

RESEARCH ARTICLE

Bound and mobile soil water isotope ratios are affected by soil texture and mineralogy, whereas extraction method influences their measurement

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Abstract

Questions persist about interpreting isotope ratios of bound and mobile soil water pools, particularly relative to clay content and extraction conditions. Interactions between pools and resulting extracted water isotope composition are presumably related to soil texture, yet few studies have manipulated the bound pool to understand its influence on soil water processes. Using a series of drying and spiking experiments, we effectively labelled bound and mobile water pools in soils with varying clay content. Soils were first vacuum dried to remove residual water, which was then replaced with heavy isotope-enriched water prior to oven drying and spiking with heavy isotope-depleted water. Water was extracted via centrifugation or cryogenic vacuum distillation (at four temperatures) and analysed for oxygen and hydrogen isotope ratios via isotope ratio mass spectrometry. Water from centrifuged samples fell along a mixing line between the two added waters but was more enriched in heavy isotopes than the depleted label, demonstrating that despite oven drying, a residual pool remains and mixes with the mobile water. Soils with higher clay + silt content appeared to have a larger bound pool. Water from vacuum distillation samples have a significant temperature effect, with high temperature extractions yielding progressively more heavy isotope-enriched values, suggesting that Rayleigh fractionation occurred at low temperatures in the vacuum line. By distinctly labelling bound and mobile soil water pools, we detected interactions between the two that were dependent on soil texture. Although neither extraction method appeared to completely extract the combined bound and mobile (total water) pool, centrifugation and high temperature cryogenic vacuum distillations were comparable for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of soil water isotope ratios.

KEYWORDS

clay mineralogy, extraction, methods, soil texture, soil water, stable isotopes, two water world hypothesis

1 | INTRODUCTION

Extraction of soil water for stable hydrogen and oxygen isotope ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) analyses has long been used to address ecological and hydrologic

questions and has been approached using a variety of methodologies (Orlowski, Pratt, & McDonnell, 2016; Walker, Woods, & Allison, 1994). Recently, there has been increased interest in the impact that soil properties, namely, clay minerals (Gaj et al., 2017; Oerter et al., 2014), organic

matter (Meißner, Köhler, Schwendenmann, Hölscher, & Dyckmans, 2014; Orłowski, Breuer, & McDonnell, 2016), and water content (Araguás-Araguás, Rozanski, Gonfiantini, & Louvat, 1995; Meißner et al., 2014; Newberry, Prechsl, Pace, & Kahmen, 2017) appear to have on measured soil water isotope ratios. In addition, lab studies under controlled conditions have revealed that sample preparation, extraction methods, and extraction conditions have the potential to alter the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of soil water (Araguás-Araguás et al., 1995; Gaj et al., 2017; Orłowski et al., 2016; Orłowski, Winkler, McDonnell, & Breuer, 2018). To determine the appropriate extraction method, interlaboratory comparisons across techniques and extraction conditions have been conducted using isotopically labelled water (Orłowski et al., 2018; Walker et al., 1994). However, regardless of soil type, extraction method, or conditions, it is rare to reproduce the isotopic composition of water directly added to soils. This makes it difficult to identify the most reliable method for obtaining an accurate characterization of soil water isotope ratios.

In addition to the influence of soil properties and extraction conditions, the “two water worlds” hypothesis (Renée Brooks, Barnard, Coulombe, & McDonnell, 2010; McDonnell, 2014) has entered the conversation. This concept is based on the idea that bound and mobile soil water are ecohydrologically separated within watersheds with important consequences for how we interpret water isotopes in these systems. The same concept might be applicable on a much smaller scale, in which bound water is described as hydration spheres associated with clay minerals and other particle surfaces, and mobile water is the “free water” in soil pores (Araguás-Araguás et al., 1995; Kučerík, Tokarski, Demyan, Merbach, & Siewert, 2018; O’Neil & Truesdell, 1991; Savin & Hsieh, 1998). Some studies also include structurally bound water within clay minerals as a distinct bound pool, separate from water adsorbed on clay and organic matter surfaces (Savin & Hsieh, 1998). Recent studies that argue for the use of soil water vapour isotopes to quantify mobile and presumably plant-available pools (Oerter, Siebert, Bowling, & Bowen, 2019) or that find that mycorrhizal association affects the isotopic composition of plant-available water (Poca et al., 2019) highlight the need to improve our understanding of the isotopic composition of various soil water pools and how these relate to important hydrologic processes.

Attempts to resolve discrepancies between expected and observed soil water isotopic composition following extraction have included the use of mineral powders (Oerter et al., 2014), salt solutions (O’Neil & Truesdell, 1991), and silica gel (Asay & Kim, 2005; Lin, Horita, & Abe, 2018) to assess apparent isotopic fractionation associated with water-surface interactions (Chen, Auerswald, & Schnyder, 2016). This is highlighted as causing predictable differences in $\delta^{18}\text{O}$ of mobile water from a reference water based on presence of particular clay minerals (Oerter et al., 2014). Gaj, Kaufhold, and McDonnell (2017) found that different clay minerals preferentially release adsorbed water at high temperatures and were more similar to the added reference water than extractions performed at lower temperatures. Although these simplified systems offer important insight into potential mechanisms, they are less complex than real soils, in which multiple processes may be occurring simultaneously. Many studies oven dry soils at or above 105°C to remove residual water from the field before subjecting them to wetting

treatments (Gaj et al., 2017; Meißner et al., 2014; Newberry et al., 2017 & 2017; Orłowski et al., 2018; Orłowski et al., 2016 & 2016; Orłowski et al., 2013; Thielemann, Gerjets, & Dyckmans, 2019; Walker et al., 1994). For high clay content soils, heating can potentially change soil structure and alter the way in which clays respond to rewetting (Jian, Berli, & Ghezzehei, 2018). On the other hand, if soils are not heated to remove residual water, this water may exchange with added water, making it difficult to assess potential extraction or handling effects. Some studies report that structural, interlayer water remains intact during drying at 105°C because this pool can only be removed at significantly higher temperature (>250°C) and under vacuum (Araguás-Araguás et al., 1995; Gaj et al., 2017; Savin & Hsieh, 1998). Studies across extraction methods, though mainly via cryogenic vacuum distillation, have noted the influence of bound water on the isotopic composition of extracted soil water (Araguás-Araguás et al., 1995; Thielemann et al., 2019; Vargas, Schaffer, Yuhong, & Sternberg, 2017; Walker et al., 1994). Residual background water appears to leave a “memory effect” that causes deviation from reference water, particularly in high clay content soils (Newberry et al., 2017). However, the magnitude of the effect that the bound pool has on the mobile pool is unknown. Few studies have effectively addressed this in full or manipulated the bound pool directly (Araguás-Araguás et al., 1995; Thielemann et al., 2019; Vargas et al., 2017; Walker et al., 1994). Resolving these uncertainties is critical to our interpretations of soil water isotope ratios based on extracted soil moisture.

In this study, we separately labelled the bound and mobile pools in soils with varying clay content in order to detect mixing between the two. In addition, we compared the most common extraction techniques, cryogenic vacuum distillation and centrifugation, in an attempt to determine which method accurately captures the total soil water (bound and mobile pools). Vacuum extractions were further conducted under a range of temperatures to observe potential temperature effects on extraction efficiency. We hypothesized that (a) soils with higher clay content would have stronger retention of labelled bound water compared with coarser textured soils; (b) cryogenic vacuum distillation would be more effective at removing total soil water (bound and mobile pools), whereas centrifugation would more readily extract the mobile fraction; and (c) distillations performed at higher temperatures would release bound and mobile water and more accurately represent total soil water compared with lower temperature extractions and centrifugation.

2 | METHODS

Soils were collected from two locations in College Station, Texas, USA (soils TB and RA) and two locations at the Oklahoma State University Range Research Station near Stillwater, Oklahoma, USA (soils CD and CG). Sand (S; Pavestone Natural Play Sand, Atlanta, GA, USA) was also included in this experiment to represent a simple soil without the influence of clay minerals or organic matter (Kaiser & Guggenberger, 2003; Keil & Mayer, 2014). Soil texture was determined via hydrometer tests (Sheldrick & Wang, 1993). To assess clay mineralogy, X-ray

diffraction (XRD) analysis was performed using a Bruker D8 diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) at the Soil Mineralogy laboratory at Texas A&M University (Theisen & Bellis, 1964). The minerals contained in the samples were identified by matching against the mineral collection data from the International Centre for Diffraction Data (www.icdd.com) using the software, EVA from Bruker (Billerica, MA, USA).

Approximately 200 g of each soil and S were air dried and sieved through a 2-mm screen sieve prior to water labelling and extraction. Soils and S were then vacuum dried (8.5 kPa, 105°C) for 4 days to constant weight to remove residual water. Samples were cooled inside the oven under vacuum in order to avoid rehydration with vapour or condensation. To label the bound pool, heavy isotope-enriched water (WaterE) of known isotopic composition ($\delta^2\text{H}$: 165.4 ± 1.6‰, $\delta^{18}\text{O}$: 19.91 ± 0.11‰; $n = 9$) was quickly added until samples were saturated. The samples were allowed to equilibrate for 72 hr in separate Whirlpak bags stored in a refrigerator (4°C) to minimize evaporation. Soils and S were then oven dried at 105°C to constant weight to remove the water, mimicking approaches used by other labs to presumably remove any mobile and bound water prior to labelling the soil water pool (Gaj et al., 2017; Newberry et al., 2017; Orłowski et al., 2016; Orłowski et al., 2016; Thielemann et al., 2019; Walker et al., 1994). Samples were again cooled inside the oven. Soils at this step could be exposed to vapour condensing from the laboratory environment while they cooled. The isotopic composition of this vapour would be on a mixing line between WaterE and the added heavy isotope-depleted water (WaterD; see below), making its potential effect on total water difficult to distinguish from WaterE (results not presented). However, the rate of condensation is expected to be low relative to the exposure time, minimizing the influence of this water source. It is worth noting that similar studies either do not control for this or tend to ignore its presence (Newberry et al., 2017; Orłowski et al., 2016 & 2016; Thielemann et al., 2019). Although it is expected to be minor, future work could address this potential complication directly through additional labelling experiments.

To label the mobile pool, the dried samples were then rewetted to saturation with WaterD of a known composition ($\delta^2\text{H}$: -93.7 ± 1.2‰, $\delta^{18}\text{O}$: -15.29 ± 0.12‰; $n = 12$), followed again by a 72-hr equilibration period in separate Whirlpak bags in the refrigerator (4°C). After homogenization, glass scintillation vials (12 ml, Wheaton-DWK Life Sciences, Millville, NJ, USA) were promptly filled with wetted soil and S, sealed, and placed in the freezer (0°C) until cryogenic vacuum distillation. Samples to be centrifuged were prepared at the same time. Pre-extraction soil weight was measured for all samples regardless of extraction method.

2.1 | Centrifugation

A double-tube centrifuge setup was designed for this experiment (Figure S1). Holes (1.5 mm) were drilled into the bottoms of 15-ml plastic centrifuge tubes (VWR International, LLC, Radnor, PA, USA). A piece of filter paper (Grade 1, 11- μm pore space, 70-mm diameter,

Whatman, Inc., Piscataway, NJ, USA) was folded and placed inside each 15-ml tube to ensure that soil or S remained in the tube but allowed water to escape. After being filled with wet sample (about 11 g for soil and 18 g for S), the assemblage was placed in a 50-ml tube (CentriStar™, Corning, Inc., Corning, NY, USA) and suspended with a washer in order to avoid contact between the sample and extracted water during centrifugation. Three replicates of each soil type were centrifuged using a Sorvall Legend RT+ (Thermo Fisher Scientific, Waltham, MA) at 5,000 rpm (2,700 g) for three 15-min intervals at 20°C. Water collected in the large Falcon tube was removed after each round, weighed, and then mixed with the extracted water from subsequent rounds. Extracted water was transferred to vials (0.3 ml, Wheaton-DWK Life Sciences, Millville, NJ, USA) for stable isotope analysis. Samples were weighed after centrifuging to calculate water recovery rate. After centrifuging, soil or S from each centrifuge tube was homogenized and transferred to individual scintillation vials for cryogenic vacuum distillation following the same protocol as described below. These distillation post centrifuge (DPC) samples were extracted at 100°C.

2.2 | Cryogenic vacuum distillation

Extractions were performed on a closed vacuum extraction line (West, Patrickson, & Ehleringer, 2006). Tubes on each port were outfitted with a metal sleeve, heating tape (Valin Thermal Solutions and Automation, Houston, TX, USA), and insulator to adjust and maintain temperature. Extractions were conducted at 80°C, 100°C, 150°C, and 200°C in order to test the extraction efficiency at varying temperatures. Thermocouples connected to a CR1000 data logger (Campbell Scientific, Logan, UT, USA) tracked the temperature of each port continuously. Extraction time varied with the amount of time that each initially frozen sample took to reach extraction temperature. Once extraction temperature was reached, the extraction continued for at least the length of time it took to reach that set temperature. This ensured that the sample spent a significant amount of time at the desired extraction temperature. The average extraction duration was 1.8 hr, with a minimum of 1.2 hr and a maximum of 3.2 hr. Extraction pressures began at 0.003 kPa. Extractions were considered complete when there was no longer vapour in the tubing, and the tube on the cold finger was clear (no further visible condensation) in addition to remaining on the vacuum line for the allotted time at the desired extraction temperature. After extraction completion, both samples and recovered water were weighed to calculate water recovery rate. Soils and S were weighed immediately post extraction and weighed again after oven drying at 105°C for 48 hr.

2.3 | Stable isotope analyses

Water recovered from centrifuged, cryogenic vacuum distillation, and DPC samples were transferred into vials for stable oxygen and hydrogen isotope analysis. Analyses were performed using a Delta V Advantage

isotope ratio mass spectrometer linked to a high-temperature conversion/elemental analyser via a Conflo IV (Thermo Fisher Scientific, Waltham, MA, USA) at the Stable Isotope for Biosphere Science (SIBS) Laboratory (<https://sibs.tamu.edu>), at Texas A&M University. Calibration was performed using in-house water standards: SIBS-wA ($\delta^2\text{H} = -390.8 \pm 1.6\text{‰}$, $\delta^{18}\text{O} = -50.09 \pm 0.33\text{‰}$) and SIBS-wP ($\delta^2\text{H} = -34.1 \pm 1.9\text{‰}$, $\delta^{18}\text{O} = -4.60 \pm 0.24\text{‰}$). Quality control was performed using an in-house water standard, SIBS-wU ($\delta^2\text{H} = -120.2 \pm 1.5\text{‰}$, $\delta^{18}\text{O} = -15.95 \pm 0.27\text{‰}$). These in-house standards were calibrated using International Atomic Energy Agency standards (Vienna standard mean ocean water 2, standard light Antarctic precipitation, and Greenland ice sheet precipitation). All isotope values are reported in Vienna standard mean ocean water–standard light Antarctic precipitation scale.

2.4 | Contribution of bound WaterE to water extracted via centrifugation

Following stable isotope analysis, we noted that the water extracted via centrifugation fell on a mixing line between WaterE and WaterD. We calculated the contribution of WaterE to $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the resulting water using a simple mixing model:

$$\text{Contribution of WaterE (\%)} = \frac{\delta_{\text{C}} - \delta_{\text{D}}}{\delta_{\text{E}} - \delta_{\text{D}}} \times 100, \quad (1)$$

where δ_{C} , δ_{D} , and δ_{E} are the isotope ratios for the water extracted by centrifugation, WaterD, and WaterE, respectively. It is important to note that the measured isotope value for WaterE may not represent the actual bound water value after drying. During drying, isotopic fractionation is expected, resulting in bound water more enriched in heavy isotopes, making the difference between WaterE and WaterD greater. The magnitude of this enrichment in heavy isotopes could vary depending on soil characteristics, temperature, and potentially a minor effect of vapour isotopic composition. We did not attempt to estimate this effect given a lack of constraint on soil texture effects. Therefore, the measured value for WaterE is the lowest possible isotope value for the bound water in each soil. Because δ_{E} is the measured WaterE value, Equation (1) potentially overestimates the contribution of bound water to the measured composition of water extracted from soils and S via centrifuging.

2.5 | Statistical evaluation

Data analysis was carried out with the statistical software R (R Core Team, 2019) run in R Studio (R Studio Team, 2019). Data were checked for normality using the Shapiro–Wilk normality test and checked for equal variance with the Brown–Forsythe test. If data was found to be normally distributed with equal variance, one-way and three-way analyses of variance were conducted to compare the individual effects and combined interactions of variables (i.e., soil type,

extraction method, extraction temperature, and extraction duration) on resulting $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. Kruskal–Wallis tests were used if data had unequal variance. Tukey honestly significant difference mean comparisons provided insight into the differences between samples and extraction conditions. Linear regressions and one- or two-sample *t* tests were also used to compare isotope results with soil properties and to other isotope results, respectively.

3 | RESULTS

3.1 | Soil texture and mineralogy

Soils RA, TB, CD, and CG ranged in clay content from 9.9% to 27.2% (Table 1). The S was found to contain 2.5% clay-sized particles and 1.4% silt-sized particles. Soil organic carbon ranged from 1.32% to 1.92%. S did not contain organic carbon. The XRD analyses revealed that the major component of all soils and S was quartz, with an average relative abundance of 93.4% (Table 1). All four soils contained small amounts of orthoclase and albite, whereas S contained orthoclase and calcite. CD and CG (Oklahoma soils) had low abundance of kaolinite, and CD contained mica as well. While the Web Soil Survey suggested that both TB and RA (Texas soils) were smectitic soils (Soil Survey Staff, 2019), montmorillonite was only detected in TB.

3.2 | Water extracted by centrifugation

Water extracted via centrifugation fell on a mixing line between the WaterE and WaterD (Figure 1). The $\delta^{18}\text{O}$ values of extracted water were significantly different from the $\delta^{18}\text{O}$ value of WaterD for all soil types ($p < 0.05$) except for CD ($t_2 = 2.62$, $p = 0.12$; Figure 1b). The $\delta^2\text{H}$ of extracted water were significantly different from WaterD for all soil types ($p < 0.05$), except for S ($t_2 = 3.02$, $p = 0.09$; Figure 1a). Although the $\delta^{18}\text{O}$ values differed among soil types ($\chi^2[4, N = 15] = 11.08$, $p = 0.03$), only TB was significantly more ^{18}O -enriched than the other samples, which were all similar to each other (Figure 1d). The $\delta^2\text{H}$ values also differed among soil types ($\chi^2[4, N = 15] = 11.10$, $p = 0.03$), with generally more deuterium-enriched water from soils with high clay + silt content. Whereas the $\delta^2\text{H}$ values increased significantly with clay content ($R^2 = 0.47$, $p < 0.01$), the relationship was stronger when considering clay + silt content ($R^2 = 0.58$, $p < 0.01$).

Mean water recovery based on extracted water weight differed with soil type. More clayey soils had lower recovery (TB = 27.3%, CG = 36.2%) compared with sandy soils (RA = 45.8%, CD = 50.3%) and S (65.5%) with higher recovery ($F(4, 10) = 5.70$, $p = 0.01$; Figure 2). Similar to the $\delta^2\text{H}$ values, water recovery decreased with clay content alone ($R^2 = 0.33$, $p = 0.03$), yet the trend was stronger with clay and silt together ($R^2 = 0.61$, $p < 0.01$). There was more variability in recovery for S and sandy soils than clayey soils.

The contribution of WaterE to the centrifuged samples is an average of 1.26%, with a range of 0.21% to 2.24% for hydrogen and 0.15% to 2.50% for oxygen (Figure 3). The size of the bound pool

TABLE 1 Characteristics of soils used in this study

	CD	CG	TB	RA	S
Location	Stillwater, OK, USA	Stillwater, OK, USA	College Station, TX, USA	College Station, TX, USA	Not applicable
Latitude, longitude	36.059600, −97.183233	36.055431, −97.190900	30.515792, −96.240623	30.574848, −96.363345	Not applicable
Taxonomic class	Fine-loamy, siliceous, active, thermic Ultic Haplustalfs	Fine-loamy, siliceous, active, thermic Ultic Haplustalfs	Fine, smectitic, thermic Ultic Paleustalfs	Fine, smectitic, thermic chromic Vertic albaqualfs	Not applicable
Clay (%)	27.2	24.4	23.4	9.9	2.5
Silt (%)	3.4	42.9	34.2	25.5	1.4
Sand (%)	69.5	32.7	42.4	64.6	96.1
Soil organic carbon (%)	1.80	1.32	1.80	1.92	0
XRD analysis (relative %)					
Quartz	93	93	92	95	94
Albite	3	3	4	2	0
Orthoclase	3	3	3	3	2
Calcite	0	0	0	0	4
Montmorillonite	0	0	2	0	0
Mica	1	0	0	0	0
Kaolinite	1	2	0	0	0
Smectite	No	No	Yes	Yes	No

Note: Soil texture was assessed using the hydrometer method (Sheldrick & Wang, 1993). Soil organic carbon was measured by dry combustion using an elemental analyser (Costech Analytical Tech, Inc, Valencia, CA, USA). Taxonomic class information was obtained from the United States Department of Agriculture Natural Resources Conservation Service Web Soil Survey (Soil Survey Staff, 2019).

Abbreviation: XRD, X-ray diffraction.

remaining after oven drying increased with clay content, but the relationship is only statistically significant for $\delta^2\text{H}$ ($R^2 = 0.47$, $p < 0.01$). When the relationship is assessed with clay and silt content combined, there is a significant increase in bound water contribution with increasing clay + silt content for $\delta^{18}\text{O}$ ($R^2 = 0.34$, $p = 0.02$) and $\delta^2\text{H}$ ($R^2 = 0.58$, $p < 0.01$).

3.3 | Water extracted by vacuum distillation

Compared with the water recovered from centrifuging, water extracted via cryogenic vacuum distillation did not fall on an isotope mixing line between WaterE and WaterD (Figure 1). Rather, the isotope values fell below the line and were overall heavy isotope depleted. However, the $\delta^{18}\text{O}$ values of CD and S were the only ones statistically different from WaterD $\delta^{18}\text{O}$ values ($t_{10} = -2.32$, $p = 0.04$ and $t_{11} = 6.02$, $p < 0.01$, respectively). All soil types were different from WaterD based on $\delta^2\text{H}$ ($p < 0.01$ for all). Across soil types, there was a significant temperature effect on $\delta^{18}\text{O}$ ($\chi^2[3, N = 48] = 37.08$, $p < 0.01$) and $\delta^2\text{H}$ values ($\chi^2[3, N = 48] = 36.54$, $p < 0.01$), with higher extraction temperatures resulting in progressively more enriched water (Figure 4). Yet extraction temperature did not impact water recovery rate based on water recovery weight ($F(3,44) = 1.40$, $p = 0.26$; Table S1) nor based on the difference between pre-extraction and post extraction soil weight ($F(3,44) = 0.16$, $p = 0.92$; Table S1).

3.4 | Distillation post centrifuge

The low water recovery (20.3–51.2% not including S; 83.1% with S) from centrifuging allowed us to extract the remaining water via vacuum distillation at 100°C. Water extracted from these samples differed in $\delta^{18}\text{O}$ across soil types, generally resulting in more heavy isotope-depleted values with decreasing sand content ($\chi^2[4, N = 14] = 12.12$, $p = 0.02$; Figure 5b). All soils with clay had similar $\delta^2\text{H}$ values, and S had the highest $\delta^2\text{H}$ value ($\chi^2[4, N = 14] = 8.27$, $p = 0.08$; Figure 5f). Across soil types, recovery for DPC samples were not significantly different based on water weight ($F(4,10) = 1.96$, $p = 0.18$) and sample weight ($F(4,10) = 0.46$, $p = 0.77$).

DPC samples were more heavy isotope depleted compared with the centrifuged and distillation samples. Overall, water extracted via DPC had similar $\delta^{18}\text{O}$ ($F(1,28) = 1.97$, $p = 0.17$) but differed in $\delta^2\text{H}$ ($\chi^2[1, N = 29] = 9.81$, $p < 0.01$) compared with their respective centrifuged samples. DPC samples differed from water extracted at 100°C via distillation (D100) for both $\delta^{18}\text{O}$ ($\chi^2[1, N = 28] = 4.03$, $p = 0.04$) and $\delta^2\text{H}$ ($\chi^2[1, N = 28] = 5.05$, $p = 0.03$).

3.5 | Centrifugation versus cryogenic vacuum distillation

Water recovery based on extracted water weight between methods were significantly different ($\chi^2[4, N = 74] = 39.05$, $p < 0.01$).

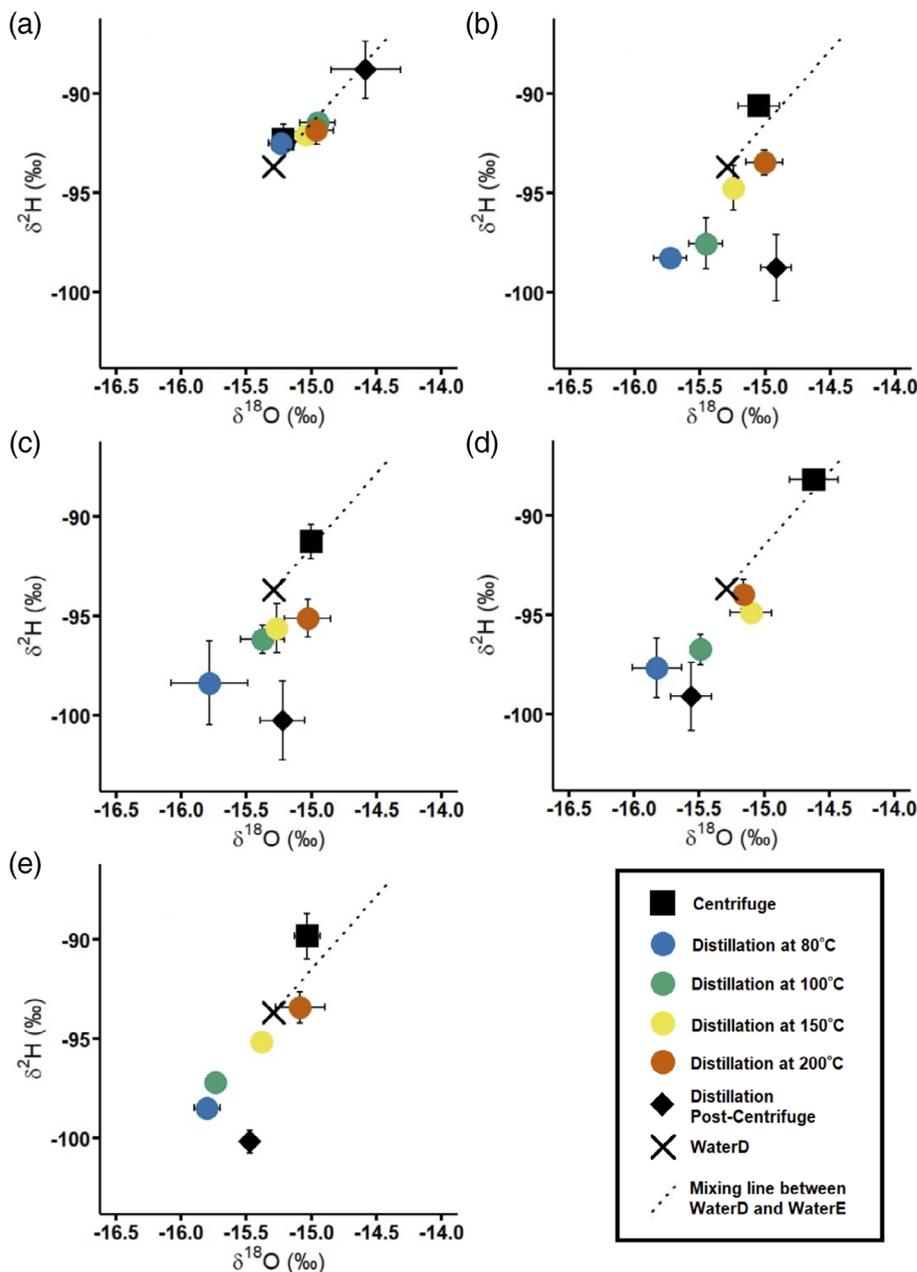


FIGURE 1 Isotope compositions of soil water extracted via centrifuging (square), vacuum distillation (circles), or distillation post centrifuge (diamond) by soil type. Distillation extraction temperatures are denoted by colour (80°C—blue, 100°C—green, 150°C—yellow, and 200°C—orange). A mixing line (dashed line) between heavy isotope-depleted water (x) and heavy isotope-enriched water is $\delta^2\text{H} = 7.359 \delta^{18}\text{O} + 18.89$. Plots are organized by soils with increasing clay + silt content (A: sand, B: CD, C: RA, D: TB, and E: CG). Error bars show the standard deviation of the three replicates for each sample

Centrifuging had an average water recovery rate of 45.0% (including S) and 39.9% (excluding S), and distillation had an average of 101.9% (including S) and 102.2% (excluding S).

Based on two-sample *t* tests, the extractions conducted at 200°C (D200) were similar to their respective centrifuged samples in terms of $\delta^{18}\text{O}$ ($F(1,28) = 0.85$, $p = 0.36$) but not $\delta^2\text{H}$ ($\chi^2[1, N = 29] = 18.08$, $p < 0.01$).

4 | DISCUSSION

4.1 | Importance of sample preparation

We directly manipulated the bound pool in these soils by vacuum drying them prior to spiking with an isotopically distinct reference water,

drying to mimic prior experimental pretreatments, and then labelling with a WaterD to label both the apparent bound and mobile pools. This allowed us to remove a large fraction of residual water from the soils that we expected to otherwise have an influence on measured soil water isotope ratios and more directly test hypotheses about mismatches between “spike” water and measured water post extraction. The vacuum-drying treatment was incorporated after a preliminary spiking experiment revealed the potential influence of residual water from the field (results not shown), consistent with reports from other studies (Araguás-Araguás et al., 1995; Newberry et al., 2017; Orlowski et al., 2018).

Our results showed that the water extracted by centrifuging falls on a mixing line between WaterE and WaterD (Figure 1). We interpret this to mean that oven drying at 105°C does not remove all bound water from soils and, while this bound water is not removed, it also

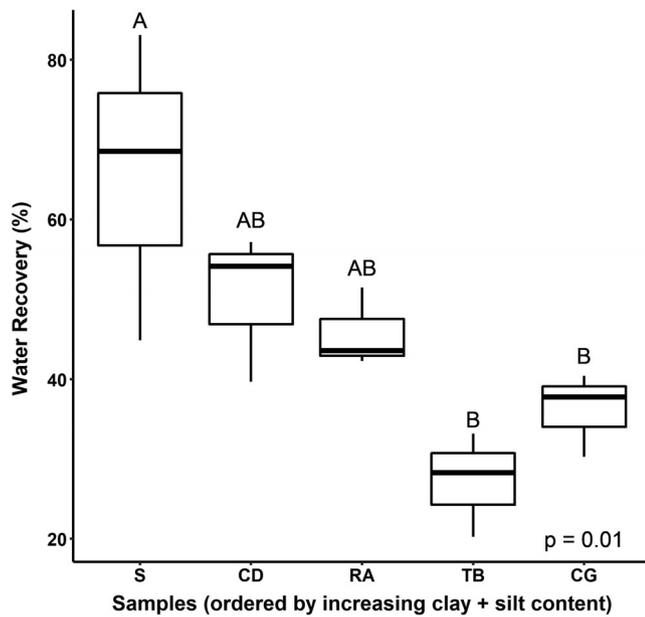


FIGURE 2 Water recovery by centrifuging. Water recovery was calculated by comparing the weight of water extracted to the calculated water in each sample. Three replicates per soil type were centrifuged. Samples on the x-axis are ordered by increasing clay + silt content

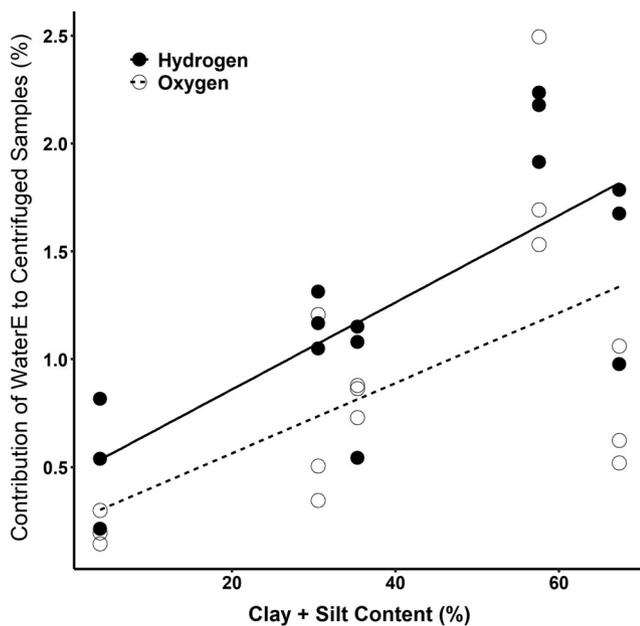


FIGURE 3 Contribution of heavy isotope-enriched water to centrifuged samples based on $\delta^2\text{H}$ (closed circles; $R^2 = 0.58$, $p < 0.01$) and $\delta^{18}\text{O}$ (open circles; $R^2 = 0.34$, $p = 0.02$) as a function of clay and silt content. (See text for discussion on heavy isotope-enriched water)

readily mixes with the presumably mobile water added subsequently (Wang, Lu, Ren, & Li, 2011). The contribution of WaterE to the centrifuged samples ranged from 0.21% to 2.24% based on hydrogen and 0.15% to 2.50% based on oxygen. Retention increased with increasing

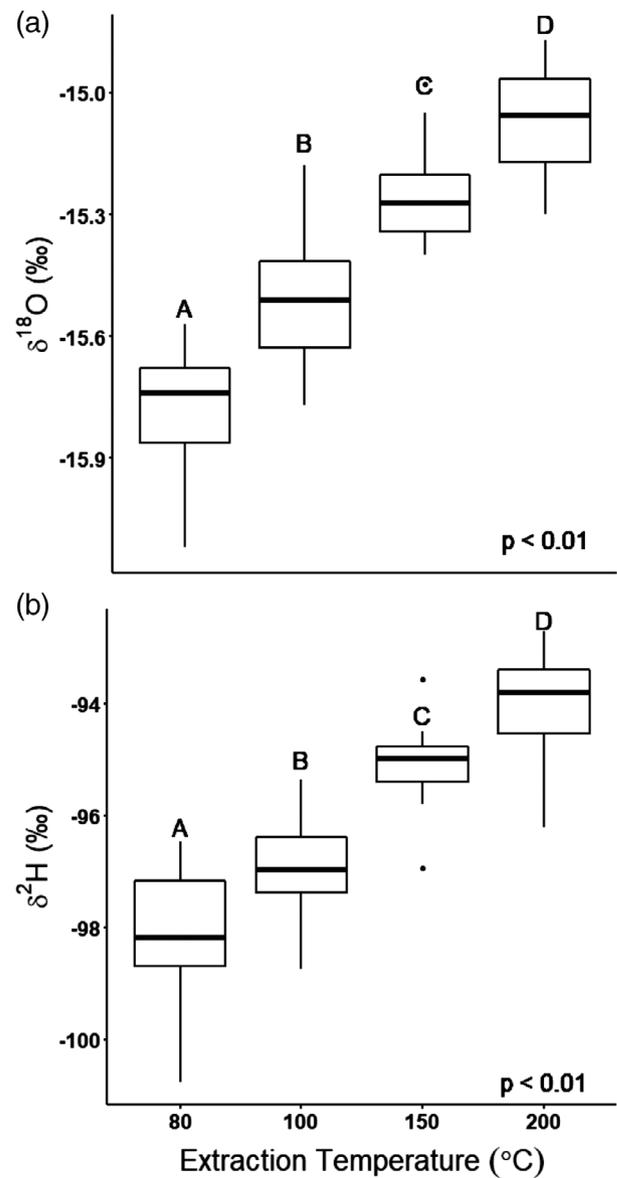


FIGURE 4 Temperature effect on $\delta^{18}\text{O}$ (a) and $\delta^2\text{H}$ (b) of water extracted from all soils via cryogenic vacuum distillation. S was not included in this comparison

clay + silt content (Figure 3). Again, the contribution of WaterE calculated using Equation (1) could overestimate the contribution of the bound water to the water extracted via centrifuging, as WaterE would have likely undergone evaporative enrichment during drying. However, the amounts calculated are in agreement with Thielemann et al. (2019), who found that soils with high clay content had bound pools accounting for 1.4% to 1.8% of the total soil water. Because the bound water and WaterD in our study are isotopically distinct from each other, only a small amount of heavy isotope-enriched bound water is needed to impact the isotopic composition of the extracted water. The calculated contribution amounts from Equation (1) exemplify this and are, therefore, useful, particularly when analysing the impact of clay on soil water processes as described later in this discussion.

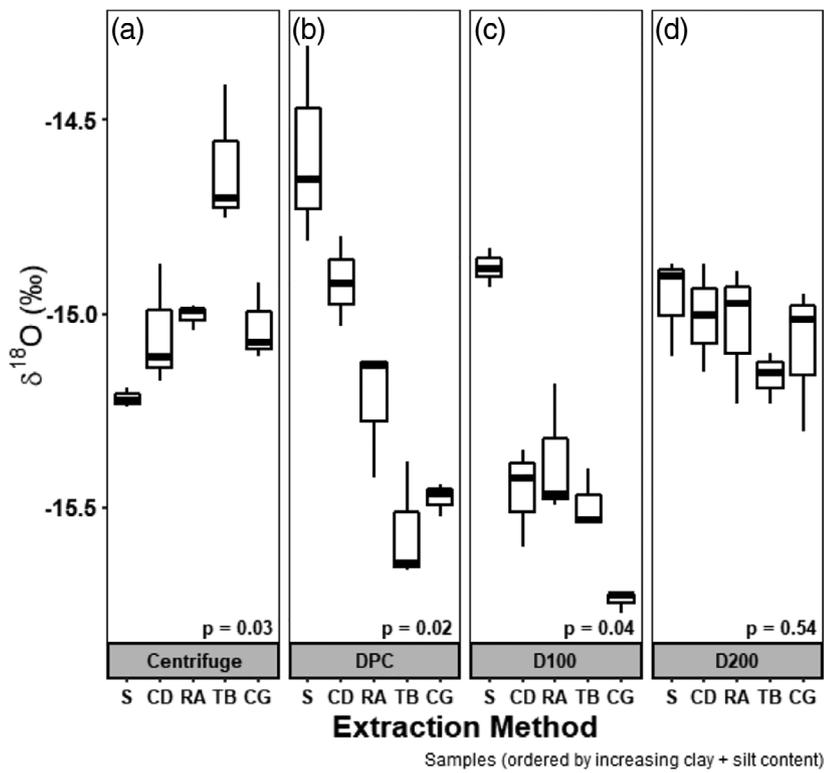
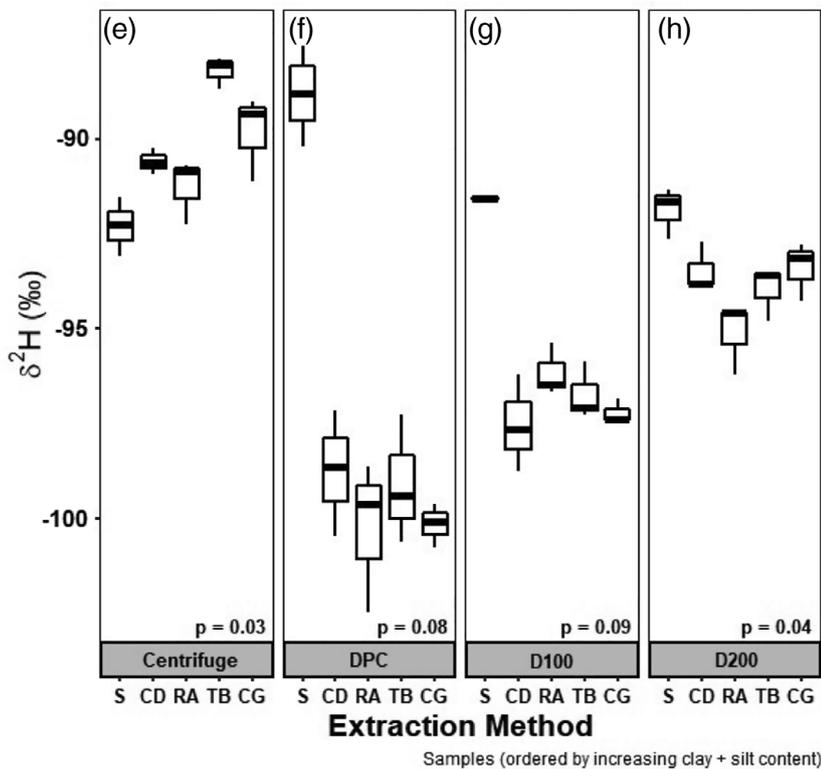


FIGURE 5 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of samples extracted by (a,e) centrifuging, (b,f) DPC, (c,g) vacuum distillation at 100°C (D100), and (d,h) vacuum distillation at 200°C (D200). Samples are ordered by increasing clay + silt content. Abbreviation: DPC, distillation post centrifuge



4.2 | Impact of clay minerals on bound water

Although we observed positive correlations between clay content and bound pool size, the type of clay minerals played an important role in these interactions. TB had only the third highest clay content and second highest clay + silt content among the soils in our study; however,

it retained the most WaterE (Figure 3). This may be explained by the fact that TB contained montmorillonite, a 2:1 phyllosilicate smectite mineral (Table 1; Barnhisel & Bertsch, 1989; O'Neil & Kharaka, 1976). Smectite is noted to have double-layered hydration spheres adsorbed to clay particles, high cation exchange capacity, and therefore, increased matric potential (Oerter et al., 2014). Although RA was

reported to also contain smectite based on the United States Department of Agriculture Web Soil Survey, the soil only contained 9.9% clay, decreasing the impact of the smectite clay minerals compared with TB (Soil Survey Staff, 2019). This is further supported by the fact that montmorillonite was not detected in the XRD analysis of RA (Table 1). According to the XRD analysis, CD and CG contained kaolinite, a common 1:1-layer mineral. Due to strong hydrogen bonding between layers, there is no interaction between soil water and these layers. Because of this, adsorption is limited to external surfaces, causing soils with 1:1 clay minerals to have low cation exchange capacity (Barton & Karathanasis, 2002). High temperature cryogenic vacuum distillation extractions on soils with kaolinite were found to produce isotope values similar to quartz, which is known to have negligible effects on soil water isotopes (Gaj et al., 2017; Longstaffe & Ayalon, 1990). Therefore, our results suggest that not only does clay content matter when evaluating relationships between bound and mobile soil water but also clay mineral compositions, particularly the presence of smectite and other 2:1-layer clay minerals, may be crucial.

4.3 | Isotopic patterns from centrifugation

Centrifuged samples showed that soils with higher clay + silt content appeared to have a larger bound pool as shown by the higher contribution of WaterE (Figure 3), which is consistent with prior reports (Araguás-Araguás et al., 1995; Gaj et al., 2017; Orłowski et al., 2016). In our experiment, finer textured soils retained more water after oven drying, likely allowing for increased exchange with the mobile WaterD during the second 72-hr equilibration period.

However, texture alone cannot explain our results. The presence of montmorillonite in TB increased the retention of WaterE, even though it has only the second highest clay + silt content (Figure 3). Studies that assessed the exchange between water bound by clay mineral cations and mobile water suggested that cations like magnesium form inner and outer layers in the hydration spheres (Sposito et al., 1999). The inner layer forms strong hydrogen bonds preferentially with water molecules that have ^{18}O , whereas the outer layer favours bonds with water molecules with ^{16}O (O'Neil & Truesdell, 1991; Oerter et al., 2014). If this mechanism is valid, one might expect that this exchange would result in lower $\delta^{18}\text{O}$ values of TB's mobile water pool relative to other soils. However, in our study, TB had the most ^{18}O -enriched water extracted via centrifugation (Figure 1d). We suggest that the explanation of this apparent contradiction is that during the equilibration period after WaterE was added, inner and outer hydration spheres were formed on montmorillonite in TB as discussed in Oerter et al., (2014), causing TB's bound pool to have more ^{18}O from WaterE than the other soils after oven drying. When WaterD was added, there was still preferential bonding; however, WaterD had significantly less ^{18}O to contribute. Therefore, the large bound pool of ^{18}O from WaterE contributed to the majority of the mixing, resulting in a net enrichment of the mobile water extracted via centrifuging. It is important to note that there have been more

studies on the isotopic effects of clay minerals on oxygen isotopes, and few have commented on interactions with hydrogen (VanDeVelde & Bowen, 2013).

4.4 | Centrifuged water does not represent the total water pool

It would be tempting to conclude that centrifuging is the "best" soil water extraction method because it captured this mixing and that water extracted with this method represents what is presumably a total water pool (bound plus mobile water). The DPC results provide additional insight to the underlying mechanisms. If there was complete mixing between the bound and mobile water pools (and no other extraction effects), the isotopic composition of the centrifuged water and the post centrifuge water should be the same. By extracting the water remaining after centrifuging on the vacuum line, we showed that water extracted via centrifuging and DPC are different from each other, particularly in hydrogen (Figure 1). S shows most clearly this effect: the centrifugation values are most similar to WaterD, and the DPC values fall along a mixing line between WaterD and WaterE (Figure 1a). The vacuum distillation values fall between these two extremes. These results suggest that centrifuged water represents a different portion of the total water pool, reflecting a mixture between the bound and mobile waters, but biased towards the mobile pool.

If the centrifuge water is biased towards the mobile pool, then the DPC water is biased towards the bound pool. This allows us to gain insight into the bound pool and the interactions between clay + silt content and clay mineralogy. In Figure 5b, it is shown that $\delta^{18}\text{O}$ declined with increasing clay + silt content, suggesting that vacuum distillation after centrifuging was able to extract the remainder of the mobile water plus an ^{18}O -depleted bound pool. For TB, if we were able to capture all bound water (^{18}O -enriched inner and ^{18}O -depleted outer hydration spheres), its respective DPC samples should be enriched in ^{18}O compared with the other samples (Oerter et al., 2014). However, this was not the case. We conclude that although vacuum distillation is able to extract bound water from clays, it is unable to access inner hydration spheres formed around particular cations at 100°C . We believe that this is related to the matric potential of the fine-grained soil particles (Trask, 1959). Interestingly, all soils have similar $\delta^2\text{H}$ values, except for S (Figure 5f). It appears that the presence of fine-grained soil particles interact with hydrogen in similar ways regardless of the amount.

To explore this further, we compared the DPC samples with the vacuum distillations performed at the same temperature (D100). For D100 samples, there were negative trends with $\delta^{18}\text{O}$ and increasing clay + silt content ($\chi^2[4, N = 14] = 9.79, p = 0.04$; Figure 5c) and significant deuterium enrichment in S relative to all the soils ($\chi^2[4, N = 14] = 8.04, p = 0.09$; Figure 5g). Although these patterns in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were similar to the DPC samples, the $\delta^{18}\text{O}$ trend is not as strong for the D100 samples. This is most likely because the D100 and DPC samples do not reflect the same pools. There is significantly more mobile water in the D100 samples compared with the DPC

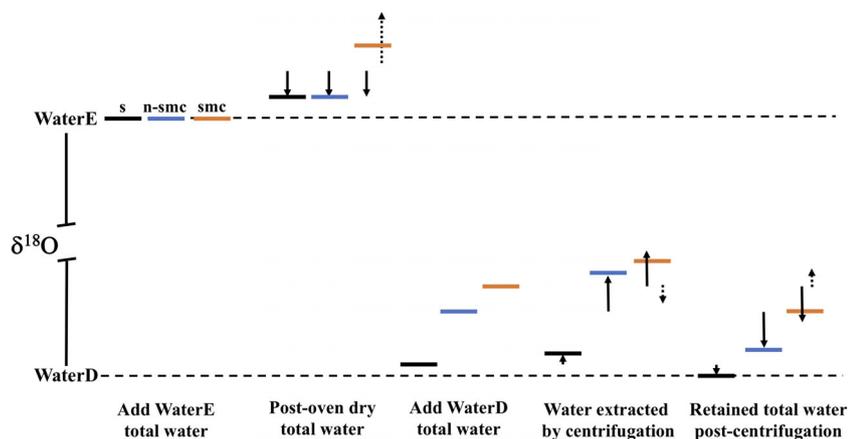


FIGURE 6 Conceptual model for observed oxygen isotope effects on the total soil water pool in sand (black bar), non-smectite soils (blue bar), and smectite soils (orange bar) at various steps in the experiment. Solid and dashed arrows indicate fractionation associated with monovalent and divalent cation hydration, respectively. The length denotes the relative degree of fractionation, incorporating the additional influence of fine-grained fraction-driven water retention on the isotopic composition of the total soil water pool. WaterD, heavy isotope-depleted water; WaterE, heavy isotope-enriched water

samples, as the DPC samples represent the pool after a large portion of the mobile water was extracted via centrifuging. Despite this, we still find distinct differences in the effects of fine-grained soil particles on oxygen and hydrogen isotopes. When comparing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for vacuum distillations conducted at 200°C (D200), there was no significant difference in $\delta^{18}\text{O}$ ($F(4,10) = 0.83$, $p = 0.54$; Figure 5d), and $\delta^2\text{H}$ became more similar to S ($\chi^2[4, N = 15] = 10.17$, $p = 0.04$; Figure 5h), with the exception of RA and TB. At higher temperatures, the matric potential effects on oxygen and hydrogen both diminish as hydrogen bonds between fine-grained soil particles and bound water are more easily broken at high temperatures (Gaj et al., 2017). This supports other studies that found that bound water is more readily released at higher temperatures (Araguás-Araguás et al., 1995; Gaj et al., 2017; Walker et al., 1994; Wang et al., 2011).

4.5 | Isotopic patterns from cryogenic vacuum distillation

There was a significant temperature effect for soils extracted on the vacuum line, with increasing extraction temperatures yielding more heavy isotope-enriched values and plotting along lines of apparent temperature-dependent fractionations, particularly for ^{18}O (Figure 1). The ^{18}O enrichment with temperature suggests that a Rayleigh-type fractionation effect occurred in the vacuum line. Rayleigh fractionation is evident if evaporation is not complete and a portion of the original water is not captured (Majoube, 1971). This alters the isotopic composition of the collected water sample, as WaterD evaporates more readily. In our study, higher extraction temperatures allowed for more water (both mobile and bound) to be released and resulted in a more complete extraction compared with those performed at lower temperatures. A similar temperature effect has been observed by other studies (Araguás-Araguás et al., 1995; Gaj et al., 2017; Orłowski et al., 2018).

Based on our calculations for water recovery for vacuum distillations, we found that the average recovery based on water weight was over 100% (Table S1). The average recovery based on sample weight

was 98.99% (Table S1). These recovery assessments suggest that the extractions performed, regardless of temperature, were “complete.” But the isotope results show that some of the extractions were not complete, particularly those performed at lower temperatures (80°C and 100°C). This is consistent with observations by Gaj et al., (2017a). During distillation, soil particles transferred to the cold finger with the extracted water, even though quartz wool was placed above samples to prevent transfer (Thielemann et al., 2019). Particles in extracted water therefore will overestimate recovery based on water weight and will underestimate recovery based on sample weight. Common mass-based recovery estimates may be insufficient to describe completeness of extractions with respect to isotope ratios of the extracted water and perhaps in part explaining variability in results from seemingly complete extractions (Orłowski et al., 2018).

4.6 | Conceptual model for total soil water

Overall, our results are consistent with previous work showing that soil properties, in particular the presence and mineralogy of clays, have an influence on the isotopic composition of bound and mobile soil water pools but that this influence remains poorly constrained, potentially limiting inferences that can be drawn from soil water isotopes in hydrological and ecological studies. Based on our results and prior published work, we developed a conceptual model of the oxygen isotope effects observed in this experiment to better understand potential mechanisms here and suggest hypotheses to guide future work (Figure 6).

The following describes the patterns observed for the sand samples, nonsmectitic soil samples, and smectitic soil samples and offers hypotheses for the underlying mechanisms. To begin, we assume that vacuum drying at 105°C removes residual mobile and bound water (including all or nearly all of the water in hydration spheres of soil cations), allowing the experiment to begin without initial isotopic influence. After vacuum oven drying, WaterE is added, and all of the soils have total soil water pools that resemble WaterE. This water, however, is expected to partition into “perturbed” and free pools as a

function of clay cation exchange capacity and the presence of adsorbed, hydrated cations (Oerter et al., 2014). When the soils are oven dried at 105°C (at ambient atmospheric pressure, mimicking common “spiking” experiment protocols), bound water in all soils and S will undergo some degree of evaporative enrichment, making the value for WaterE the lowest possible value for the bound water pool. At the same time, the nonsmectitic soils (and sands to a lesser extent) preferentially retain ^{16}O in the bound, hydration spheres of adsorbed minerals associated with kaolinite clay minerals, expected to be dominated by monovalent cations like Na^+ and K^+ . For the soils with smectite, the same depletion occurs for monovalent cations, as well as for the outer hydration spheres of divalent cations. However, a retention of ^{18}O in the inner hydration spheres of divalent cations is expected. This partitioning of ^{18}O to the inner hydration spheres is expected to have a relatively stronger heavy isotope-enrichment effect on retained water, resulting in a net enrichment of the total soil water pools in smectite soils compared with the other soils and WaterE following oven drying. When WaterD is subsequently added, it is a large fraction of the total water, causing overall heavy isotope depletion of the total water pools. At this point, the amount of WaterE retained after oven drying matters to the isotopic composition of the total water pool based on mass balance. As shown in Figure 3, S retained the least WaterE, whereas the soil with smectite (TB) retained the most. These differences in soil texture plus clay mineralogy result in enrichment of the total soil water compared with WaterD, with S being the least enriched and smectite soils being the most (high clay content plus retention of ^{18}O -enriched water in hydration spheres). In addition, during this step, we believe that mobile WaterD exchanges with the heavy isotope-enriched bound water, contributing WaterE to the “free” water. During centrifugation, this mobile water is removed, with sand having the highest average water recovery (65.5%) and the smectite samples having the lowest (27.3%; Figure 2). Water extracted by the centrifuge should access the mobile pool only. For all soils, we expect some enrichment of the mobile pool as the fractionated, bound WaterE pool exchanges with WaterD in the prior step. The degree of enrichment increases with a larger fine-grained fraction and the presence of smectitic clays. After centrifugation, the remaining water is biased towards WaterE as a function of soil matric potential (resisting water removal by centrifugation) and the isotope effects associated with cation hydration spheres and exchange with the added WaterD.

If this conceptual model is correct, one prediction is that the total water pool for all samples will not fall on a mixing line in $\delta^2\text{H}$ - $\delta^{18}\text{O}$ space between the two reference waters because we do not expect the isotope effects of ion hydration and exchange to be the same for $\delta^2\text{H}$ and $\delta^{18}\text{O}$. It is important to note that although there is evidence for these underlying mechanisms for oxygen isotopes (Oerter et al., 2014), hydrogen isotope interactions in soils are less understood. This makes it difficult to accurately calculate the isotopic composition of the total water pool for both $\delta^2\text{H}$ and $\delta^{18}\text{O}$, preventing us from making strong statements about the best extraction method. However, according to the model, the total soil water pool should be between WaterE and WaterD, though somewhat offset from a mixing line. In

general, the water extracted via centrifuging, distillation at 150°C, and distillation at 200°C fall to the right of WaterD on the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ plots (Figure 1). The differences between these three extraction methods are relatively small for all of the soils with limited or no montmorillonite, suggesting that centrifugation and high temperature distillations reasonably represent total soil water for nonsmectitic clay soils. We suggest that future studies employ a similar sample preparation method to ours to control the isotopic composition of bound and mobile pools in order to directly study soil water extraction effects without the influence of residual water from the field. Further, studies should not only focus on clay content but also include soils with a wide range of clay types in order to directly assess the impacts of mineralogy and organic matter on soil water isotope composition. Extraction temperature is clearly important for cryogenic vacuum distillations in this and other studies; therefore, future studies should avoid extractions at one temperature. Other common soil water extraction methods (for example, lysimeters) should also be considered to compare with distillation and centrifuging.

5 | CONCLUSIONS

Consistent with prior reports, we demonstrated that oven drying is inefficient in removing residual water from soils. By labelling this apparently bound water, we were further able to detect interactions between bound and mobile soil water pools. The isotope ratios of soil water obtained by centrifugation were consistent with bound and mobile water mixing, but this mixing appeared to be incomplete, as shown by cryogenic vacuum extraction of water remaining after centrifugation. Cryogenic vacuum distillations had substantially higher water recovery, but the isotopic composition of extracted water was affected by temperature-dependent effects and was different from that obtained by centrifugation. High temperature (between 150°C and 200°C) distillations yielded water that was most similar to the WaterD value; however, water derived by centrifugation suggested the presence of a residual pool not clearly reflected in the distillation water. Based on these results, we suggest a conceptual model for water isotope fractionation in soils linked to both clay content and mineralogy but point out that important uncertainties remain. Future work evaluating extraction methods should include explicit characterization of clay mineralogy. In addition, our work implies caution in interpreting isotope ratios of extracted soil water and a need to better characterize processes that govern soil water fractionation.

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DATA AVAILABILITY STATEMENT

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

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