing and interacting (i.e., isotopic exchange via water vapor) water pools in the soil. Thielemann et al. (2019) considered the idea that the water pools in the soil are not in isotopic equilibrium as unlikely. The extracted soil water in their study differed from the spike water due to exchanges with residual soil water. Since elimination of residual water might require drying the soil at very high temperatures (∼>200˚C; Thielemann et al., 2019; Wen et al., 2021) changing its physicochemical properties in the process, the suitability of spike experiments to investigate soil-related isotopic fractionation could be questioned. Considering the collected evidence so far, pointing toward spatial and temporal heterogeneity of the isotopic composition of water in the soil, spike experiments might be just part of an experimental strategy when studying soil-related isotopic fractionation.

Finally, it could be argued that certain methods might not be suitable for root water uptake studies since plants might access water held at higher soil tensions (McDonnell, 2014) not extractable with these methods (e.g., CF). Since the debate regarding soil-related isotopic fractionation and the role of moisture history in the interactions of isotopically distinct soil water pools is still open, we agree with the statement of Penna et al. (2020): "it is important to sample potential soil source water that is held across the variability of soil water tensions and at multiple times." That is, we might be able to describe better the spatial and temporal variability of soil water isotopic composition and of root water uptake if we use several isotopic methods in the same study.

4 | CONCLUSIONS

Soil water fractionation during water extraction or resulting from physicochemical interactions with the soil matrix are two intertwined phenomena that add significant uncertainties to quantification and spatio-temporal distribution analysis of root water uptake and of soil water isotopes. Disentangling these processes and measuring their impact in soil water isotopic analysis would contribute to a better understanding and description of water fluxes in the soil–plant–atmosphere continuum. By using "isotopically inert" soils, we aimed at exploring soil water mixing processes, soil-tension-related

isotopic fractionation and methodological constrains of some of the established water extraction techniques. We partially accepted null hypothesis (a), that is, remaining tap water in the soil did mix with the newly added, isotopically enriched water. However, the observed zigzagging pattern in the time series of stage B extraction in the memory effect experiment points toward a certain degree of incomplete mixing in some areas. We rejected null hypothesis (b): the isotopic composition of soil water changed as a function of the modeled soil water potential value (i.e., from saturation to residual water content). The explanation for these differences was of a methodological nature and potentially caused or enhanced by low soil water potential values. No quantitative assessment of a soil-tension fractionating effect could be done. Likewise, we rejected hypothesis (c): there were considerable differences between the measurements from three destructive methods (CF, DVE, and CVD) and the in situ online method. The in situ online method had the best repeatability, followed by CF. However, we could not extract soil water via CF from dry soil samples (i.e., soil water content < 4%). The discrepancies in the isotopic determinations (either among methods or with reference water) were mostly related to moisture history, spatial heterogeneity, and potential methodological issues than to soil-texture or soil-tension fractionating effects. Spike experiments, comparison between isotopic methodologies (especially between those relying on destructive sampling and in situ ones), and complementary use of these techniques for the characterization of (soil-texture and soil-tension-related) isotopic fractionation can enhance the accuracy of soil water isotopic measurements. Ultimately, this will contribute to the validation and standardization of water stable isotopic monitoring in (eco)hydrological studies.

AUTHOR CONTRIBUTIONS
Paulina Deseano Diaz: Conceptualization; data curation; formal analysis; methodology; validation; visualization; writing—original draft. **Thai Nong**: Conceptualization; methodology. **Nicolas Brüggemann**: Resources; supervision; visualization; writing—review and editing. **Maren Dubbert**: Funding acquisition; investigation; project administration; supervision; visualization; writing—review and editing. **Mathieu Javaux**: Visualization; writing—review and editing. **Natalie Orlowski**: Data curation; formal analysis; validation; visualization; writing—review and editing. **Harry Vereecken**: Resources; writing—review and editing. **Youri Rothfuss**: Conceptualization; data curation; formal analysis; funding acquisition; project administration; resources; supervision; validation; visualization; writing—review and editing.

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CONFLICT OF INTEREST STATEMENT
The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT
Upon acceptance, all of the research data that were required to create the plots will be available from reliable FAIR-aligned data repositories with assigned DOIs. The data is also available upon request.

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