On-Site Calibration for High Precision Measurements of Water Vapor Isotope Ratios Using Off-Axis Cavity-Enhanced Absorption Spectroscopy

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ABSTRACT

Stable isotope ratio measurements of atmospheric water vapor ($\delta^{18}O_v$ and $\delta^2H_v$) are scarce relative to those in precipitation. This limitation is rapidly changing due to advances in absorption spectroscopy technology and the development of automatically calibrated field-deployable instrument systems. These systems allow high throughput, in situ monitoring of the temporal variability in $\delta^{18}O_v$ and $\delta^2H_v$. This paper presents a robust calibration procedure for reliable, high-precision $\delta^{18}O_v$ and $\delta^2H_v$ measurements at less than hourly intervals in this study. The method described here was developed and tested using a coupled system consisting of a commercial water vapor isotopic source device and a commercial water vapor isotope analyzer [Los Gatos Research (LGR) model WVIA-24] based on the off-axis integrated cavity output spectroscopy (off-axis ICOS) technique. The isotope analyzer shows a time-dependent response that varies with water vapor mixing ratio, suggesting the need of regular (hourly) calibration achievable by a single reference water source evaluated at a range of mixing ratios. By using a three-point calibration procedure with a range of user-specified water vapor mixing ratios, the authors were able to produce hourly $\delta^{18}O_v$ and $\delta^2H_v$ measurements with an overall accuracy ($\pm 0.2\%$ for $\delta^{18}O_v$, $\pm 0.5\%$ for $\delta^2H_v$) and precision ($\pm 0.3\%$ for $\delta^{18}O_v$, $\pm 3.0\%$ for $\delta^2H_v$) in the laboratory. The calibration procedure reliably produced data that were consistent with those collected by the conventional cryogenic method in an old-growth forest.

1. Introduction

Isotope-enabled general circulation models (GCMs) are a unique tool to compare the stable isotope ratios in precipitation ($\delta^{18}O$ and $\delta^2H$) in contemporary and palaeoclimatic conditions (Joussaume et al. 1984). GCMs are able to simulate regional distributions of atmospheric water vapor and its stable isotope ratios ({$\delta^{18}O_v$ and $\delta^2H_v$}), but these model simulations are difficult to validate, and rarely do so, because of the scarcity of direct and continuous $\delta^{18}O$ and $\delta^2H$ measurements. As a result, GCM model outputs are often compared to ground-based, time-integrated $\delta^{18}O$ and $\delta^2H$ in precipitation such as those in the Global Network of Isotopes in Precipitation (GNIP; Hoffmann et al. 1998; Joussaume et al. 1984; Jouzel et al. 1987; Sturm et al. 2005). Breakthroughs in absorption spectroscopy technology lead to the popularity of commercially available optical-based isotope spectroscopy analyzers. Next-generation gas analyzers are field-deployable and have the potential for in situ stable isotope ratio measurements of atmospheric trace gases. Data comparison between spectroscopy analyzers and isotope ratio mass spectrometry are important and should be chronically reported by diverse research groups conducting experiments in a wide range of laboratory and environmental conditions, as these spectroscopy analyzers continue to improve.

Recent studies examined the performance of cavity-enhanced absorption spectroscopy instruments for water vapor isotope ratio measurements using a variety of calibration protocols (Gupta et al. 2009; Iannone et al. 2010; Schmidt et al. 2010; Sturm and Knohl 2010; Wang et al. 2009). Previously a dewpoint generator (Li-Cor 610, Lincoln, Nebraska) was used to produce a reference vapor stream of known isotopic composition (Wang et al. 2009).
et al. 2009). The dewpoint generator has been shown as a nonideal Rayleigh distillation device (Lee et al. 2005).

In addition, the reference water requires at least 12 h to reach equilibrium in the condenser block inside the dewpoint generator, and it cannot be run more than 24 h without interruption (Wang et al. 2009). These limitations prohibit the use of a dewpoint generator for unattended field sampling. To overcome this problem, a continuous, steady water vapor source of consistent isotopic composition is necessary. This led to the development of a “dripper” system, which completely vaporizes an aliquot without fractionating the stable isotopologues of reference liquid water, to calibrate water vapor samples in a tunable diode laser absorption spectroscopy analyzer (Campbell Scientific, Inc., TGA 100A, Logan, Utah; Lee et al. 2005). Similar to this idea, recent studies (Gupta et al. 2009; Schmidt et al. 2010; Sturm and Knohl 2010) used a modified injection/evacuation system to introduce a completely vaporized reference water sample into a heated dry-air mixing chamber. Periodically, an absorption spectroscopy analyzer samples the reference mixture to monitor instrumental drift, and makes corrections to the unknown air samples based on the known isotopic composition of the reference water.

In this study we described a calibration routine for in situ $\delta^{18}O_v$ and $\delta^2H_v$, measurements made by a commercial water vapor isotope analyzer [WVIA; Los Gatos Research, Inc. (LGR), model WVIA-24] coupled with a reference vapor source device [water vapor isotopic standard source (WVISS)]. An earlier version of LGR’s WVIA was evaluated in temperature controllable growth chambers. Upon calibration, good precision was reported (Sturm and Knohl 2010). In their experiments, water vapor mixing ratios of the sample air had a relatively slow and smooth transition. When sampling in a fast-changing environment where water vapor mixing ratios of the ambient air are likely to fluctuate drastically and rapidly, a field-ready calibration routine for high resolution $\delta^{18}O_v$ and $\delta^2H_v$ measurements has not yet been adequately demonstrated.

Here we present a user-configurable calibration procedure achievable by the use of a single reference water source at a range of mixing ratios in field conditions. We first present experiments that determined the accuracy and precision of the analyzer in the laboratory. Using the calibration routine developed in the laboratory, the system was field-tested in an old-growth coniferous forest. We show that the LGR water vapor isotope ratio system (WVIA calibrated regularly by WVISS) reliably operated over the range of water vapor mixing ratios from 5000 to 24 000 ppm during our experimental period.

2. Methods

We evaluated the commercially available Los Gatos Research Water Vapor Isotope Analyzer (model WVIA-24) in laboratory and field conditions. The analyzer provides simultaneous mixing ratio measurements of water isotopologues in water vapor at a maximal scan rate of 2 Hz. The analyzer uses a near-infrared diode laser scanning over three absorption lines near the 1.4-$\mu$m wavelength for $H_2O$, HDO, and $H_2^{18}O$. The analyzer is based on an off-axis integrated cavity output spectroscopy (OA-ICOS) technique described in detail by Baer et al. (2002). The long pathlength of the LGR OA-ICOS analyzer (a ~5000 increase in the ratio of pathlength to cell length) provides high sensitivity and precision for isotopologue ratio measurements in atmospheric trace gases. The OA-ICOS absorption spectroscopy was shown capable of handling water isotopologue ratio measurements in extremely low mixing ratio environments (Sayres et al. 2009).

a. Water vapor isotope standard source system

A WVISS unit manufactured by Los Gatos Research provides steady reference vapor streams to calibrate the WVIA. The WVISS offers the potential of performing automated, unattended calibrations for prolonged durations. An external diaphragm vacuum pump (KNF, N920AP.29.18) downstream of the analyzer draws air into the WVIA at a typical flow rate of 800 mL min$^{-1}$ in our experiments (pump 2; Fig. 1). A three-way valve inside the WVISS controls airflow by switching between ambient inlets and WVISS reference air. During calibration ambient air is drawn by a compressor and passed through a two-stage desiccation process lowering water vapor mixing ratios below 10 ppm. A mass flow controller regulates the flow of dry air into a 1-L mixing chamber heated to 80°C. A nebulizer administers a mist of reference water into the heated chamber, providing complete vaporization without fractionating the reference water. Once the calibration cycle completes, the three-way valve automatically switches back to its default position to resume air sampling from ambient inlets. A user-configurable program in the WVIA fully and automatically controls the valve switching inside the WVISS and the intervals and durations of a calibration cycle.

b. Calibration protocol

We used a three-point calibration procedure spanning a range of reference water vapor mixing ratios encompassing those observed in the ambient air. Every hour, reference gas (air containing isotopically known water
vapor) was introduced at three levels of mixing ratios: 16 000, 10 000, and 5500 ppm, each for 260 s. Figure 2 shows an example of the mixing ratios measured from four ambient inlets bracketed by hourly reference gases aforementioned. For each duration of a given reference level, readings from the first 80 s were discarded and the data from the subsequent 170 s were averaged to produce hourly $^{18}$O and $^2$H ratios at three reference mixing ratio levels.

c. Laboratory evaluation

To determine the WVIA’s accuracy and precision, we performed a laboratory experiment in which two water bottles of known isotopic composition were repeatedly measured in 10 separate rounds. One bottle served as a reference producing average $^{18}$O and $^2$H ratios at three levels of water vapor mixing ratios. The other bottle was treated as an unknown. We alternated the connection between the two bottles of water with the WVISS, which generated unfractionated vapor streams ($\delta^{18}$O = $-15.9_{\%o}$ ± 0.2_{\%o} and $\delta^2$H = $-121.0_{\%o}$ ± 0.5_{\%o}) that were subsequently measured by the WVIA at 25°C ± 3°C in the laboratory. For each round of the experiment, we ran the reference gas for 6 min at each of the three levels of mixing ratios (22 000, 14 000, and 6000 ppm). To ensure no memory effects from the residual water, we purged the system by running dried air through the WVISS until the mixing ratio dropped below 500 ppm. The system was then switched to measuring the unknown water bottle. Vapor streams from the unknown water bottle were measured at a high (~17 000 ppm) and a low (~7600 ppm) range, each for 10 min, followed by a purge of dry air before returning to measuring the reference water bottle. The same procedure was repeated 10 times using the two water bottles with dry air purged between runs.

d. Calibration curves for data correction

Uncalibrated readings recorded by the WVIA were analyzed to examine the sensitivity of water vapor isotope ratios to changes in mixing ratios. A second-order polynomial function was fitted to the mean of the recorded isotope ratios at the three designated levels of reference water vapor mixing ratios. Calibration curves were developed separately to characterize the response to variations in the $^2$H and $^{18}$O measurements recorded by the instrument as a function of the water vapor mixing ratio, using the formula below:

\[
\delta^{18}O = a + b \times \text{mixing ratio} + c \times \text{mixing ratio}^2
\]

\[
\delta^2H = d + e \times \text{mixing ratio} + f \times \text{mixing ratio}^2
\]

**FIG. 1.** A schematic of experimental setup. In the field experiment, ambient air samples were pulled from three heights by a diaphragm pump (pump 1) and passed through the WVISS unit before entering the WVIA. An additional heated Teflon tube (HT) was installed at 1 m.
a \ oceans, and 16O are known.

\[
\alpha = \frac{(^{18}O)_{\text{raw}}}{(^{16}O)_{\text{known}}} = f_O(w) = a_Ow^2 + b_Ow + c_O
\]

(1a)

\[
\alpha = \frac{(^{2}H)_{\text{raw}}}{(^{1}H)_{\text{known}}} = f_H(w) = a_Hw^2 + b_Hw + c_H
\]

(1b)

where \( \alpha \) represents the ratio between the isotopic composition reported by the WVIA and the true value of the reference water, and \( w \) is the water vapor mixing ratio reported by the WVIA. Values of \( \alpha \) vary as a function of the mixing ratio as described by a second-order polynomial equation. The \(^2\H\H\) and \(^{18}\O\O\) ratios recorded by the WVIA show distinct sensitivity to changes in the mixing ratio which required different sets of polynomial coefficients \( a, b, \) and \( c \). Using Eq. (1), errors in the WVIA-reported isotopic composition can be evaluated based on WVIA-recorded mixing ratios. The isotopic composition of an unknown air sample can be corrected following the equations given by

\[
\left(\frac{^{18}O}{^{16}O}\right)_{\text{corrected}} = \frac{1}{\alpha} \left(\frac{^{18}O}{^{16}O}\right)_{\text{raw}},
\]

(2a)

\[
\left(\frac{^{2}H}{^{1}H}\right)_{\text{corrected}} = \frac{1}{\alpha} \left(\frac{^{2}H}{^{1}H}\right)_{\text{raw}},
\]

(2b)

where \((^{18}O/^{16}O)_{\text{raw}}\) and \((^{2}H/^{1}H)_{\text{raw}}\) represent WVIA-reported isotopic composition in the sample air. We report the corrected isotopic composition in the delta notation \( \delta \) relative to the Vienna Standard Mean Ocean Water described by (Coplen 1996):

\[
\delta = \left(\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1\right) \times 1000,
\]

(3)

where \( R \) is the molar ratio of heavy to light isotopes.

de. Field evaluation

1) STUDY SITE

We installed the water vapor isotope system in the Wind River Experimental Forest near Carson, Washington, in late August 2010, to evaluate its performance based on the calibration protocol developed in the laboratory. The Wind River site is a 500-yr-old-growth coniferous forest and has been an active research station for stable carbon and water isotope studies as a part of the AmeriFlux network (Lai and Ehleringer 2011; Lai et al. 2006, 2005, 2004). Dominant species include Douglas fir (Pseudotsuga menziesii), western hemlock (Tsuga heterophylla), and western red cedar (Thuja plicata) with an average canopy height of approximately 60 m. Temperature and rainfall variations are highly seasonal, ranging from a mean minimum -3.7°C in January to a mean maximum 26.9°C in July (Bauerle et al. 1999).

2) EXPERIMENTAL SETUP FOR AIR SAMPLING

Ambient air was drawn from three different heights (1, 10, and 60 m) through \(\frac{1}{4}\)" diameter polytetrafluoroethylene (PTFE) tubing using a diaphragm pump at a flow rate of 0.5 L min\(^{-1}\) (KNF Neuberger Model UN811 KNI, FIG. 2. In situ sample data collected from four inlets with hourly calibrations lasting 15 min. The upper graph represents a 90-min period spanning two calibrations to reveal our automatic step-down calibration scheme.
115-V, 60-Hz; pump 1 in Fig. 1). A 0.2-μm filter with PTFE membrane in a polypropylene housing (Polycap 36 TF ½" FTG, VWR) was installed on the front end of each tube. Cautions were taken to prevent condensation at the inlets by wrapping 1” cylindrical insulation foam around the PTFE tubing approximately 24” toward the filter. A customized heated Teflon tube (Clayborn Laboratory, Truckee, California), kept constantly 5°C above the ambient temperature, was separately installed at 1 m as a reference to compare with the air drawn through the three unheated PTFE tubes. The unheated PTFE tube at 1 m was extended approximately 20 m away from the dry shack into the understory. The heated tube of 3 m in length was attached to the base of the crane tower with zip ties. The four sampling tubes were connected to a manifold housing solenoid valves (Clippard single-sided six-station manifold; 12-V, normally closed, two-way, manifold mount valves, Clippard Instrument Laboratory, Inc., Cincinnati, Ohio) inside a dry shack below the crane tower. Two thermal couples were used to measure room air temperature. A relay board (Campbell A6REL-12 Relay Board) connected to a CR3000 datalogger (Campbell Scientific, Inc, Logan, Utah) controls the switching of the solenoid valves that alternate airflow from the four inlets, each for 10 min, into the WVISS. The first 5 min of data recorded by the WVISS for each 10-min sampling cycle from an inlet were discarded. The remaining 5 min of the data recorded by the WVISS were corrected and reported as an hourly average at the top of the hour. This results in a calibration duty cycle of 20 min h⁻¹.

Reference gases generated by the WVISS were measured in the WVISS following the same protocol developed in the laboratory. Every hour, reference gases were introduced at three levels of mixing ratios encompassing the range of ambient water vapor mixing ratios. Each level of reference gases ran for 260 s. The first 80 s of the readings recorded by the WVISS were discarded, and the subsequent 170 s of the data (with the last 10 s discarded) were computed to produce three average values separately for 18O/16O and 2H/1H at the three predetermined mixing ratios. Two calibration curves, one for 18O/16O and the other for 2H/1H, were calculated each hour and the ambient air data recorded by the WVISS within the hour were corrected following the procedure as outlined in the method section.

3. Results

a. WVISS accuracy and precision from laboratory experiments

Regular calibration is necessary for the LGR water vapor isotope analyzer (model WVISS-24) for maximum accuracy due to the observed variability in the laboratory-controlled experiment. Figure 3 shows the results from the laboratory experiment in which two water bottles of known isotopic composition were repeatedly measured as outlined in the methods. The run-to-run variability observed in both 18O and 2H suggest two general patterns. First, uncalibrated 18O readings recorded by the WVISS constantly underestimate the true values, while the uncalibrated 2H readings recorded by the WVISS overestimate the true value. Second, deviations from the true values show a nonlinear, water-vapor mixing ratio–dependent response. The WVISS appeared to have smaller 2H biases at higher mixing ratios, but no such trend was detectable for 18O. The observed variability suggests the need of regular calibration if the analyzer is to be employed in field experiments when rapid changes in the atmospheric water vapor mixing ratios and large environmental fluctuations can be expected.

Figure 4 shows the comparison between corrected and uncorrected δ18O and δ2H values from the bottle-switching experiment. The results shown are for two levels of mixing ratios represented by the averages of all 10 unknown runs. The uncorrected readings reported by the WVISS underestimated the true δ18O value by
1.2% ± 0.5% at both high and low mixing ratios, while overestimated the true δ²H value by 1.1% ± 0.5% at high mixing ratios and by 2.8% ± 0.4% at low mixing ratios. Using the three-point calibration, we were able to improve the errors to within ±0.02% for δ¹⁸O and ±0.2% for δ²H with a precision of ±0.3% for δ¹⁸O and ±3.0% for δ²H in the laboratory. These numbers are comparable or better than those reported by the manufacturer. It is interesting to note that while the calibration protocol significantly (p < 0.05) improved the accuracy for both δ¹⁸O and δ²H, the precision was slightly worse for δ²H after the correction in our laboratory experiment. This was likely due to other types of errors introduced during the experiment (e.g., operator errors, sample transfer and storage, uncertainties in the reference waters, etc.).

b. Temperature sensitivity of WVIA (uncalibrated) in field experiments

From late August to early October 2010, the water vapor isotope system was installed in the Wind River Experimental Forest for δ¹⁸O and δ²H measurements within and above the canopy. Unlike the laboratory experiment under which the room temperature did not considerably change, the WVIA experienced daily temperature fluctuations spanning between 13.5°C and 29.9°C during the field study period. Figure 5 shows the uncalibrated WVIA’s sensitivity to the temperature fluctuation inside the dry shack at two levels of mixing ratios. These temperature relationships were compiled from the reference gases generated by the same reference water bottle (δ¹⁸O = −15.9‰ ± 0.2‰ and δ²H = −121.0‰ ± 0.5‰) and subsequently introduced to the WVIA hourly during the month-long experiment. We separated the hourly temperatures into a low (13°C–24°C) and a high (24°C–30°C) range and there were distinct relationships between room temperatures and the isotope readings recorded by the WVIA for the three levels of mixing ratios. The statistical analyses of these linear relationships were summarized in Table 1.

Uncalibrated readings recorded by the WVIA showed different temperature responses at the two temperature ranges. Ten out of the 12 slopes evaluated were significantly different from zero (Table 1). The temperature dependences for δ¹⁸O and δ²H measurements differed. At the low temperature range (13°C–24°C), strong (1.17°C ± 2.1, p = 0.0001, R² = 0.54) temperature sensitivity was found for δ²H at the low mixing ratio. This temperature sensitivity decreases as the mixing ratio increases, and becomes statistically insignificant (20.04°C ± 2.1, p = 0.052, R² = 0.01) when the reference gas increased to 16 000 ppm (Table 1; Fig. 5). No to low significant relationship was found for δ¹⁸O at the low temperature range.

In contrast, strong (varying between 20.2 and 20.4°C from high to low levels of mixing ratios) temperature sensitivity was found for δ¹⁸O at the high temperature range (24°C–30°C). The WVIA’s temperature sensitivity of δ²H was somewhat mediated but still statistically significant at higher temperatures (Table 1; Fig. 5). Our laboratory results showed that the bias resulting from WVIA’s temperature sensitivity can be fully removed by a multipoint calibration routine when operated in conjunction with a WVISS.

4. Discussion

In this study we presented a calibration protocol for in situ, high precision water isotopologue measurements by an OA-ICOS instrument. The primary finding of the study is that the calibration protocol described herein allows accurate and precise measurements to be recorded by the LGR water vapor isotope analyzer when it operates in conjunction with the water vapor isotope...
standard source unit. We have shown that routine measurements of known isotopic water vapor reference samples effectively compensate for the finite temperature response of the WVIA (model WVIA-24). For maximum accuracy and precision, we recommend using a three-point calibration routine. A three-point calibration scheme was regularly used for trace gas monitoring (Bollenbacher et al. 2000). A unique feature of the calibration protocol described here is that the uncertainty in the isotope ratios reported by the analyzer is

**Table 1.** Temperature sensitivity of the uncalibrated water vapor isotope analyzer (model WVIA-24) evaluated at three levels of mixing ratios in field experiments. Slopes from a linear regression, \( \delta = s \times T_r + b \), that significantly differ from zero \((p < 0.05, F\text{ test})\) are indicated by an asterisk.

<table>
<thead>
<tr>
<th>Room temperature ((T_r))</th>
<th>Isotopes</th>
<th>Mixing ratio</th>
<th>Slope ((s))</th>
<th>Intercept</th>
<th>(R^2)</th>
<th>(p) value</th>
<th>Degrees of freedom</th>
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<tr>
<td>12°–24°C</td>
<td>(\delta^{18}O)</td>
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<td>−14.2</td>
<td>0.001</td>
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<td>305</td>
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<td></td>
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<td>0.0003</td>
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<td></td>
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<td>−14.2</td>
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<td>305</td>
</tr>
<tr>
<td></td>
<td>(\delta^2H)</td>
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<td>−121.5</td>
<td>0.01</td>
<td>0.0525</td>
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<td></td>
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<td>−130.0</td>
<td>0.14</td>
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<td>305</td>
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<td></td>
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<td>1.17*</td>
<td>−146.7</td>
<td>0.54</td>
<td>&lt;0.0001</td>
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<td>24°–30°C</td>
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<td>16 000</td>
<td>−0.2*</td>
<td>−8.0</td>
<td>0.29</td>
<td>&lt;0.0001</td>
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<td>&lt;0.0001</td>
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</table>

**Fig. 5.** The uncalibrated WVIA’s temperature sensitivity for two ranges of room temperature in the field experiment. Each data point represents an hourly average for a total of 663 h of data points. The lines represent least squares linear regression with the statistics summarized in Table 1. Only data from two levels of mixing ratios were shown.
characterized by changes in the mixing ratio rather than the isotopic composition of the reference gas, allowing users to develop finite calibration functions with only one reference water bottle of known isotopic composition. This mixing ratio-based calibration procedure is user-configurable and can be applied to a specific range of mixing ratios in the ambient air over a wide range of environmental conditions. Using the calibration protocol described herein, we were able to measure unknown water to errors within $\pm 0.02^\circ\text{o}$ for $\delta^{18}\text{O}$ and $\pm 0.2^\circ\text{o}$ for $\delta^2\text{H}$, with a precision $\pm 0.3^\circ\text{o}$ for $\delta^{18}\text{O}$ and $\pm 3.0^\circ\text{o}$ for $\delta^2\text{H}$ in the laboratory. Including errors in our laboratory reference water ($\pm 0.2^\circ\text{o}$ for $\delta^{18}\text{O}$ and $\pm 0.5^\circ\text{o}$ for $\delta^2\text{H}$), the overall accuracy for the hourly water vapor isotope ratio measurements were $\pm 0.2^\circ\text{o}$ for $\delta^{18}\text{O}$ and $\pm 0.5^\circ\text{o}$ for $\delta^2\text{H}$. Applying the three-point calibration, we were able to obtain hourly average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements with a similar precision for water vapor mixing ratios spanning between 4000 and 25 000 ppm in field experiments. Our laboratory results likely represent the optimal performance of the instrument. Long-term stability of field measurements will be evaluated in a future study.

To demonstrate how regular calibration using the WVISS improves a WVIA’s accuracy in producing hydrologically important stable isotope information, Fig. 6 shows an example of the deuterium excess ($d$ excess) derived from hourly $\delta^2\text{H}$ and $\delta^{18}\text{O}$ observations made above the Wind River Forest canopy over a 24-h period. Deuterium excess, defined by Dansgaard (1964) as 

$$d = \delta^2\text{H} - 8 \times \delta^{18}\text{O},$$

has traditionally been used as a diagnostic tracer to identify the origin of vapor sources and moisture recycling (Gat 2000). Figure 6 compares values of the $d$ excess before and after correcting biases in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ recorded by the WVIA. Values of the $d$ excess derived from uncorrected readings were approximately $30^\circ\text{o}$ lower than those derived from the corrected data. The $d$ excess derived from the corrected data (Fig. 6a, insert) showed a diel pattern similar in magnitude to those previously reported in this forest (Lai and Ehleringer 2011). The diel pattern of $d$ excess derived from corrected $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values shows a remarkable agreement with that observed by cryogenic trapping (Fig. 6b). Using an H$_2$O isotope balance model developed by Lai et al. (2006) and Lai and Ehleringer (2011) showed that atmospheric mixing largely explained the diel pattern in the observed $d$ excess in this forest. Lower $d$-excess values in the early morning can be attributed to air entrainment from the free troposphere as the boundary layer rapidly developed because of surface heating. The higher $d$-excess values observed in the midday can be explained by the horizontal advection of surface evapotranspiration from the upwind area. Evaporation was shown to increase $d$-excess values in the atmospheric moisture over the Great Lakes and the Mediterranean Sea (Gat et al. 1994, 2003). The uncorrected $d$ excess would have shown negative values throughout this day, clearly a bias due to errors in the uncalibrated $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values reported.

![Fig. 6](image_url)
by the WVIA. In that regard, having accurate $\delta^{18}O$ measurements is critical to the estimate of $d$-excess values because any errors in the $\delta^{18}O$ would be amplified 8 times when the isotope ratios are reported as $d$ excess.

The absorption cell inside the WVIA was heated to $-50^{\circ}\mathrm{C}$, a design aiming to minimize the effect of ambient temperature fluctuations on the WVIA’s performance. Nevertheless, results from our field experiment showed considerable temperature sensitivity (Fig. 5). Previous studies (Sturm and Knohl 2010) reported a temperature sensitivity of an earlier version of the WVIA as $-0.37\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$ for $\delta^2H$ and $-0.24\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$ for $\delta^{18}O$ in a temperature range of $19^{\circ}-29^{\circ}\mathrm{C}$. They also noted that the temperature control of the WVIA’s cavity did not reach the set temperature when the ambient air temperature dropped below $22^{\circ}\mathrm{C}$. Our results suggested varying agreement with previous findings (Sturm and Knohl 2010). We show that the WVIA’s temperature sensitivity varied with mixing ratios, generally, with a stronger sensitivity at lower mixing ratios. At 5500 ppm, the WVIA showed a sensitivity of $-0.32\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$ for $\delta^2H$ and $-0.40\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$ for $\delta^{18}O$ in a temperature range of $24^{\circ}-30^{\circ}\mathrm{C}$ (Table 1). These values were similar to previous results (Sturm and Knohl 2010). The temperature sensitivity became weaker at higher mixing ratios. At 16 000 ppm, the WVIA showed a sensitivity of 0.15$\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$ for $\delta^2H$ and $-0.20\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$ for $\delta^{18}O$ under the same temperature range.

In the low temperature range ($12^{\circ}-24^{\circ}\mathrm{C}$), the WVIA showed no significant sensitivity to temperature fluctuation at high levels of mixing ratio (Table 1). The WVIA showed a small but statistically significant response for $\delta^{18}O$ at lower mixing ratios ($0.04\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}, p < 0.05$). The greatest sensitivity was found for $\delta^2H$ ($1.17\%_{\text{oo}}^{\circ}\mathrm{C}^{-1}$) at 5500 ppm. Overall, our results showed that the temperature sensitivity of LGR’s WVIA has limited improvement from an earlier version (Sturm and Knohl 2010). Using the three-point calibration, we were able to explicitly characterize the temperature-mixing ratio relationship, which was fully incorporated into the second-order polynomial functions shown in Eq. (1).

The WVIA may be subject to a more pronounced anomaly if the analyzer experiences a greater temperature fluctuation in field conditions. To address this concern, we plotted the hour-to-hour variability of the reference gases reported by the WVIA operated in field conditions (data not shown). Comparing field data collected on a typical day with the laboratory results (Fig. 3), we found the magnitude of the run-to-run variability to be similar ($2\%_{\text{oo}}$ versus $2\%_{\text{oo}}$ for $^{18}O/^{16}O$ and $14\%_{\text{oo}}$ versus $11\%_{\text{oo}}$ for $^2H/^H$) between the laboratory and field experiments. Run-to-run variations in the field data were well characterized by second-order polynomial response curves. Regular runs of reference gases can be used to capture and correct for short-term instrument response to temperature fluctuations.

The WVIA, when operated in conjunction with a commercially available water vapor isotopic source unit capable of delivering known vapor flows at multiple mixing ratios, can accurately and precisely provide in situ $\delta^{18}O$, and $\delta^2H$ measurements in field experiments.

We recommend that users of water vapor isotopic instrumentation fully characterize the instrumentation response of $\delta^{18}O$, and $\delta^2H$ measurements carefully over the range of water vapor mixing ratios encountered. Regular checks at a single mixing ratio may be sufficient to reliably correct for time-dependent variation in response (due to drift), but for optimum data quality, we recommend a three-point calibration routine as outlined in the methods. As with all isotopic specific measurements, users of laser-based instrumentation should regularly calibrate using a known (traceable) isotopic source in order to properly report accurate values.

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