Lessons from and best practices for the deployment of the Soil Water Isotope Storage System

Rachel E. Havranek¹, Kathryn Snell¹, Sebastian Kopf¹, Brett Davidheiser-Kroll², Valerie Morris³, Bruce Vaughn³
¹Geological Sciences, University of Colorado Boulder, Boulder, 80303, USA
²Thermo Fisher Scientific (Bremen) GmbH, Bremen, Germany
³Institute of Arctic and Alpine Research, University of Colorado Boulder, Boulder, 80303, USA

Correspondence to: Rachel Havranek (rachel.havranek@colorado.edu)

Abstract. Soil water isotope datasets are useful for understanding connections between the hydrosphere, atmosphere, biosphere, and geosphere. However, they have been underproduced because of technical challenges associated with collecting those datasets. Here, we present the full testing and automation of the Soil Water Isotope Storage System (SWISS). The unique innovation of the SWISS is that we are able to automatically collect water vapor from the critical zone at a regular time interval and then store that water vapor until it can be measured back in a laboratory setting. Through a series of quality assurance and quality control tests, we rigorously tested that the SWISS is resistant to both atmospheric intrusion and leaking in both laboratory and field settings. We assessed the accuracy and precision of the SWISS through a series of experiments where water vapor of known composition was introduced into the flasks, stored for 14 days, and then measured. From these experiments, after applying an offset correction, we assess the precision of the SWISS at 0.9‰ and 3.7‰ for δ¹⁸O and δ²H, respectively. We deployed three SWISS units to three different field sites to demonstrate that the SWISS stores water vapor reliably enough that we are able to differentiate dynamics both between the sites as well within a single soil column. Overall, we demonstrate that the SWISS is able to faithfully retain the stable isotope composition of soil water vapor for long enough to allow researchers to address a wide range of ecohydrologic questions.

1 Introduction

Understanding soil water dynamics across a range of environments and soil properties is critical to food and water security (e.g. Mahindawansha et al., 2018; Quade et al., 2019; Rothfuss et al., 2021); understanding biogeochemical cycles, such as the nitrogen and phosphorus cycles (e.g. Hinckley et al., 2014; Harms and Ludwig, 2016); and understanding connections between the hydrosphere, biosphere, geosphere and atmosphere (e.g. Vereeken et al., 2022). One approach that can be used to understand water use and movement in the critical zone is the stable isotope geochemistry of soil water (e.g. Sprenger et al., 2016; Bowen et al., 2019). Variations in the stable isotope ratios of oxygen and hydrogen of soil water (δ¹⁸O, δ²H) track physical processes like infiltration, root uptake
and evaporation. In particular, stable water isotopes are useful for disentangling complex mixtures of water from multiple sources (e.g. Dawson and Ehleringer, 1991; Brooks et al., 2010; Soderberg et al., 2012; Good et al., 2015; Bowen et al., 2018; Gomez-Navarro et al., 2019; Sprenger and Allen 2020). Despite the long-recognized utility of measuring soil water isotopes for understanding a range of processes (e.g. Zimmerman et al., 1966; Peterson & Fry., 1987), soil water isotope datasets have been under-produced as compared to groundwater and meteoric water isotope datasets (Bowen et al., 2019).

The primary barrier to producing soil water isotope datasets has been the arduous nature of collecting samples. Traditionally, soil water samples are taken by digging a pit, and collecting a mass of soil to bring back to the lab for subsequent water extraction, disrupting the soil profile each time a sample is collected. To circumvent issues related to this style of sampling, the ecohydrology community has developed a variety of in situ water sampling methods over the last 10 years (e.g. Rothfuss et al., 2013; Volkmann and Weiler, 2014; Gaj et al., 2015; Oerter et al., 2016; Beyer et al., 2020). These methods have helped to shed light on a range of ecohydrologic questions from evaporation and water use dynamics in managed soils (e.g. Oerter et al., 2017; Quade et al., 2019) to better understanding where plants and trees source their water (e.g. Beyer et al., 2020).

The expansion in situ sampling methods allows for a greater understanding of ecohydrologic dynamics temporally, but with current methods these studies are often done in close proximity to the institutions performing the studies because of logistical constraints. The spatial constraints limit what we can learn about soil hydrology in remote and traditionally understudied landscapes. Beyond the ecohydrology community, the creation of high temporal resolution soil water isotope data sets is useful to a broader set of stakeholders. For example, long-term temporal records of soil water can be used to better understand geologic proxy development (e.g. stable isotope records from pedogenic carbonate, br-GDGTs, etc.). These projects, however, commonly have environmental constraints like soil type or local climate state that may not be located near institutions performing those studies, creating the need for a system that is capable of collecting water vapor from remote settings in an automated way.

In this contribution, we report on the further development and testing of a field deployable system first introduced in Havranek et al., (2020). This system is now capable of independently sampling soil water vapor in situ, storing that water vapor for a period of time until the samples can be brought back to a laboratory to be measured. In our case, we used a Picarro L-2130i water isotope analyzer (Picarro, Inc. Santa Clara, CA) to measure both water concentration and the oxygen and hydrogen isotope ratios of the soil water vapor. The combination of the autonomous sampler and the CRDS instrument offers a flexible and reliable solution to obtain data that is otherwise difficult to collect from soil profiles. Here, we present the testing and optimization of the Soil Water Isotope Storage System (SWISS). First, we present a quality assurance and quality control (QA/QC) procedure that we strongly recommend any future user to complete prior to deploying this kind of system for either a field or lab experiment. Second, we demonstrate the viability of this system under field-conditions through two field suitability experiments. Lastly, we sampled three different field sites to show that the automation schema works on a monthly timescale and that the system preserves soil water vapor isotopes signals with sufficient precision to distinguish between three different field settings and vertical profile differences.
2 Background

In recent years, a number of technical innovations have made it easier to sample and measure soil water for stable isotope analysis. Advances in laser-based instrumentation (e.g. cavity ring-down spectroscopy, CRDS) have made high throughput, high precision measurements of both water concentration and water stable isotopes possible. Field deployments with laser-based instruments are technically possible and have been conducted successfully (e.g. Oerter et al., 2017; Quade et al., 2019; Künhammer et al., 2021), but require uninterrupted AC power, adequate shelter as well as safe and stable operating environments for best results. These prerequisites are not often available at most field sites, especially in more remote locations and for longer sampling time frames.

Second, the testing and adoption of vapor permeable tubing provides a way to sample soil water vapor with minimal disturbance to the soil profile (e.g. Rothfuss et al., 2013; Quade et al., 2018; Oerter and Bowen, 2019; Beyer et al., 2020; Kubert et al., 2020). This method works by flushing dry nitrogen (or dry air) through the vapor permeable membrane (Accurrell PP V8/2HF, 3M, Germany), creating a water vapor gradient from inside the probe to the soil, thus inducing water vapor movement across the membrane. Water vapor is then entrained in the dry nitrogen and flushed to either a CRDS system or into a storage container. The adoption of vapor permeable tubing has been a large step forward for the ecohydrology community, and opened the possibility of creating long-term soil water stable isotope records, particularly when paired with measurement in the field by spectroscopic instruments.

While this application is a major advancement, it has many practical limitations for remote field sites, therefore, we aimed to develop a system, termed the SWISS, that is capable of independently collecting samples and can then store those samples for a period of time before being returned to the lab for analysis.

2.1 Soil Water Isotope Storage System details and previous work

The Soil Water Isotope Storage System (SWISS) uses three basic components for water vapor storage of multiple samples: glass flasks, stainless steel tubing and a flask selector valve (Fig. 1, Supplementary Table 1). The ability of the SWISS to reliably store water vapor for up to 30 days was demonstrated previously using a series of lab experiments (Havranek et al., 2020). This proof of concept demonstrated that the flasks retain original water isotope values, but the laboratory system was not field deployable or have customizable automation. Here, we present a fully autonomous, field-ready system that has been thoroughly tested under both laboratory conditions and field conditions, including development and testing of a solar-powered, battery backed automation system that enables pre-scheduled water vapor sampling without manual intervention in remote field locations.

2.2 Field Sites:

2.2.1 Site Set-Up

In figure 1 we show the field-setup employed at all of our field sites. At each site we dug two holes. One hole is instrumented with soil moisture and temperature data loggers at 25 cm, 50 cm, 75 cm, and 100 cm depths, as well as the water vapor permeable probes at 25 cm, 50 cm and 75 cm depths (Fig 1A). All probes were deployed >9 months before the first samples were collected to allow the soil to settle and return to natural conditions as much as possible. During probe deployment we took care to retain the original soil horizon sequence and horizon depths as
Figure 1. A) The sampling flow path. To sample soil water, dry nitrogen is regulated at a specific rate using a mass flow controller, and then directed to one of the three sampling depths, or the soil bypass loop using a set of solenoid valves. Both the mass flow controller and solenoid valves are housed inside the SWISS. Once directed to the correct sampling depth, dry nitrogen is carried to the vapor permeable probes via gas impermeable tubing that is buried approximately 15 cm depth. After passing through the vapor permeable probe, the entrained soil water vapor is carried back to the SWISS where it is directed to the correct flask using a Valco multiselector valve. B) Photos of a built-out SWISS and the layout of a field site. Each of the system components (i.e. solar panel, battery, N2 tank, SWISS, PVC tube) are labeled, in addition to the location of the instrumented hole in which all of the probes are buried. The hole which houses the SWISS, power, and N2 tank is approximately 1.5 m wide.
much as possible. The second hole is where the SWISS unit, dry nitrogen tank, and associated components to power
the SWISS are stored (Fig 1B). The water vapor probes, which connect to the SWISS with Bev-A-Line impermeable
tubing, are run through a PVC pipe buried at approximately 15 cm depth. We chose to run the impermeable tubing
to the SWISS underground to limit the effect of diurnal temperature variability on the impermeable tubing, so as to
limit condensation as water travels from the relatively warm soil to the SWISS.

2.2.2 Site description
We deployed the SWISS at three field locations: Oglala National Grassland, Nebraska, USA; Briggsdale,
Colorado, USA; and Seibert, Colorado, USA.

The Oglala National Grassland site (Lat: 42.9600/Long: -103.5979/elev: 1117 m) is located in
northwestern Nebraska, USA in a cold semi-arid climate. The soil at this site is described as an aridisol with a silt-
loam texture. It is part of the Olney series (Natural Resources Conservation Service, 2022).

The Briggsdale site (Lat: 40.5947/Long: -104.3190/elev: 1480 m) is located in northeastern Colorado, USA
in a cold semi-arid climate. The soil at this site is described as an alfisol with a loamy sand - sandy loam texture. It is
part of the Olnest series (Natural Resources Conservation Service, 2022).

The Seibert site (Lat: 39.1187/Long: -102.9250/Elev: 1479 m) is located in eastern Colorado, USA in a
cold semi-arid climate. The soil at this site has been described as an alfisol, that has a sand loam texture in the top 50
cm of the profile, and a silt loam texture between 50 - 100 cm. It is part of the Stoneham series (Natural Resources

3 Materials

3.1 SWISS Hardware components
In each SWISS there are 15 custom made ~650 ml flasks. These flasks are designed similarly to those used
for other water vapor applications. For example, a similar flask is currently used in an unmanned aerial vehicle to
collect atmospheric water vapor samples for stable isotope analysis (Rozmiarek et al., 2021). The flasks have one
long inlet tube that extends into the flask almost to the base, and one shorter outlet tube so that vapor exiting the
flask is well mixed and representative of the whole flask (Fig. 1A). The large flask volume is advantageous because
there is a low glass surface area to volume ratio, and therefore we are able to reliably measure vapor from the flasks
on a CRDS instrument without interacting with vapor bound to the flask walls. The 15 glass flasks are connected to
a 16-port, multi-selector Valco valve. We chose to use a Valco valve because these have previously been shown to
sufficiently seal off sample volumes for subsequent stable isotope analysis (Theis et al., 2004). The valve and flasks
are connected by ¼ inch stainless steel tubing and stainless steel ¼ inch to ¼ inch union Swagelok fittings; we use
PTFE ferrules on the glass flasks with the Swagelok fittings. The first port of the valco valve is ⅛th inch stainless
steel tubing that serves as a flask bypass loop, which enables flushing of either dry air or water vapor through the
system without interacting with a flask. All components are contained in a 61 cm x 61 cm x 61 cm Pelican case with
foam. This case is insulated, and provides enough protection to allow reliable transport of the SWISS by vehicle to field sites.

3.2 Soil Probes

There are three components for the collection and interpretation of soil water vapor: vapor permeable probes, soil temperature loggers, and soil moisture sensors (Fig 1B, Supp. Table 1). Here, we use a vapor permeable membrane (ACCURELL PP V8/2HF, 3M, Germany) that was first tested by Rothfuss et al., (2013). We opted to use this tubing because it has been shown to deliver reliable data over time (i.e. Rothfuss et al., 2015), and is easy to use and customize to individual needs. We previously observed that variability in the length of the vapor permeable tubing can lead to systematic offsets in the stable isotope composition of measured waters (Havranek et al., 2020). Therefore, we were careful to construct all probes such that the length of the Accurrell vapor permeable tubing was 10 cm long, and the impermeable Bev-A-Line IV connected on each side of the vapor permeable tubing was 2 m long. We also constructed the vapor permeable probes to be used in the lab setting for standards in an identical fashion. Soil temperature loggers (Onset HOBO MX2201), used for applying a temperature correction to all soil water vapor data, were buried at the same depths as the vapor permeable probes. Soil moisture sensors (Onset S-SMD-M005) were also buried at the same depths as the vapor permeable probes.

3.3 Automation components, code style, and remote setting power

The philosophy behind the automation of the SWISS was to make it as easy to reproduce as possible, and as flexible as possible to meet different users’ sampling needs. We therefore use widely available hardware components and electronics parts; for each product there are numerous alternatives which should be equally viable and could be swapped to better meet each user’s needs. In an effort to make our system as accessible and customizable as possible for the scientific community, all automation code is completely open source and will continue to be refined for future applications and hardware improvements. We note that all code is provided as is and should be tested carefully for use in other experiments.

The overall sampling scheme used in this paper is described in figure 2 and table 1. Our experimental goal was to create a time series of soil water vapor data from three discrete sampling depths (25 cm, 50 cm, 75 cm). Prior to sampling any soil water vapor, we flushed away any water vapor present in the lines within the SWISS prior to flushing the sample loops. Then, at the start of sampling for each depth, we also flushed the water vapor probe to remove condensation or ‘old’ water vapor. The gas from both of those steps was expelled via the flask bypass loop. Each soil depth was then sampled for 45 minutes by flushing through the next flask designated in the sequence.

Supplement Figure SI 1 shows the components of the automation system. To automate and program the sampling scheme, we used: (1) a microcontroller to run the automation script; (2) a coin-cell battery powered real time clock so that the microcontroller was always capable of keeping track of time through power losses, and therefore maintain the sampling schedule; (3) an RS-232 to TTL converter for serial communication with the Valco valve; (4) solenoid valves that were used to control which depth was being sampled and the associated VDC power relay; (5) a mass flow controller used to control the rate at which dry nitrogen (1 ppm H2O) is flushed through the
Figure 2. Flow chart of the instrument schedule used for sampling during all field experiments.

<table>
<thead>
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<th>Code</th>
<th>Wake-up</th>
<th>Flush internal lines</th>
<th>Sample depth 1</th>
<th>Sample depth 1</th>
<th>Flush depth 2</th>
<th>Sample depth 2</th>
<th>Sample depth 3</th>
<th>Sample depth 3</th>
<th>Flush internal lines</th>
<th>Sleep</th>
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<td>10</td>
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<td>10</td>
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<td>1</td>
</tr>
<tr>
<td>Valco valve position</td>
<td>flask bypass</td>
<td>flask bypass</td>
<td>flask bypass</td>
<td>flush bypass</td>
<td>flush bypass</td>
<td>flush bypass</td>
<td>flush bypass</td>
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<td>flush bypass</td>
<td>flask bypass</td>
</tr>
<tr>
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<td>25 cm</td>
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<td>50 cm</td>
<td>75 cm</td>
<td>75 cm</td>
<td>soil bypass</td>
<td>none</td>
</tr>
</tbody>
</table>

Table 1. Description of soil water sampling steps

probes; and (6) a power relay used to power the Valco valve and mass flow controller. All parts are described in detail in Supplemental Table 2.

In a remote setting, the SWISS units are powered using the combination of a 12V deep-cycle battery and a 12VDC, 100W solar panel that is used to charge the battery. The solar panel is mounted to a piece of plywood that covers the hole where the SWISS is deployed (note, the hole is uncovered in Fig. 1B for illustrative purposes). We opted for this setup because the underground storage of all parts of the system creates a discreet field site that attracts minimal attention from other land users. In the field, we used a 12VDC-120VAC power inverter to provide simple plug and play power for the Valco valve and mass flow controller. This simple combination was suitable for summertime in the Western U.S. where there are a great number of sunny hours, and the solar panel was able to easily charge the 12V battery. This setup may need to be adjusted based on location and desired sampling time. Like the automation system, there are many commercial options available for products, and they can be easily adjusted for users’ needs; example parts are described in detail in Supplemental Table 2. We also note that in areas where it is possible to plug into a power grid, the deep cycle battery, solar panel and power inverter can be removed.
4 Methods

4.1 QA/QC: Testing the SWISS under lab conditions

The highest order concern for the SWISS is that it remains leak-free because any leaks introduce potential for fractionation or mixing of atmosphere that would alter the stable isotope ratio of the water vapor in the flask. So, we developed a three-part quality assurance and quality control (QA/QC) procedure that must be completed for each new SWISS prior to the first deployment. The first step detects any significant leaks using helium detection methods; the second step is to perform a dry air test to detect medium scale leaks; and the third step is to perform a water vapor test to detect slow leaks. Below, we quickly summarize each of these QA/QC steps. Full procedural descriptions are available in supplementary material and the data processing code is available via github.

4.1.1 Step 1: using helium to detect large scale leaks

After initial assembly of the SWISS plumbing, we filled the flasks with helium and used a helium leak detector to find large leaks. Typically, the kinds of leaks we were able to detect with this method were due to cracking of the inlet or outlet on the glass flask that occurred while tightening the swagelok fittings. Another easy alternative is to complete a short dry air test (described below) that requires on the order of 12-24 hours.

4.1.2 Step 2: dry air tests detect medium scale leaks

Once we felt sure that there were no major leaks in our systems, we completed a dry air test. The goal of this test was to catch any second order, medium-scale leaks. Typically, this test found swagelok fittings that had been under tightened. The advantage of this kind of test is that it is easy and quick to complete. This test started with a dry air fill. A dry air fill consists of flushing flasks with air that is filtered through drierite (which has a water vapor mole fraction of less than 500 ppm), at 2 L/min for 5 minutes. With a flask volume of 650 ml, this means the volume of the flask is turned over 15 times. Flasks were then sealed and left to sit for seven days.

At the end of the seven-day period we measured each flask using the dead-end pull sample introduction (note, italicized terms are specific methods, and are explained in greater detail in supplementary material) method on a Picarro L2130-i Isotope and Gas Concentration Analyzer. For this sample introduction method, the inlet to the valco valve was sealed with a ¼” swagelok cap and there was no introduction of a carrier gas. As a result, air was removed from the flask based on the flow rate of the Picarro CRDS (typically 27 - 31 ml/min).

We found that in a low-humidity environment, we needed a week to really see leaks, but this timescale would likely be shorter in more humid locations. Additionally, this test could be modified based on available equipment (for example, if an instrument is available to measure trace atmospheric gases, that could be used instead). To ensure that SWISS units continue to operate as expected, this test should be done between field deployments on every SWISS unit.

We repeated dry air tests until the majority (typically at least 13/15) flasks had a water vapor mole fraction value of less than 500 ppm at the end of the seven day experiment. Water vapor values from the CRDS have not been independently calibrated, but relative variations are believed to be reliable.
4.1.3 Step 3: Water vapor tests detect small scale leaks

The purpose of this experiment was to mimic storage of water vapor at concentrations similar to what we might expect in a soil, and for durations similar to those of our field experiments. Additionally, these tests were used to demonstrate that flasks that were filled early in the sampling sequence did not lead by the time the samples were returned to the lab for measurement. For this experiment, flasks were filled with water vapor of known isotopic composition and known concentration, sealed for 14 days, and then we measured the water vapor concentration and isotope values.

Prior to putting any water vapor into the flasks (either in the field or in the lab), we completed a dry air fill (as defined above) that served to purge the flasks of any prior water vapor that might exchange with the new sample. To supply water vapor to the flasks, we used the vapor permeable tubing immersed in water. Across three different measurement sessions, we used three different waters that are used as tertiary standards in the INSTAAR SIL lab to complete these experiments: a light water made from melting and filtering Rocky Mountain snow (-25.5‰ and -187.5‰ VSMOW, for δ¹⁸O and δ²H, respectively), an intermediate water that is deionized (DI) water from the University of Colorado Boulder Campus (~-16.2‰ and -120.7‰ VSMOW for δ¹⁸O and δ²H, respectively) and a heavy water that is filtered water sourced from Florida, USA (~ -0.8‰ and -2.8‰ VSMOW for δ¹⁸O and δ²H, respectively). All secondary lab standards are characterized relative to international primary standards obtained from the International Atomic Energy Agency and are reported relative to the V-SMOW/SLAP standard isotope scale.

We flushed the flasks at a rate of 150 ml/min for 30 minutes, and measured the δ¹⁸O and δ²H values and mole fraction of water vapor as each flask was filled. To calculate the input value, we averaged δ¹⁸O and δ²H over the last three minutes of the filling period.

At the end of the 14-day storage period, we measured each flask to evaluate if the isotope composition had significantly changed over the storage period. To mitigate memory effects between flasks, we ran dry air via the flask bypass loop (port 1 of every Valco valve) for 5 minutes between each flask measurement. During this 5 minute window, we used a heat gun to manually warm each flask. The purpose of the heating was to help create a longer, more stable window of measurement time. While the temperature of the flask was not strictly controlled or regulated, they were all warm to the touch.

Once the flask was warmed and the impermeable tubing dried, water vapor was introduced to the CRDS using one of two methods: 1) the dead-end pull method described above, or 2) a dry air carrier gas sample introduction method. The dead-end pull method is preferable when the water vapor mole fraction inside the flask is low (~17,000 ppm). But, the major downside of the dead-end pull method is that condensation forms in the stainless steel tubing that connects the flasks to the Valco valve, as well as the Valco valve itself, far more commonly as compared to the dry air carrier gas method. During the dry air carrier gas method, dry air is continuously flowing through the flask at a rate of 27-31 ml/min for the entire 12 minute measurement period. Additionally, to reach a water vapor mole fraction of approximately 25,000 ppm (the optimal humidity range for the CRDS), we diluted the water vapor with dry air at a rate of 10 ml/min. Without dilution, the concentration out of the flasks is as high as 35,000 - 40,000 ppm, which leads to saturation issues on a Picarro L2130-i. Providing a carrier gas prevents condensation from forming in the Valco valve and tubing, and prevents fractionation that may occur because of
changing pressure within the flask. The dry air carrier gas method is our preferred method for sample introduction in most cases.

For each flask we looked at signal stability individually, and for approximately 90% of the flasks we found that after excluding the first three minutes of measurement of each flask, the subsequent three minutes were the most stable and consistent. For some flasks, using either a later portion of the measurement period, or slightly earlier offered a more stable signal.

During these experiments, instrument drift and stability were monitored using a suite of four waters of known composition that were introduced to the CRDS using a flash evaporator system, described in detail by Rozmiarek and others (2021). Additionally, instrument stability was assessed by measuring water vapor of known composition that was produced using the vapor probes, in a fashion that is identical to how the flasks were flushed.

4.2 Field suitability and Field application experiments:

4.2.1 Field suitability experiment #1: Long term field leak test

As a complement to the QA/QC we did under lab conditions, we also completed long term dry air tests at our field sites. The purpose of these experiments was to demonstrate that even under field conditions the flasks are still resistant to atmospheric intrusion. Furthermore, this leak test was used to demonstrate that the flasks filled last during the sampling sequence had not taken on an atmospheric isotope composition prior to sampling.

Like all field deployments, we started with a dry air fill, and then one SWISS was deployed to each of our three field sites. No soil water was collected during these deployments. The duration between filling the flasks with dry air to measuring the flasks was anywhere between 34 - 52 days.

4.2.2 Field suitability experiment #2: Mock field tests

To demonstrate that the automation code and sampling scheme we propose worked as expected on short, observable timescales, we set up an experiment to simulate field deployment of one SWISS unit (Meringue) near the University of Colorado Boulder. This test used the automation components and remote power setup described in the materials section. During this field-simulation experiment, our goal was to collect three discrete samples each sampling period, to simulate collection of samples from three depths at each field site. Importantly, we wanted to demonstrate that the sampling scheme does not introduce significant memory effects between samples.

Over the course of 25 hours, all 15 flasks were filled with three different vapors. Two were water vapors, created from the light water and intermediate water as described above in the water vapor test section. The third was water vapor from the ambient atmosphere. For this experiment we filled three flasks per cycle with each one of the waters (e.g. Flask 2 = light, Flask 3 = intermediate, Flask 4 = Atmosphere).

For seven days, the SWISS unit was stored in a simulated field setting, while the water vapor remained in the flasks. At the end of the seven days, flasks with a higher water vapor mole fraction (light and intermediate water vapor samples) were measured using the carrier gas sample introduction method, whereas those with a low water vapor mole fraction (atmosphere) were measured using the dead end pull sample introduction method. We used equations 2A and 2B from Rothfuss et al., (2013) to convert from water vapor to liquid values. Then, using tertiary
standards, data were corrected into the VSMOW data frame. Finally, the SWISS unit offset correction (detailed below) was applied.

4.2.3 Full field deployment experiment: One month period

We deployed one SWISS unit each to the three field sites described. We sampled at three depths (25 cm, 50 cm, and 75 cm) on each sampling day, following the protocol in figure 2. We sampled at each depth every 5 days (protocol length = 25 days total). At the end of a 28 day period, the SWISS units were returned to the lab, and measured. The measurement protocol and data reduction protocol follows the procedures described in the water vapor QA/QC test section above. The data correction scheme follows as in the section above.

5 Results

5.1 QA/QC Results

5.1.1 Dry air test

Figure 3 shows the results of a seven-day dry air test for three SWISS units (marked by the box name) (SI Table 3). For all three SWISS units, at least 13/15 of the flasks maintained a water vapor mole fraction value of less than 500 ppm over the seven day period. In two of the three SWISS units (Lindt and Raclette), the water vapor mole fraction for flasks was randomly distributed around approximately 350 ppm. In Toblerone there was a systematic decrease in water vapor mole fraction from flask 2 through flask 16, matching the order in which the flasks were filled with dry air initially. In both Lindt and Toblerone, flask 2 had the highest water vapor mole fraction of all the flasks.

Figure 3. Results of a dry air test from three different SWISS units named: Lindt, Raclette and Toblerone. The majority of the flasks maintain a water vapor mixing ratio of less than 500 ppm.

5.1.2. Water vapor test

In panels a and b of figures 4 and 5, we show the results of 11 different water vapor tests performed across three analytical sessions using 6 different SWISS units. This dataset includes water vapor tests using three different water vapors (light, intermediate and heavy) and uses both the dead-end pull and dry-air carrier gas methods to introduce water vapor to the CRDS. Across these three sessions, we measured 164 flasks while filling them with...
water vapor and at the end of the two week hold period. After correcting for instrument drift, we calculated the difference between the starting and end values to assess drift in water vapor isotope values due to leaking or other measurement bias.

Ideally, we expect a normal distribution centered about 0 within the uncertainty limits of the water vapor probes (Oerter et al., 2016). For δ¹⁸O, the mean difference between the start and end values for the flasks is 1.1‰ with a standard deviation of 0.72‰ (outliers removed). There is a consistent positive offset, with a few clear outliers (Fig. 4A). We do not observe a consistent difference between water vapor sample introduction methods (Supp. Fig. 2). After removing outliers (< Q1 - 1.5*IQR or > Q3 + 1.5*IQR, n = 15) from the dataset, we compared the kernel density estimate shape to a normal distribution calculated from the mean and standard deviation of the dataset to assess dataset normality (Fig. 4B). A normal distribution slightly overestimates the center of the data, but captures the overall shape fairly well. Therefore, we used the median offset (1.0‰) to correct our water vapor isotope values, and used the interquartile range of the dataset (outliers removed) to estimate uncertainty of the SWISS as ± 0.9‰.

In figure 5C, for simplicity, we just present the results from 45 flasks (three SWISS units), with the 1.0‰ offset correction applied. After correction, data are randomly distributed about 0, and are within the uncertainty range of ± 0.9‰ (Supp. Table 4).

For δ²H, the mean difference between the start and end values is 2.63‰ with a standard deviation of 2.85‰ (outliers removed). Similarly to δ¹⁸O, we ideally expected a normal distribution of differences centered around 0. As with δ¹⁸O, there was a consistent positive offset with some outliers (i.e. < Q1 - 1.5*IQR or > Q3 + 1.5*IQR) (Fig. 5A). After removing outliers (n = 26) from the dataset, we compared the kernel density estimate to a normal distribution calculated from the mean and standard deviation of the dataset to assess dataset normality (Fig. 5B). As for δ¹⁸O, the center of the dataset is overestimated by the mean, but the overall peak shape is roughly captured. We therefore use the median value of 2.3‰ as an offset correction, and estimate uncertainty at ±3.7‰ for δ²H from the interquartile range. In figure 5C, we present the results from 45 flasks (three SWISS units), with the 2.3‰ offset correction applied. Data are randomly distributed about 0, and are within the uncertainty range of ± 3.7‰ (Supp. Table 4).

5.2 Field suitability and field deployment experiment results

5.2.1. Dry air test

Figure 6A shows the result of placing SWISS units that were flushed with dry air out into field conditions over the course of 34 - 52 days (SI Table 3). We chose these time intervals because they bracket the typical length of a deployment, which helped us determine how quickly flasks should be measured after bringing a SWISS back to the lab. At the timescale of 34 - 43 days, 13 of the 15 flasks typically maintained a water vapor mole fraction of less than 1000 ppm. At the timescale of 52 days, eight of the 15 flasks had a water vapor mole fraction between 1000 - 2500 ppm, and the remaining seven flasks had a water vapor mole fraction of less than 1000 ppm. Given that these tests were completed with different SWISS units, these data also include some of the inter-unit variability.
Figure 4. Results of the water vapor tests. A) Boxplot of the difference between the starting $\delta^{18}O$ value and the final $\delta^{18}O$ value of all 164 flasks. B) After removing the outliers from the dataset, the kernel density estimate (black line) and the normal distribution calculated from the dataset (dashed green) are shown. C) After applying the offset correction of 1.0‰, the difference between the starting $\delta^{18}O$ value and the final $\delta^{18}O$ value for three boxes from the August 2022 session are shown. An uncertainty of $\pm$ 0.9‰ is marked with a dashed line, and data points that fall outside that uncertainty are colored red.

Figure 5. Results of the water vapor tests. A) Boxplot of the difference between the starting $\delta^2H$ value and the final $\delta^2H$ value of all 164 flasks. B) After removing the outliers from the dataset, the kernel density estimate (black line) and the normal distribution calculated from the dataset (dashed green) are shown. C) The difference between the starting $\delta^2H$ value and the final $\delta^2H$ value for three boxes from the August 2022 session are shown after applying the offset correction of 2.3‰. An uncertainty of $\pm$ 3.7‰ is marked with a dashed line, and data points that fall outside that uncertainty are colored red.
Figure 6. A) Results from three different field-based long dry air tests. B) Results from the automation field suitability tests using the SWISS unit named Meringue. Flasks that sampled atmosphere are shown in blue, flasks that sampled deionized water (DI) are shown in pink, and flasks that sampled the light water are shown in yellow. The top plot shows the $\delta^{18}$O results, and the bottom plot shows the $\delta^2$H results.
5.2.2. Automation test

Figure 6B shows the result of using the automation code to collect and store water vapor of known composition for seven days (Table 2). In both plots, the known values of the water are shown as a long-dash line. Uncertainty on those measurements is estimated at 0.5‰ and 2.4‰ for δ¹⁸O and δ²H respectively (Oerter et al., 2016), shown as the dotted lines. We estimated the isotope value of the atmosphere at the time of sampling with data from the CRDS in the lab. The corrected isotope value of each flask is shown, with uncertainty associated with the SWISS units estimated at 0.9‰ and 3.7‰ for δ¹⁸O and δ²H, respectively.

Seven of the nine flasks filled with water vapor overlap within uncertainty of the known δ¹⁸O value for those standards (top plot, Fig. 6B), and four of the five flasks filled with atmospheric vapor overlap within uncertainty of our estimated δ¹⁸O value. Flasks that fall outside of the bounds of uncertainty tend to have lower δ¹⁸O values than the expected value. For δ²H, (bottom plot, Fig. 6B) only three of the nine flasks filled with water vapor overlap within uncertainty of the known value of those standards, while four of the five flasks filled with atmospheric vapor overlap within uncertainty of the estimated δ²H value. Flasks that fall outside of the bounds of uncertainty typically have higher δ²H values than the expected value.

<table>
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<tr>
<th>SWISS</th>
<th>Flask</th>
<th>water</th>
<th>δ¹⁸O (‰)</th>
<th>δ²H (‰)</th>
</tr>
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<tr>
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<td>DI</td>
<td>-14.4</td>
<td>-122.2</td>
<td></td>
</tr>
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<td>Atmosphere</td>
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<td>-105.6</td>
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<td>Meringue 4</td>
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<td>-193.7</td>
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<tr>
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<td>DI</td>
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<td>-130.8</td>
<td></td>
</tr>
<tr>
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<td>Atmosphere</td>
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<td>-103.4</td>
<td></td>
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<tr>
<td>Meringue 7</td>
<td>Light</td>
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<td>-201.5</td>
<td></td>
</tr>
<tr>
<td>Meringue 8</td>
<td>DI</td>
<td>-17.3</td>
<td>-140.5</td>
<td></td>
</tr>
<tr>
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<td>Atmosphere</td>
<td>-9.1</td>
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<td>-200.7</td>
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<tr>
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<td>DI</td>
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<td>-122.5</td>
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<td>Atmosphere</td>
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<td>Light</td>
<td>-23.3</td>
<td>-192.9</td>
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</tr>
</tbody>
</table>

Table 2. Results of the Automation test

5.2.3 Field deployment

Figure 7 shows the results from three field deployments in Oglala National Grassland, Nebraska; Briggsdale, Colorado; and Seibert, Colorado (Table 3).
Figure 7. Results from all three field deployments to Oglala National Grassland, NE, Briggsdale, CO and Seibert, CO. Note, the y-axis scale for all three plots is different.

There are 15 samples from Oglala National Grassland (Fig. 7); five from 25 cm depth and five from 75 cm depth. Samples were taken approximately every five days from 2022-06-25 to 2022-07-14. Four of the five samples from 25 cm overlap within uncertainty in δ18O value, and all five samples overlap with uncertainty in δ2H value. There is a significant decrease in the δ18O value at 25 cm between 2022-06-25 and 2022-06-29. There is no similar shift in δ2H value over the same time period. The first three samples from 50 cm overlap in both δ18O and δ2H values, then the final two samples drift to higher isotope values. All five samples from 75 cm overlap in δ18O and δ2H values. Similar to the samples from 50 cm, there is a trend towards higher δ2H values for the last three samples. Overall, δ18O and δ2H values from 25 cm are significantly higher than the values from 50 and 75 cm depth. Generally, samples from 50 cm depth have lower δ18O and δ2H values than samples from 75 cm depth.

There are 10 samples from Briggsdale, CO (Fig. 7); five samples are from a vapor probe buried at 50 cm depth and five samples are from a vapor probe buried at 75 cm depth. Data from 25 cm at Briggsdale, CO were excluded because the water vapor mole fraction from all of the flasks with samples at this depth had extremely low water vapor mole fractions (<13,000 ppm), and so those data may either represent atmosphere or soil gas from an extremely dry soil. Samples were taken every five days between 2022-07-17 and 2022-08-06. All samples overlap within uncertainty in both δ18O and δ2H values, however samples from 50 cm are clearly offset to higher values for both δ18O and δ2H as compared to samples from 75 cm.

There are 8 samples from Seibert, CO (Fig. 7); four samples are from a vapor probe buried at 25 cm depth and four samples are from a vapor probe buried at 50 cm depth. Samples collected from 75 cm depth at Seibert, CO were discarded because there were significant problems with condensation while measuring these flasks, and so all data were considered spurious. Samples were collected every five days between 2022-06-19 and 2022-07-04. At 25 cm depth, δ18O values of three of the four samples overlap within uncertainty; the 25 cm sample from 2022-06-29 that does not overlap has a higher δ18O value than the other three samples. At 25 cm depth, δ2H values overlap...
within uncertainty for all four samples. At 50 cm depth, there is a steady decrease in δ¹⁸O value over the sampling period, while δ²H values for all four samples remain steady.

6 Discussion

6.1 QA/QC and field suitability tests

6.1.1 Dry Air tests

For the seven day dry air tests, the flasks were able to maintain a water vapor mole fraction typically less than 400 ppm, and all flasks maintain a water vapor mole fraction of less than 700 ppm (Fig. 4). In Colorado, the ambient atmosphere during the summertime typically sits at a water vapor mole fraction between 10,000 - 20,000 ppm, and in winter the water vapor mole fraction can drop as low as 4000 ppm. If the flasks allowed in a significant amount of atmosphere, the flasks would have had much higher water vapor molar fractions. This suggests that the system is resistant to atmospheric intrusion.

There seems to be a systemic bias towards a high water vapor mole fraction for the first flask that is measured (flask 2). There are two potential analytical sources of this. First, it's possible that during the filling phase, not all of the atmospheric vapor has been flushed out of the system before starting the fill process. Similarly, it is possible that not all of the atmospheric water vapor was flushed from the line that connects to the CRDS prior to the start of the measurements.

6.1.2 Water vapor tests

The in-lab water vapor tests served three functions: 1) they allowed us to test the best method for measuring soil water vapor at fairly high water vapor mole fractions that might be representative of field conditions (i.e. > 25,000 ppm), 2) to test if there is any systemic bias introduced through the building materials or measurement schema, and, 3) test whether soil water vapor samples can yield reliable stable isotope values.

We completed 11 water vapor tests using 6 SWISS units and three analytical sessions, resulting in 164 measurements of water vapor. Across the three analytical sessions, three waters with different isotopic compositions were used to produce water vapor (1 heavy, 1 intermediate, and 1 light). If there was alteration of original values due to leaky flasks, we might expect the δ¹⁸O and δ²H values to converge on the δ¹⁸O and δ²H value of the atmosphere. For example, we might expect water vapor from the light water test to have the most significant change in isotope value, towards that of the ambient atmosphere.

Figures 4 and 5 demonstrate that there is a consistent offset in both δ¹⁸O and δ²H of the water vapor from the start of storage to the end for all three analytical sessions. After removing outliers from the dataset, there remains a consistent bias across all SWISS boxes and analytical sessions (Figs 5B, 6B). The consistency across >135 flasks, different starting water vapor isotope values, sample introduction methods, and multiple analytical sessions suggests that this difference is a function of the storage and measurement. Additionally, the normality of the distribution
Table 3. Results from the three field deployments of SWISS.
suggests that there is a systematic bias that we can reliably correct for. We chose to use the median value as an offset correction over the mean of the normal distribution, because the median is not biased by higher isotope difference values that are a complex combination of systematic bias and slow leaking. The calculated average offset is 1.0‰ and 2.6‰ for δ\(^{18}\)O and δ\(^{2}\)H, respectively.

Based on the results of the water vapor tests, we estimate the uncertainty of the SWISS at 0.9‰ and 3.7‰ for δ\(^{18}\)O and δ\(^{2}\)H, respectively using the interquartile range (IQR) of the water vapor test results after removing outliers from the dataset. We prefer the IQR over the calculated standard deviation of the normal distribution, because IQR is not biased by outlier values. In figures 5C and 6C, we show the results of 3 water vapor tests from the August 2022 analytical session, with an offset correction applied. 43 of the 45 measured flasks faithfully retained the starting δ\(^{18}\)O value of the water vapor, and 37 of the 45 measured flasks faithfully retained the starting δ\(^{2}\)H value of the water vapor. Additionally, after the offset correction was applied, most flasks also fall within the uncertainty of the water vapor permeable probes (δ\(^{18}\)O = 0.5‰ and δ\(^{2}\)H = 2.4‰).

Supplemental figure 3 shows a kernel density estimate plot of the results from two water vapor test sessions, with the offset correction applied. During the March 2022 session, flasks were measured using the dead-end pull sample introduction method and during the August 2022 session, flasks were measured using the dry air carrier gas sample introduction method. There is no significant difference in the measured difference between the two sample introduction methods. We prefer the dry air carrier gas method, because it is far simpler to control the water vapor mixing ratio, and optimize the concentration to be around 25,000 ppm, which is the concentration at which the Picarro L2130-i is most reliable. The dry air carrier gas method also makes it far easier to control for and monitor for condensation in the stainless steel tubing and vapor impermeable tubing, which can bias a measurement.

6.1.3 Field suitability tests

In Figure 7A, we observe that the flasks typically maintained a low water vapor mole fraction (< 1000 ppm) under field conditions, and at timescales relevant to 4-6 week field deployments (34 - 43 days). The 34 day test was done during June 2022, and therefore tests the SWISS under warm summertime conditions. The 43 day test was done in October 2021, which included nights where temperatures fell below 0°C, and therefore tests the suitability of the SWISS to maintain integrity under freezing conditions. We observe that the SWISS did considerably worse at maintaining a low water vapor mole fraction over a 52 day time period during similar summertime conditions as compared to the 34 - 43 day time period. Over the 52 days, seven flasks maintained a water vapor mole fraction less than 1000 ppm and the remaining 8 had a water vapor mole fraction between 1000 - 2500 ppm. Though the SWISS performed considerably worse after 52 days than it did from 34 - 43 days, it is important to note that the atmospheric water vapor mole fraction during the storage time period was likely 15,000 - 20,000 ppm, and so the measured values demonstrate that the SWISS are still quite resistant to atmospheric intrusion at that timescale.

In figure 7B, the data show that the flasks faithfully preserved the δ\(^{18}\)O value of both water vapor produced using the vapor permeable probe and the atmosphere over a seven day period. One flask was removed from the dataset (flask eight), because there was noticeable condensation in the impermeable tubing during the measurement.
phase, with an increase of > 5‰ for δ\(^{18}\)O during the measurement period. Notably, the two flasks whose δ\(^{18}\)O oxygen isotope values do not overlap within uncertainty are more negative than expected, rather than drifting towards atmospheric values or values expected with kinetic fractionation. It is possible that those samples were also affected by condensation at the start of the experiment; during condensation, we expect that \(^{18}\)O will preferentially go into the liquid phase, and that the water vapor that enters the flask will have a lower than expected δ\(^{18}\)O value.

Surprisingly, only 3 flasks filled with either DI or light water vapor overlap within uncertainty of the known δ\(^2\)H values, while four of the five flasks overlap within uncertainty of the estimated atmosphere isotope value. The flasks tend to drift towards the value of the atmosphere, but retain the overall data pattern from the oxygen isotope values.

6.1.4 Lessons learned and recommendations from the QA/QC and field suitability tests:

The dry air test is a time-efficient method for identifying flasks that are leaky and will not preserve the sampled water vapor value, therefore we recommend these tests as a required step prior to field deployment of future SWISS units. For example, supplemental figure 4 shows that it is possible to drastically reduce the water vapor mole fraction in a flask filled with dry air between tests by tightening and/or replacing problematic fittings (both those attached to the glass flasks and those on the valco valve) and in some cases the glass flask itself. This shows we can reduce the leakiness of the flasks. The dry air test is also an easy baseline test that also allowed us to test building materials. For example, in supplemental figure 5, we tested using PTFE swagelok fittings with \(\frac{1}{8}\)" PTFE tubing rather than stainless steel. These materials would be advantageous because they are much easier to install and are significantly lighter. We found that these fittings and tubing may be sufficient to store water for up to a single week, but on longer timescales (e.g. 27 days) we observed greater exchange and leaking than the stainless steel. We encourage any future user using this modification to rigorously test these fittings on a timescale appropriate for their application.

From the water vapor tests, we get a sense of the accuracy and precision of the SWISS. The calculated uncertainty of the flasks (0.9‰ and 3.7‰ for δ\(^{18}\)O and δ\(^2\)H, respectively) is somewhat larger than the uncertainty associated just with the use of the water vapor probes (0.5‰ and 2.4 ‰ for δ\(^{18}\)O and δ\(^2\)H, respectively, Oerter et al., 2016), but is sufficient for many critical zone applications, given the magnitude of seasonal variability that can be observed in natural systems (e.g. Oerter et al., 2017; Quade et al., 2019).

We opted to use a large flask volume because it allows us to measure a sample for long enough on a CRDS that we get reliable data, without interacting with vapor bound to the flask walls. The drawback of this, however, is that we must sample soil water vapor for a relatively long period of time (45 minutes). In supplemental figure 6, we show that the sampling regime, and particularly the length of time we pump dry air through the tubing, does not significantly alter the soil moisture content of the soil. Additionally, we demonstrate that the sampling regime we use does not introduce significant memory effects.

Based on the results of the long, field dry air test, we recommend that the water vapor storage time doesn’t exceed 40 days for reliable results, or that the user undertake multiple dry air tests with lower concentration benchmarks if deployments may exceed 40 days.
Overall, the quality control and quality assurance as well as the field suitability tests demonstrate that the SWISS are able to faithfully retain the isotope value of water vapor collected using water vapor permeable probes. Like many other systems that measure dual isotopes, each system (i.e. $\delta^{18}O$ and $\delta^2H$) must be evaluated separately. In general, we interpret oxygen isotope data with a higher degree of confidence than the hydrogen isotope data. As the automation test revealed however, even when the absolute $\delta^2H$ value is not correct, the general pattern can reveal information about soil water dynamics. One particular challenge with the vapor permeable probes, that others have noted, is condensation in any portion of the system (e.g. Quade et al., 2019; Kühnhammer et al., 2019). As much as possible, it is helpful to have the impermeable tubing at warmer temperatures than the soil or water it is sampling. In many situations it may be worthwhile to warm the transfer tubing, but this should be done in a way that does not alter the thermal structure of the soil, and in remote settings, can operate safely independently. Additionally, taking care to ensure that the SWISS is evenly and lightly warmed in the lab setting helps to prevent condensation from forming in the stainless steel tubing and Valco valve.

6.2 Field Deployments

In Figure 7 we show the results of three field deployments completed during summer 2022 (table 3). At the Oglala National Grassland site, we used the SWISS named Lindt to collect samples. During the August 2022 water vapor test on Lindt, all of the oxygen isotope values fall within uncertainty of the system, and nine of the fifteen flasks fall within uncertainty of the system. Therefore, we interpret the $\delta^{18}O$ values with a higher amount of confidence and the $\delta^2H$ values with a lower amount of confidence (Figs. 4C and 5C). We note that most of the $\delta^{18}O$ and $\delta^2H$ values follow the same trends, and fall on the global meteoric water line (Figs. 7 and 8A). In general, soil water from 25 cm had higher $\delta^{18}O$ and $\delta^2H$ values than soil water from both 50 and 75 cm (Fig. 8A). Given that 4 of the 5 samples from 25 cm overlap with the GMWL and have a d-excess that overlaps within error of 10‰, the soil water from that depth may reflect summer precipitation with higher $\delta^{18}O$ and $\delta^2H$ values. Soil water from 75 cm had intermediate $\delta^{18}O$ and $\delta^2H$ values for most of the study period, and soil water from 50 cm depth had the lowest $\delta^{18}O$ and $\delta^2H$ values for most of the study period, which may reflect a more mean-annual or winter precipitation biased value. The d-excess value of soil water collected from 75 cm is centered around a global meteoric water line value of 10‰ (Fig. 8B). Based on data available from the National Weather Service (Chadron, NE), there were likely significant precipitation events on 2022-06-25 and 2022-07-08 at the field site. There is a significant shift to lower $\delta^{18}O$ values at a sampling depth of 25 cm between 2022-06-25 and 2022-06-29, as well as a marked increase in the d-excess value (Fig. 8A). We interpret this shift as infiltration of precipitation with lower $\delta^{18}O$ values, and is supported by a return of d-excess values to ~10‰ (Fig. 8A). The National Weather Service reported 0.84 inches of rain at Chadron Municipal Airport, approximately 50 km from the study site on 2022-07-08, which likely was associated with at least some precipitation at our field site. Following the significant rain event on 2022-07-08, we observe a marked increase in the stable isotope value of water vapor from a sampling depth of 50 cm, towards values that are much closer to those at 25 cm depth. This indicates that after a large precipitation event, there is mixing and the creation of a far more uniform soil water isotope profile to a depth of 50 cm, but at the depth of 75 cm, the oxygen isotope data remain fairly uniform across the sampling period.
At Briggsdale, CO we used the SWISS named Raclette to collect soil water vapor samples. Data from 25 cm depth at Briggsdale, CO were discarded because the water vapor mole fraction was much lower than would be expected given the soil temperature (i.e. < 15,000 ppm). The gravimetric water concentration at that soil depth at the time of sampling was approximately 4% through the sampling period. Given the low water concentration, it is possible that there was simply not enough water vapor to sufficiently sample. Based on the results of the August 2022 water vapor test done on Raclette where all flasks fell within uncertainty of the SWISS system for both $\delta^{18}$O and $\delta^2$H, except for flask 11 (Figs. 4C and 5C), which corresponds to the 25 cm depth sample from 2022-07-27, we interpret all of the data with a higher level of confidence. This sample was already removed from the dataset because of low water vapor mole fraction associated with the very dry soil. The soil water $\delta^{18}$O and $\delta^2$H values from a sampling depth of 50 cm and 75 cm overlap within uncertainty, but the soil water $\delta^{18}$O and $\delta^2$H values from 50 cm have a higher isotopic value than the samples from 75 cm. All of the data from within each sampling depth group (i.e. 50 cm and 75 cm) overlap within uncertainty, conforming to the expectation that soil water from these sampling depths should be fairly invariant (e.g. Oerter et al., 2017). There were precipitation events at the study site on 2022-
07-24, 2022-07-28 and 2022-07-31. It is possible that the slight negative shift in both $\delta^{18}O$ and $\delta^2H$ on 2022-08-01 reflects infiltration of precipitation to those depths, but this is not certain given that all of the measurements from within a sampling depth overlap within uncertainty.

At Seibert, CO we used the SWISS named Toblerone to collect soil water vapor samples. Data from 75 cm depth at Seibert, CO were discarded because of evidence of condensation during the measurement of the flasks associated with that sampling depth. Based on the results of the August 2022 water vapor test done on Toblerone, we interpret all of the data with a high degree of confidence, except for Flask 3, which is the 50 cm sample from 2022-06-19 (Figs. 4C and 5C). Unlike data from the other two field sites, soil water from 25 cm and 50 cm overlap within uncertainty. There were two precipitation events at the field site during the sampling period on 2022-06-25 and 2022-07-01, but both events were quite small (<0.02 inches, CoAgMet). There is no significant influence of the precipitation events on the $\delta^{18}O$ and $\delta^2H$ values. The >1.0‰ increase in $\delta^{18}O$ values on 2022-06-29 is surprising given that there is not a comparable magnitude increase in $\delta^2H$ value, and that the values measured from 2022-07-04 more closely match the $\delta^{18}O$ and $\delta^2H$ values from the two earlier sampling days. There are two potential explanations for this data. First, that is a real signal from an evaporation driven increase in $\delta^{18}O$ value, and the reset to a lighter $\delta^{18}O$ value on 2022-07-04 is due to the infiltration of precipitation. This explanation is corroborated by a low d-excess value associated with this measurement (Fig. SI 9). The second possible explanation is that the 25 cm sample from 2022-06-29 is influenced by condensation at the time of sampling. Dew point at the field site on 2022-06-29 significantly decreased as compared to the other sampling days to a monthly minimum of 20.6°C. It is possible that environmental conditions encouraged the formation of condensation in the impermeable tubing at the time of sampling. There were no obvious signs of condensation during the time of measurement in the lab. These results highlight the utility of having broad contextual environmental data to aid in the interpretation of soil water isotope data.

All together, these three soil water isotope datasets demonstrate two main findings. First, data from these samples show that the differences between field sites is easily resolvable using the SWISS. For example, at 50 cm depth the oxygen isotopes range between -14.4 to -16.3‰, -9.9 to -10.3‰, and -7.4 to -9.3‰ for the Oglala, Briggsdale and Seibert sites, respectively. These differences likely reflect differences in the stable isotope composition of precipitation and evaporation dynamics. Second, the sample data retrieved from a SWISS are sufficiently precise to be able to meaningfully resolve vertical profile soil water isotope data. For example, at the Oglala National Grassland field site, soil water from 25 cm clearly has higher $\delta^{18}O$ and $\delta^2H$ values as compared to soil water from a depth of 50 and 75 cm.

6.3 Future improvements

One significant SWISS unit hardware improvement that could be made would be to install a heating implement to the flasks. One source of uncertainty on the current system is the potential effect of uneven heating of the flasks prior to measurement. This could be improved in subsequent iterations of the SWISS with the addition of heat tape or blankets that can deliver controlled and consistent amounts of heat. This improvement could also help
limit the amount of manual intervention needed during measurement, and could improve automation of flask
measurement.

In addition, we have made a few improvements to the automation system that were not implemented for the
data presented in this contribution, but will be part of future deployments. First, we will track conditions inside the
SWISS with a temperature and relative humidity sensor inside the case. Second, we plan to eliminate the power
inverter by powering both the Valco valve and mass flow controller with VDC using a power step up controller.
Lastly, we will add an IoT cellular router to be able to remotely monitor and control the SWISS units.

Finally, there are two future considerations for field deployments. The first is finding a way to safely and
automatically heat the impermeable tubing that connects the water vapor probes and the SWISS in a way that
doesn’t change the inherent thermal structure of the soil, and is safe for unmonitored use. Additionally, we plan to
test SWISS unit resilience during air travel so that these units can be used at field sites that are not within driving
distance of a research facility.

Conclusions

We presented the evolution of the soil water isotope storage system (SWISS) from a prototype to a fully
built out and tested system. We also presented a quality control and quality assurance procedure that can be used to
ensure the reliable storage of soil water vapor over long time periods (up to 40 days). In addition, these quality
control and quality assurance tests shed light on the accuracy and precision of the SWISS. After applying an offset
correction, we determine the overall precision of the SWISS to be 0.9‰ and 3.7‰ for δ¹⁸O and δ²H, respectively. In
a field setting, flasks reliably resist atmospheric intrusion. Additionally, the proposed sampling schema does not
introduce significant memory effects. Lastly, we demonstrate that the precision of the SWISS still allows us to
distinguish between field sites and between soil water dynamics within a single soil column. Taken as a whole, these
data show that the SWISS can be used as a tool to answer many emerging ecohydrological questions, and will
enhance researchers’ ability to collect soil water isotope datasets from more remote and traditionally understudied
field sites.

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Author contribution

Rachel E. Havranek: original draft, conceptualization, methodology, investigation, formal analysis, funding acquisition. Kathryn E. Snell: Conceptualization, Methodology, Writing – review & editing, funding acquisition. Sebastian H. Kopf: Conceptualization, Methodology, Writing – review & editing. Brett Davidheiser-Kroll: Conceptualization, Methodology, Writing – review & editing. Valerie Morris: Methodology, Writing – review & editing. Bruce Vaugh: Methodology, Writing – review & editing.

Competing interests

The authors declare no competing interests.
Works Cited


