Water vapor δ^2H, δ^{18}O and δ^{17}O measurements using an off-axis integrated cavity output spectrometer – sensitivity to water vapor concentration, delta value and averaging-time

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RATIONALE: High-precision analysis of atmospheric water vapor isotope compositions, especially $\delta^{17}O$, can be used to improve our understanding of multiple hydrological and meteorological processes (e.g., differentiate equilibrium or kinetic fractionation). This study focused on assessing, for the first time, how the accuracy and precision of vapor $\delta^{17}O$ laser spectroscopy measurements depend on vapor concentration, delta range, and averaging-time.

METHODS: A Triple Water Vapor Isotope Analyzer (T-WVIA) was used to evaluate the accuracy and precision of $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$ measurements. The sensitivity of accuracy and precision to water vapor concentration was evaluated using two international standards (GISP and SLAP2). The sensitivity of precision to delta value was evaluated using four working standards spanning a large delta range. The sensitivity of precision to averaging time was assessed by measuring one standard continuously for 24 hours.

RESULTS: Overall, the accuracy and precision of the $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$ measurements were high. Across all vapor concentrations, the accuracy of $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$ observations ranged from 0.10‰ to 1.84‰, 0.08‰ to 0.86‰ and 0.06‰ to 0.62‰, respectively, and the precision ranged from 0.099‰ to 0.430‰, 0.009‰ to 0.080‰ and 0.022‰ to 0.054‰, respectively. The accuracy and precision of all isotope measurements were sensitive to concentration, with higher accuracy and precision generally observed under moderate vapor concentrations (i.e., 10000-15000 ppm) for all isotopes. Precision was also sensitive to the range of delta values, though the effect was not as large when compared to the sensitivity to concentration. The precision was much less sensitive to averaging time when compared with concentration and delta range effects.

CONCLUSIONS: The accuracy and precision performance of the T-WVIA depends on concentration but depends less on the delta value and averaging-time. The instrument can

simultaneously and continuously measure δ^2H, $\delta^{18}O$ and $\delta^{17}O$ values in water vapor, opening a new window to better understand ecological, hydrological and meteorological processes.

Keywords: $\delta^{17}O$, accuracy, averaging-time dependence, concentration dependence, delta range dependence, ecohydrology, isotope, laser, precision

INTRODUCTION

Phase changes of water tend to fractionate against heavier isotopes (e.g., ^2H, ^{18}O and ^{17}O relative to ^1H and ^{16}O). Therefore, water isotopes are natural tracers of hydrological cycles and can be widely utilized to investigate temporal and spatial variations in ecohydrological processes[1-8]. Recently, there has been growing interest in a new hydrological tracer $\delta^{17}O$, accompanied by the development of high-precision analytical methods[9, 10]. Similar to δ^2H and $\delta^{18}O$, $\delta^{17}O$ can be used to infer the degree of isotope enrichment during transpiration[11], serve as tracer in different water bodies (e.g., meteoric water and ice cores)[12-14], and characterize evaporative regimes. Furthermore, the ^{17}O-excess (^{17}O-excess$=\ln(\delta^{17}O + 1) - 0.528\ln(\delta^{18}O + 1)$) is also used to probe kinetic fractionation processes. While this metric is similar to d-excess (d-excess$=\delta^2H$ - $8\delta^{18}O$), ^{17}O-excess is relatively less sensitive to temperature effects and equilibrium fractionation during the formation and transport of rainfall[15, 16]. As a consequence, ^{17}O-excess is independent of temperature and can be used as a proxy for humidity. It is particularly useful for constraining oceanic humidity because of a strong negative correlation between ^{17}O-excess and relative humidity[12]. ^{17}O-excess thus provides an additional constraint to quantify the balance between equilibrium and kinetic effects, and also has been applied to reconstruct atmospheric trajectories and past climate[13, 17].

Due to the low natural abundance of ^{17}O, it has historically been challenging to obtain $\delta^{17}O$ measurements with acceptable accuracy and precision, particularly in the vapor phase. The traditional Isotope Ratio Mass Spectrometry (IRMS) technique requires the vapor first be trapped using cryogenic trapping or collection with a molecular sieve[18]. In addition, the technique requires water to be converted to O_2 rather than CO_2 or CO, which is a laborious process [19-21]. As a result, $\delta^{17}O$ measurements derived from the IRMS technique are complicated, expensive and time-consuming, and can only be done in a small number (< 10) of laboratories worldwide[9, 10, 21, 22].

Other work has focused on obtaining liquid-water $\delta^{17}O$ measurements using both IRMS and newer laser absorption spectroscopy (LAS) techniques. For instance, Barkan and Luz[21] as well as Schoenemann et al.[22] measured two international water standards (Greenland Ice Sheet Precipitation, GISP and Standard Light Arctic Precipitation, SLAP/SLAP2) from the International Atomic Energy Agency (IAEA) using a conventional IRMS technique. Berman et al.[9] measured GISP utilizing a Triple Isotope Water Analyzer (TIWA) relying on the Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique. They showed that the OA-ICOS technique, which is energy efficient and requires no sample conversion, can measure δ^2H, $\delta^{18}O$ and $\delta^{17}O$ values with a precision comparable to the IRMS technique. Later, Steig et al.[10] measured the same standard (GISP) using the Cavity Ring Down Spectroscopy (CRDS) technique, demonstrating that this instrument could also measure $\delta^{17}O$ values with high precision. While the results of that study were encouraging, the CRDS technique requires high power and dry air or N_2 as carrier gas, potentially making remote deployment difficult.

There are several reasons that the dependence of instrument performance on water vapor concentration and delta value should be evaluated. First, in order to study the temporal and spatial dynamics of water vapor $\delta^{17}O$ values in field settings where different water vapor concentrations

and various delta values often occur, we need to evaluate the accuracy and precision of laser-based instruments in complex and volatile environments. Second, in previous observations, the trends in accuracy and precision of δ^2H and $\delta^{18}O$ measurements with increasing water vapor concentrations were different for different measuring techniques and instruments[10, 23-25], and even for the same sample for different isotopes[23, 25]. Third, the fundamental principle of LAS techniques (e.g., OA-ICOS and CRDS techniques) is measuring the mixing ratio of different isotopes. So in theory, "delta stretching", which results from the mismatch in delta value between the standard and sample (an important consideration in IRMS measurements), is not significant in LAS measurements[5]. However, in practice, the precision has been found to depend on delta values and the performance varied using different techniques and instruments[9, 26]. Therefore, based on the above reasons, in order to completely understand an instrument performance, the tests under different water vapor concentrations and delta values are required.

To our knowledge, no previous work has quantified how the accuracy and precision of vapor-phase $\delta^{17}O$ measurements depend on water vapor concentration, delta ranges and averaging-time. In order to utilize $\delta^{18}O$ and $\delta^{17}O$ concurrently for potential ^{17}O-exess calculation, δ^2H and $\delta^{18}O$ measurements should also be evaluated due to anticipated differences in instrument performance for the three isotopes. To fill these knowledge gaps, the objectives of this study are to: 1) assess the accuracy and precision of water vapor δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements and their concentration dependence, 2) assess the precision delta dependence of water vapor δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements, and 3) assess the precision averaging-time dependence of water vapor δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements. Knowing the effects of these three important factors (concentration[23, 24], delta range[9, 26] and averaging-time[10, 27]) on instrument performance will improve our capacity to interpret observations of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ from complex environments.

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EXPERIMENTAL

Instruments and water standards

In this study, we evaluated the accuracy and precision of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements obtained from a Triple Water Vapor Isotope Analyzer (T-WVIA-45-EP, Los Gatos Research Inc. (LGR), Mountain View, CA, USA), which is based on the OA-ICOS principle. Water vapor standards were introduced into the T-WVIA using a Water Vapor Isotope Standard Source (WVISS, LGR, Mountain View, CA, USA). The WVISS is a vaporization device that does not induce isotope fractionation in liquid waters, and was used to create water vapor of known isotopic composition under a range of concentrations. Thus, through the combined operation of the WVISS and T-WVIA instruments, we continually and simultaneously measured $^2H/^1H$, $^{18}O/^{16}O$, and $^{17}O/^{16}O$ ratios from liquid standards with known isotopic compositions. The water vapor isotopic ratios were expressed in δ-notation as a deviation from a reference ratio[23],

$$\delta = \frac{R}{R_{\text{VSMOW}}} - 1 \ , \tag{1}$$

where R is the atomic ratio (e.g., $^2H/H$, $^{18}O/^{16}O$ or $^{17}O/^{16}O$) of the sample, and R_{VSMOW} is the respective isotope ratio of the international standard Vienna Standard Mean Ocean Water (VSMOW).

In order to assess if the accuracy and precision of the T-WVIA depends on water vapor concentration, two IAEA water standards (GISP and SLAP2) were used to generate water vapor samples that spanned a range of vapor concentrations (5000, 10000, 15000, 20000 and 25000 ppm) through WVISS. To evaluate how precision of the observations depends on delta value, we used four commercially available working standards from LGR with a range of -154‰ to -52‰, -20‰ to -8‰ and -10‰ to -4‰ for δ^2H, $\delta^{18}O$ and $\delta^{17}O$, respectively. The analytical accuracy was defined

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as the difference between the measured and true value. The analytical precision was defined as the standard deviation of multiple measurements of the same sample.

The true δ^2H and $\delta^{18}O$ values of GISP[28] and SLAP2[29] were obtained from IAEA. Specifically, the δ^2H and $\delta^{18}O$ true values of GISP are -189.50±1.20‰ and -24.76±0.09‰, respectively. The δ^2H and $\delta^{18}O$ true values of SLAP2 are -427.50±0.30‰ and -55.50±0.02‰, respectively. Since IAEA has not yet assigned true $\delta^{17}O$ values of the two standards, we summarized values from published resources and used the mean values as the "true" values (Table 1). Accordingly, the $\delta^{17}O$ true value was assumed to be -12.90±0.24‰ and -29.18±0.43‰ for GISP and SLAP2, respectively.

[Table 1 here]

In order to evaluate if precision was sensitive to averaging time, one laboratory working standard was measured under a water vapor concentration of 15000 ppm continuously for 24 hours. We characterized the time-dependent stability of the instrument using Allan variance curves[23, 30], which were created from the continuous δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements. The Allan variance ($\sigma^2_A(\tau)$) measures the average temporal variability of a signal over a certain averaging time (τ)[27], and is defined as

$$\sigma_A^2(\tau) = \frac{1}{2n-1} \sum_{i=1}^{n} Y(\tau)_{i+1} - Y(\tau)_i)^2 \quad , \qquad (2)$$

where τ is the time-interval (e.g., 10 seconds, minute and hour), Y_i is the average value of the measurement in averaging interval i, and n is the total number of averaging intervals for a given τ.

Assessment procedures

For each measurement, the WVISS was preheated to 80 °C to ensure a complete vaporization of the liquid standard without inducing isotope fractionation between liquid and vapor phase. This process usually takes about two hours when the ambient temperature is around 25 °C. The T-WVIA was turned on about two hours before the measurements to ensure ideal measuring conditions with gas pressure and chamber temperature being around 40 Torr and 50 °C, respectively. To avoid condensation of water vapor between the WVISS and T-WVIA, the Teflon tubing connecting WVISS and T-WVIA was heated using pipe-heating cable. The data output frequency was set to 1 Hz.

In order to avoid memory effects from residual water, the WVISS nebulizer was purged for at least two minutes after each measurement. Next, the "stabilize" option of the device was turned on for two minutes to expel residual air inside the vaporizing chamber. Different vapor concentrations were created by adjusting the "dilution control" knob, which controls the flow rates of dry air and the liquid water sample. Each sample was run for about two minutes and the 1-Hz data were averaged over the two-minute interval. For the averaging-time assessment, results of continuous measurements were used.

RESULTS

The dependence of isotope measurement accuracy on water vapor concentrations

To assess how accuracy of the δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements depends on concentration, two international water standards (GISP and SLAP2) were repeatedly measured by T-WVIA under different water vapor concentrations ranging from 5000 ppm to 25000 ppm. All of the measured values and true values of the two standards under different water vapor concentrations are summarized in Table 2. In addition, the accuracy trends of the two standards under different water vapor concentrations are shown in Figure 1.

[Table 2 here]

[Figure 1 here]

The relationship between accuracy and water vapor concentration of δ^2H differed between the GISP and SLAP standards, though in general higher accuracy was observed when water vapor concentration was relatively low (5000-10000 ppm, Figure 1A). As water vapor concentration increased, the measured GISP δ^2H first increased to the maximum value of -188.50±0.05‰ at 15000 ppm, then decreased to the minimum value of -190.51±0.56‰ at 25000 ppm (Table 2). When considering analytical error of the IAEA reported values, these observations were within the range of the true value for all concentrations except the highest (e.g., 25000 ppm). The SLAP δ^2H tended to decrease as water vapor increased, with measured values ranging from -427.34±1.28‰ to -429.34±1.15‰ (Table 2). Overall, our measurements underestimated GISP δ^2H values by 0.32‰ and 1.01‰ at 5000 ppm and 25000 ppm, respectively, and overestimated GISP δ^2H by 0.10‰ to 1.00‰ under the other concentrations (Figure 1A). The highest accuracy for the GISP standard was 0.10‰ at 10000 ppm and the lowest accuracy was 1.01‰ at 25000 ppm. The highest accuracy for the SLAP2 δ^2H was observed at a vapor concentration of 5000 ppm, where the observations

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overestimated the true value by only 0.16‰. Under other concentrations, the observations underestimated the true value by 0.75‰ to 1.84‰, with the lowest accuracy observed at the highest concentration.

The relationship between the accuracy of the $\delta^{18}O$ measurements and water vapor concentration also differed between the GISP and SLAP2, though in both cases the highest accuracy was observed when water vapor concentration was 5000 ppm (Figure 1B). The maximum and minimum measured GISP $\delta^{18}O$ values were -23.90±0.01‰ at 15000 ppm and -24.84±0.02‰ at 5000 ppm, respectively (Table 2), and the range exceeded the reported IAEA true value range. The observed SLAP2 $\delta^{18}O$ generally decreased from -55.39±0.20‰ to -56.31±0.22‰ as water vapor concentration increased (Table 2). Overall, the observations underestimated the true GISP $\delta^{18}O$ value at 5000 ppm by 0.08‰ (the highest accuracy), but overestimated it by 0.37‰ to 0.86‰ under the higher concentrations (Figure 1B). The observations overestimated the true SLAP2 $\delta^{18}O$ value by around 0.10‰ at 5000 ppm (the highest accuracy), and then consistently underestimated the true value by 0.17‰ to 0.81‰ under higher vapor concentrations (Figure 1B).

With respect to $\delta^{17}O$, the accuracy trends were again inconsistent between the GISP and SLAP2, though for both standards the highest accuracy was observed at a water vapor concentration of 10000 ppm (Figure 1C). Notably, for both standards, the trend in $\delta^{17}O$ accuracy along the gradient of increasing water vapor concentration differed substantially from the observed trends for δ^2H and $\delta^{18}O$ (Figure 1). As water vapor concentration increased, the GISP $\delta^{17}O$ measurements first gradually decreased from a maximum value of -12.63±0.01‰ at 5000 ppm to a minimum value of -13.33±0.01‰ at 15000 ppm (Table 2), and then fluctuated under the higher concentrations. The SLAP2 $\delta^{17}O$ measurements declined slightly as vapor concentration increased from 5000 ppm to 15000 ppm, but then increased significantly from -29.00±0.01‰ to -28.56±0.12‰

under higher concentrations (Table 2). The observations overestimated the GISP $\delta^{17}O$ true value by 0.06‰ to 0.27‰ under lower concentrations (5000-10000 ppm), but underestimated the true value by 0.12‰ to 0.43‰ under higher concentrations. The highest accuracy was 0.06‰ at 10000 ppm and the lowest accuracy was 0.43‰ at 15000 ppm (Figure 1C). With respect to SLAP2, the observations overestimated the $\delta^{17}O$ true value across all concentration ranges. Interestingly, the accuracy of the SLAP2 $\delta^{17}O$ reduced from 0.18‰ to 0.62‰ as water vapor concentration increased (Figure 1C), which is a result that was not observed in the case of $\delta^{2}H$ and $\delta^{18}O$. SLAP2 $\delta^{17}O$ accuracy was the highest at 10000-15000 ppm, when it equaled 0.18‰, and the lowest at the highest concentration (25000 ppm), when it was 0.62‰ (Figure 1C).

The dependence of isotope measurement precision on water vapor concentrations

No monotonic trends for the precision of $\delta^{2}H$ observations for GISP and SLAP2 with the increasing water vapor concentrations were observed. However, for both standards, the measurement values were similar under higher concentrations (15000-25000 ppm) and the higher precision was observed under modest concentrations (10000-15000 ppm) (Figure 2). The $\delta^{2}H$ precision of GISP was highest at 10000 ppm, when it equaled 0.099‰, and was lowest at 20000 ppm, when it equaled 0.334‰. In the case of SLAP2, the $\delta^{2}H$ precision was lowest at 10000 ppm (0.430‰) and highest at 15000 ppm (0.136‰).

[Figure 2 here]

Similarly, the precision of $\delta^{18}O$ measurements did not change monotonically with increasing water vapor concentration for either standard (Figure 2B). However, for both standards, the highest precisions were observed when water vapor concentration was between 15000 ppm and 20000

ppm. The trends for SLAP2 $\delta^{18}O$ and δ^2H precision were similar, but not for GISP (Figure 2A and 2B). The precision of GISP $\delta^{18}O$ was low when water vapor concentration was low (5000-10000 ppm), was highest when concentration was 20000 ppm (0.028‰), and was lowest when concentration reached 25000 ppm (0.073‰). The lowest precision of SLAP2 of 0.080‰ was also observed at 25000 ppm, but the highest precision of 0.009‰ was observed at 15000 ppm.

With respect to $\delta^{17}O$, the trends in precision with increasing water vapor concentration were indistinguishable between the two standards. The highest observed precision for both standards (0.022‰ and 0.025‰ for GISP and SLAP2, respectively) was observed at the same concentration (20000 ppm). The precision of both standards gradually increased with increasing water vapor concentration when concentration was low (5000-20000 ppm) and then worsened at the highest concentration (25000 ppm). The lowest precision for both standards was observed at 25000 ppm, when precision was 0.046‰ for GISP and 0.054‰ for SLAP2. Importantly, regardless of the standards used, precisions were not significantly different across all concentration ranges.

The dependence of precision on the range of delta values

To characterize the instrument precision under different delta values, we conducted analyses using four working standards with a range of delta values (ranging from -154‰ to -52‰ for δ^2H, -20‰ to -8‰ for $\delta^{18}O$ and -10‰ to -4‰ for $\delta^{17}O$). As described above, GISP and SLAP2 showed the lowest accuracy and precision at the highest water vapor concentration (25000 ppm). Therefore, the highest concentration was removed when the working standards were evaluated under different concentrations (5000-20000 ppm). Figure 3 depicts the precision dependence of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ on the delta values.

[Figure 3 here]

For δ^2H, the higher precision values were always observed under the mid-range delta values (-124‰ to -95‰) regardless of the concentrations (Figure 3A). Furthermore, the relationship between precision and delta values was similar for all concentrations except 20000 ppm (Figure 3A). When concentration was < 20000 ppm, as the delta value increased, precision improved (from 0.143‰-0.384‰ to 0.070-0.167‰) as delta value increased from -154.4‰ to -96.5‰, but then worsened at the highest delta value. Precision was generally worse when water vapor concentration was 20000 ppm for all delta values, ranging from 0.250‰ to 0.412‰.

Similarly, the precision of the $\delta^{18}O$ measurements was higher at mid-range delta values, and was similar provided water vapor concentration was < 20000 ppm (Figure 3B). The precision variation was small for all the concentrations, and the values were very similar when the delta value was greater than -16.5‰, though some differences were noted when delta value was low (Figure 3B). In addition, Figure 3A and Figure 3B illustrate that the $\delta^{18}O$ precision was higher than δ^2H. When concentration was < 20000 ppm, the precision improved from 0.052‰-0.105‰ to 0.014‰-0.038‰ as delta value increased from -19.1‰ to -15.3‰, but worsened when delta value was > -12.6‰. When water vapor concentration was 20000 ppm, the precision improved from 0.081‰ to 0.046‰ as delta value increased from -21.1‰ to -12.5‰, and then fluctuated as delta value increased further.

The precisions of the $\delta^{17}O$ measurements were similar (~0.03‰) across all delta values (-11.8‰ to -5.2‰) when water vapor concentration was modest (10000-15000 ppm) (Figure 3C). The precisions of the $\delta^{17}O$ measurements were lower with different trends at 5000 and 20000 ppm. When concentration was 5000 ppm, the precision continuously improved with increasing delta value from the lowest precision of 0.075‰ to the highest precision of 0.045‰. At 20000 ppm, the

precision of the $\delta^{17}O$ measurements slightly worsened with increasing delta value to the lowest precision of 0.062‰ then improved to the highest precision of 0.039‰, as the delta value increased.

The dependence of precision on the averaging times

The Allan deviation (i.e., the square root of the Allan variance) curves were created based on the time-series of the 24 h continuous observations (Supplementary Fig. S1, see Supporting Information). The Allan deviation curves revealed similar patterns in the dependence of precision on averaging time for the three isotopes (Figure 4). The precision first improved with increasing averaging times and then worsened under longer averaging times. The optimum averaging time occurred at 260 s, 210 s and 160 s for δ^2H, $\delta^{18}O$ and $\delta^{17}O$, respectively. The corresponding precision was 0.050‰, 0.016‰ and 0.023‰ for δ^2H, $\delta^{18}O$ and $\delta^{17}O$, respectively.

[Figure 4 here]

DISCUSSION

The accuracy dependence on water vapor concentrations

An important aspect of vapor isotope measurements is the instrument response to changing water vapor concentrations[23, 24]. In our study, the accuracy of the δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements did not change monotonically as water vapor concentrations increased from 5000 ppm to 25000 ppm. The relationship between accuracy and concentration was more similar for δ^2H and $\delta^{18}O$ when compared to $\delta^{17}O$, but for all three isotopes the accuracy was generally highest when water vapor concentration was low (Figure 1).

Several previous studies[23-25] relied on WVIA instruments to evaluate the relationship between water vapor concentration and the accuracy of δ^2H observations. The results of this study tend to agree with those reported by Rambo et al.[25] (model WVIA-24, water δ^2H true value was -121.0±0.5‰), in which the measured values underestimated the true value at low concentration (7640 ppm) and overestimated the true value at high concentration (16980 ppm). On the other hand, results from Kurita et al.[24] (model DLT-100, version 908-0004, δ^2H true value was -78‰) reported trends similar to our SLAP2 measurements (δ^2H measured values slightly decreased from 5000 ppm to 10000 ppm). In addition, Sturm and Knohl[23] (model DLT-100, version March 2009, δ^2H true values ranged from -190‰ to -80‰) reported a unimodal relationship between measured δ^2H values and concentrations, which is different from our results as concentration increased from 5000 ppm to 25000 ppm. Our reported trend of decreasing SLAP2 $\delta^{18}O$ with increasing concentration (10000-25000 ppm) is similar to that reported by Strum & Knohl[23]. The SLAP2 $\delta^{18}O$ accuracy trend is also consistent with that reported by Rambo et al.[25], in which the measured values overestimated the true values at low concentration (7640 ppm) and underestimated the true values at high concentration (16980 ppm). To our best knowledge, there is no assessment on the vapor concentration dependence for $\delta^{17}O$ accuracy, so we cannot compare our observed trend with others. Based on these earlier reports and our own assessment, it appears that the measurement accuracy does depend on concentration but no clear monotonic trends emerged. The δ^2H accuracy (0.10‰-1.84‰) of this assessment is comparable to what was reported by Steig et al.[10] (0.52‰) using the CRDS technique. The $\delta^{18}O$ and $\delta^{17}O$ accuracy (0.08‰-0.86‰ and 0.06‰-0.62‰) across all concentration ranges is also comparable to that measured by Schoenemann et al.[22] (0.75‰-1.63‰; 0.17‰-0.36‰) using a conventional IRMS technique.

The precision dependence on water vapor concentrations

Similar to the trends for accuracy, no monotonic trend in precision with increasing concentration was observed, and patterns differed between δ^2H, $\delta^{18}O$ and $\delta^{17}O$ measurements. These results are in contrast with those from Sturm and Knohl[23], which reported similar relationships between precision and concentration for δ^2H and $\delta^{18}O$. In contrast to the results for accuracy, the precisions values had small variations and the trends were similar between GISP and SLAP2, especially for $\delta^{18}O$ and $\delta^{17}O$, although our measurement precisions of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ depend on the water vapor concentrations.

The δ^2H and $\delta^{18}O$ precision (0.099‰-0.430‰ and 0.009‰-0.080‰) of both standards observed here are within the precision range or better than that reported by Sturm and Knohl[23] using a WVIA instrument (model DLT-100, version March 2009), in which the reported precision was 0-0.47‰ for δ^2H and 0-0.27‰ for $\delta^{18}O$ (4500-16000 ppm). However, that study reported a decline in precision with increasing concentration, in contrast to the results presented here.

The precision of δ^2H and $\delta^{18}O$ reported here are much better than the previous results using a WVIA instrument [25] (model WVIA-24, the precision was ±3.0‰ for δ^2H and ±0.3‰ for $\delta^{18}O$ from 6000 ppm to 22000 ppm) and LWIA[31] instruments (model DLT-100, version 908-0008 and 908-0008-2000). In those previous studies, precision ranged from ±0.56‰ to ±1.80‰ and ±0.10‰ to ±0.27‰ for δ^2H and $\delta^{18}O$, respectively. As reported by Berman et al.[9], the GISP $\delta^{18}O$ and $\delta^{17}O$ precision was ±0.07‰ and ±0.05‰ when measured by a TIWA-45EP instrument, which is close to the results reported here across all concentrations (0.009‰-0.080‰ and 0.022‰-0.054‰ for $\delta^{18}O$ and $\delta^{17}O$, respectively). The precision estimates reported here are also comparable to what was reported by Steig et al.[10] using the CRDS technique (the precision was < 0.2‰, < 0.03‰ and

< 0.02‰ for δ^2H, δ^{18}O and δ^{17}O, respectively). Therefore, the precisions obtained with the T-WVIA instrument are comparable to previous results based on OA-ICOS and CRDS techniques.

In order to avoid drawing conclusions just based on the relatively depleted values for all three isotopes (GISP and SLAP2), we also conducted additional testing for the relationship between precision and concentrations using four working standards from LGR. Similar to the results based on GISP and SLAP2 measurements, the working standard results indicated their precision trends were also different with increasing water vapor concentrations, and the higher precision was observed at 15000 ppm. Therefore, taking into account the results of all standards (both the two international standards and four working standards), the precisions of all three isotopes (δ^2H, δ^{18}O and δ^{17}O) depend on concentrations, and in general, the higher precision often appeared at 15000 ppm.

The dependence of precision on the range of delta values

The relationship between precision and delta value varied with water vapor concentration and across the different isotopes. The observed δ^2H and δ^{18}O precision (0.070‰-0.412‰ and 0.014‰-0.105‰ for δ^2H and δ^{18}O, respectively) reported here is better than that reported in previous study (about 0.5‰-0.7‰ and 0.20‰-0.26‰ for δ^2H and δ^{18}O, respectively) using a WVIA[26] instrument (model DLT-100, version March 2011) with water vapor concentration of 18000 ppm and similar delta values. In addition, our δ^{18}O and δ^{17}O precision (0.014‰-0.105‰ and 0.024‰-0.075‰ for δ^{18}O and δ^{17}O, respectively) is comparable to that reported by Berman et al.,[9] who used a TIWA-45EP instrument (delta values ranging from -24.7‰ to -2.25‰ and -13.1‰ to -1.2‰ for δ^{18}O and δ^{17}O, respectively) in which the precision ranged from 0.05‰ to 0.15‰ and 0.04‰ to 0.10‰ for δ^{18}O and δ^{17}O, respectively. Therefore, precision of the measurements reported here

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are comparable to, or better than those reported in previous studies relying on WVIA and TIWA-45EP instruments.

The dependence of precision on the averaging times

The time-dependent stability of the instrument is an important characteristic. The highest precision of δ^2H and $\delta^{18}O$ (0.05‰ and 0.016‰) reported here is comparable with previous results using a WVIA[23] instrument at 14000 ppm (0.04‰; 0.03‰) as well as L2130-i-C (0.04‰; 0.03‰) and L2140-i (0.07‰; 0.015‰) instruments (Picarro Inc. water isotope analyzers) based on the CRDS technique[10]. In addition, the highest $\delta^{17}O$ precision (0.023‰) in the present study is better than that measured by L2130-i-C instrument (0.03‰)[10], though it is worse than measured by L2140-i (0.015‰)[10] and TIWA-45EP (0.01‰)[9] instruments. Therefore, the performance of our testing instrument also depends on averaging time, but the precision is much less sensitive to averaging time compared with concentration and delta range effects.

The practical considerations and limitations of the current calibration

The study results suggest that the accuracy and precision of the T-WVIA instrument depend on water vapor concentration, delta range and averaging-time. The accuracy was relatively high at 10000 ppm and relatively low at 25000 ppm for all isotopes across the concentration range. Moreover, similar to results reported by Sturm and Knohl[23], under vapor concentrations lower than 5000 ppm and higher than 25000 ppm, the δ^2H and $\delta^{18}O$ measured values were relatively unstable. Here, a similar trend for $\delta^{17}O$ was also observed. Therefore the measurements should be taken with caution under these concentrations. Overall, the precision also depended on the delta values for all three isotopes. However, considering the effects of both water vapor concentrations and delta dependence, the concentration has a much stronger effect, and the instrument precision

is the best under a concentration of 15000 ppm. Informed by our testing results, there are some practical considerations, which will help achieve higher accuracy and precision. Although the concentration has a stronger influence on the instrument performance compared with the influence of the other two factors, all of the factors should be considered in order to obtain the best accuracy and precision. Based on our observations, the instrument performance is not affected by the room temperature variations due to the internal temperature control of the instrument. However, before calibration or liquid water measurement, the WVISS should be preheated to 80 °C to ensure a complete vaporization and the T-WVIA should be turned on about two hours before the measurement to ensure ideal measuring conditions (gas pressure, ~40 Torr and chamber temperature, ~50 °C). Meanwhile, the Teflon tubing connecting WVISS and T-WVIA should be heated using pipe-heating cable to avoid condensation of water vapor. If T-WVIA and WVISS is used for liquid water measurements and not merely for calibration, the instrument should be used under moderate vapor concentrations (i.e., between 10000 ppm and 15000 ppm) to obtain the high accuracy and precision. In this situation, the accuracy of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ should be better than 1.26‰, 0.86‰, and 0.43‰, respectively, and the precision could reach up to 0.099‰, 0.009‰ and 0.027‰, respectively. Also the standards should have similar isotopic compositions to the samples. Since the precision and accuracy of the T-WVIA technique compare favorable with those previously reported for IRMS or LAS techniques, T-WVIA measurements show promise for their use in investigating various ecohydrological processes, including transpiration isotope enrichment and the source of rainfall and non-rainfall waters.

One limitation of our calibration method is the difficulty of distinguishing the error source between the testing instrument and the calibration unit. This is a standard issue for most calibration studies relying on a range of calibration units[24-27]. The issue could be reduced by comparing

multiple calibration units with different operating principles. Another limitation of evaluating the instrument performance is the source of the $\delta^{17}O$ true values of the two international standards, which were not assigned by IAEA. This might affect the absolute accuracy assessment, but should not affect the trends describing how accuracy and precision depend on concentration, delta range and averaging time. In addition, the true values of the four working standards from LGR have not been widely recognized as "true values." Therefore, in order to avoid biases in the assessment of how accuracy depends on the delta value, we only used them to assess how precision depends on delta value.

CONCLUSIONS

In this study, we evaluated, for the first time, the vapor $\delta^{17}O$ performance of a commercially available Triple Water Vapor Isotope Analyzer (T-WVIA-45-EP) in terms of accuracy and precision and in relation to water vapor concentrations, delta range and averaging-time response. We found that the accuracy ranged from 0.10‰ to 1.84‰, 0.08‰ to 0.86‰ and 0.06‰ to 0.62‰ for $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$, respectively, across the various water vapor concentrations. These results comparable to those reported using CRDS[10] and conventional IRMS[22] techniques. The precision across all concentrations ranged from 0.099‰ to 0.430‰, 0.009‰ to 0.080‰ and 0.022‰ to 0.054‰ for $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$, respectively, which is comparable to previous liquid water results based on OA-ICOS[9, 23, 25, 31] and CRDS[10] techniques. In addition, the highest accuracy and precision was generally observed at moderate water vapor concentrations of 10000-15000 ppm. The precision across all delta values ranged from 0.070‰ to 0.412‰, 0.014‰ to 0.105‰, 0.024‰ to 0.075‰ for $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$, respectively. These results are comparable, or represent an improvement to, results from a previous study using WVIA[26] and TIWA-45EP[9] instruments. The highest time-dependent precision was 0.050‰, 0.016‰ and 0.023‰ for $\delta^{2}H$, $\delta^{18}O$ and $\delta^{17}O$,

respectively, which are comparable with that measured by the WVIA[23] instrument and CRDS[10] technique. In conclusion, the accuracy and precision of the T-WVIA instrument depends on all three important factors (vapor concentration, delta range and averaging-time), but are more sensitive to water vapor concentration than delta range, and largely insensitive to averaging-time.

Clearly the current evaluation does not close discussion and assessments for vapor $\delta^{17}O$ measurements. Because laser-based $\delta^{17}O$ measurements have only been commercially available for a couple of years, there remains a need for more intensive calibrations and comparisons under a wider range of environmental conditions, and even for more individual instruments. More importantly, we need to continually evaluate the $\delta^{17}O$ measurements, and in particular there is a need to revisit the dependent of accuracy on water vapor concentration when more recognized international standards of $\delta^{17}O$ become available. Based on the current assessments, the T-WVIA can simultaneously and continuously measure δ^2H, $\delta^{18}O$ and $\delta^{17}O$ values in water vapor with high precision and accuracy to conduct long-term and remote research, opening a new prospect for better understanding ecological and hydrological processes.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article at the publisher's website.

Table 1. Summary of measured $\delta^{18}O$ and $\delta^{17}O$ values (average ± stdev (1σ)) of GISP and SLAP2 (‰) from different studies.

References	Method	GISP		SLAP/*SLAP2*	
		$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$
Li et al.[32]	BrF5	-24.83±0.10	-13.14±0.10	-55.82±0.08	-29.90±0.16
Jabeen and Kusakabe[33]	BrF5	-23.94±0.10	-12.59±0.10	-53.54±0.17	-28.58±0.18
Barkan and Luz[21]	COF3	-24.73±0.02	-13.12±0.01	-55.11±0.12	-29.48±0.07
Kusakabe and Matsuhisa[34]	BrF5	-24.41±0.07	-12.91±0.07	-54.65±0.06	-29.21±0.07
Schoenemann et al.[22]	COF3	-24.01±0.27	-12.73±0.18	-53.87±0.35	-28.82±0.22
Lin et al.[35]	BrF5			-54.38±0.12	-29.06±0.07
Lin et al.[35]	BrF5			*-54.59±0.25*	*-29.19±0.14*
Average ± Std		-24.38±0.41	-12.90±0.24	-54.57±0.76	-29.18±0.43
IAEA[28]		-24.76±0.09			
IAEA[29]				*-55.50±0.02*	

Note: The values in italics are SLAP2 isotopic values.

Table 2. Measured values and true values (average ± stdev (1σ)) of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ for GISP and SLAP2 (‰) under different water vapor concentrations. Ensemble averages were created from three measurements.

|	H₂O	δ^2H		$\delta^{18}O$		$\delta^{17}O$	
	(ppm)	Measured values	True values	Measured values	True values	Measured values	True values
GISP	5000	-189.82±0.23		-24.84±0.02		-12.63±0.01	
	10000	-189.40±0.06		-24.39±0.01		-12.84±0.02	
	15000	-188.50±0.05	-189.5±1.2	-23.90±0.01	-24.76±0.09	-13.33±0.01	-12.90±0.24
	20000	-189.07±0.04		-23.99±0.02		-13.02±0.01	
	25000	-190.51±0.56		-24.29±0.12		-13.16±0.07	
SLAP2	5000	-427.34±1.28		-55.40±0.09		-28.95±0.07	
	10000	-428.25±0.71		-55.39±0.20		-29.00±0.12	
	15000	-428.76±0.47	-427.5±0.3	-55.67±0.02	-55.50±0.02	-29.00±0.01	-29.18±0.43
	20000	-428.32±0.27		-55.67±0.04		-28.67±0.03	
	25000	-429.34±1.15		-56.31±0.22		-28.56±0.12	
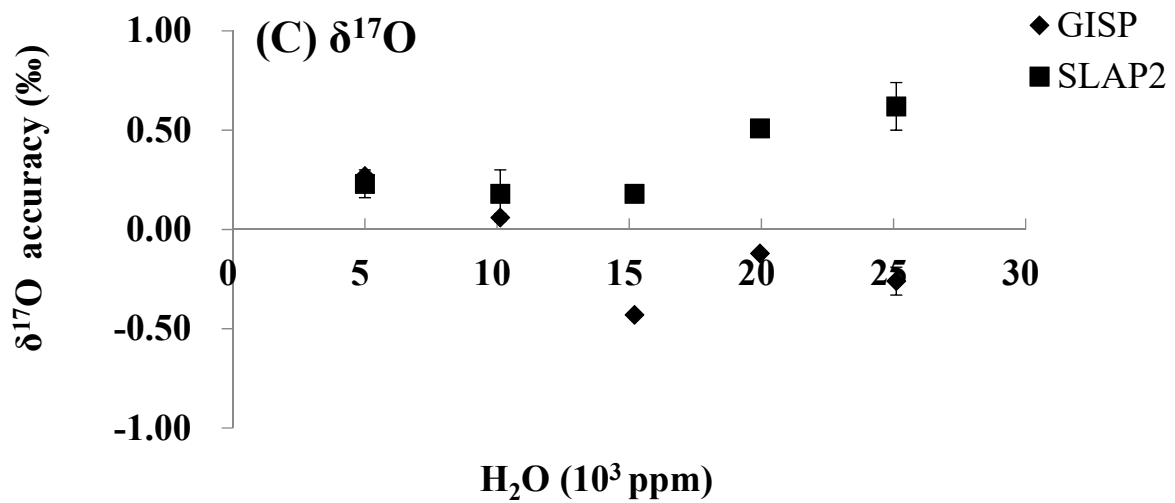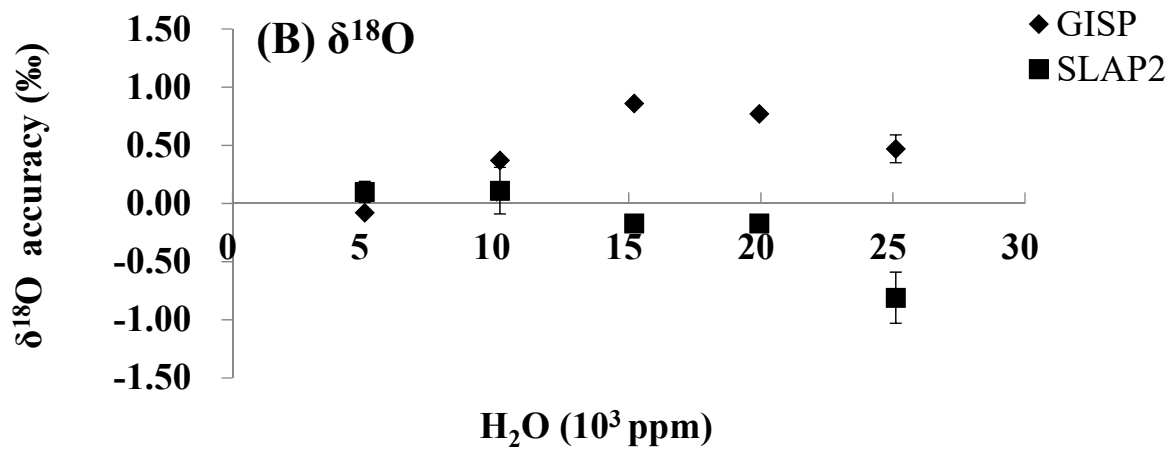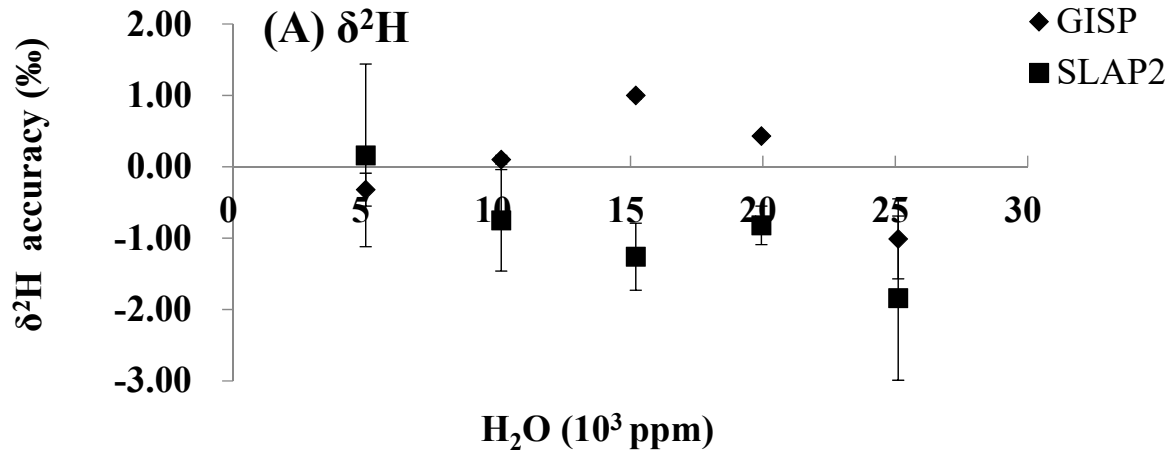
Figure 1. The accuracy dependence of δ^2H (A), $\delta^{18}O$ (B) and $\delta^{17}O$ (C) on water vapor concentrations for GISP and SLAP2 (‰). Each data point represents an average of nine repeated experiments. Error bars indicate one standard deviation (1σ) of the average (n=9).

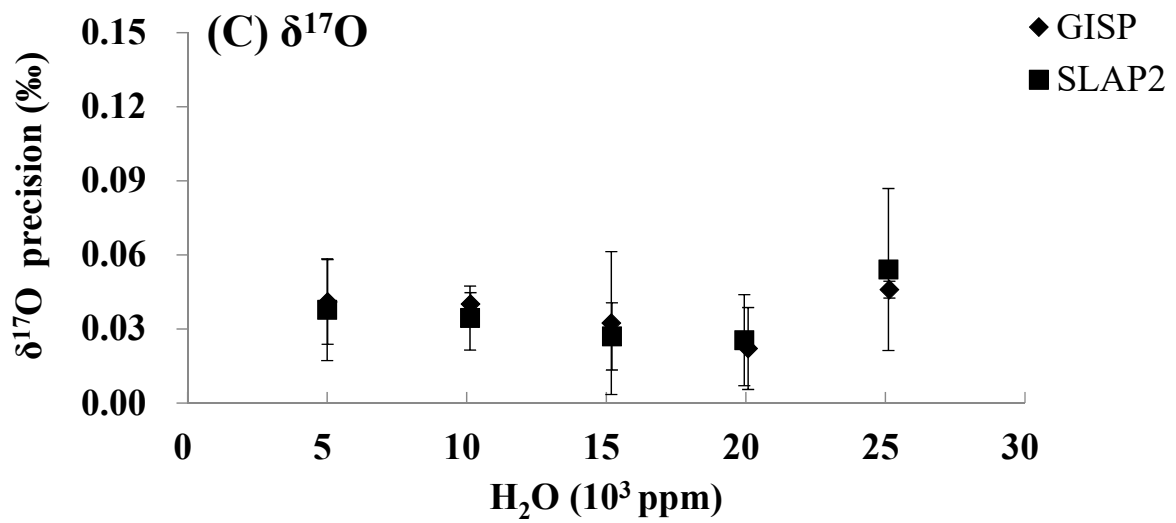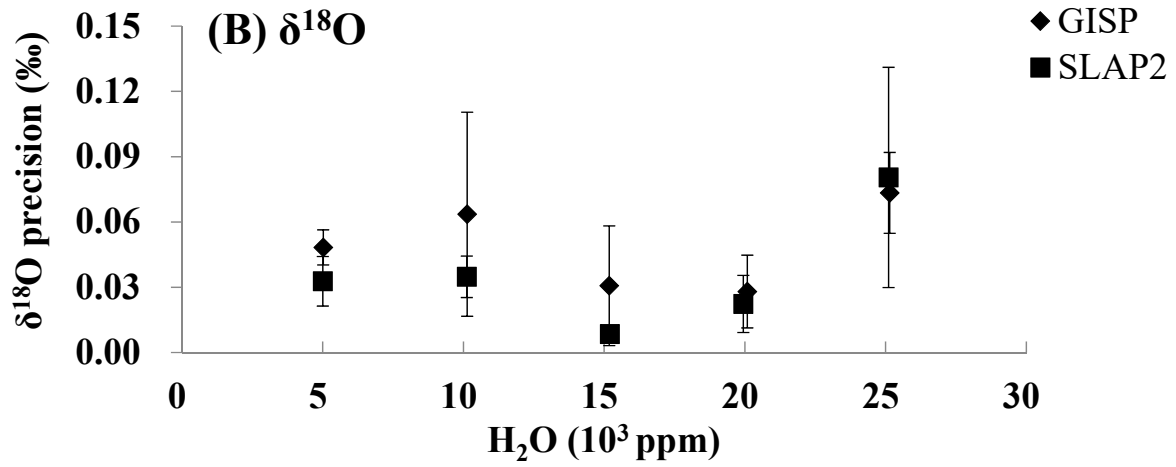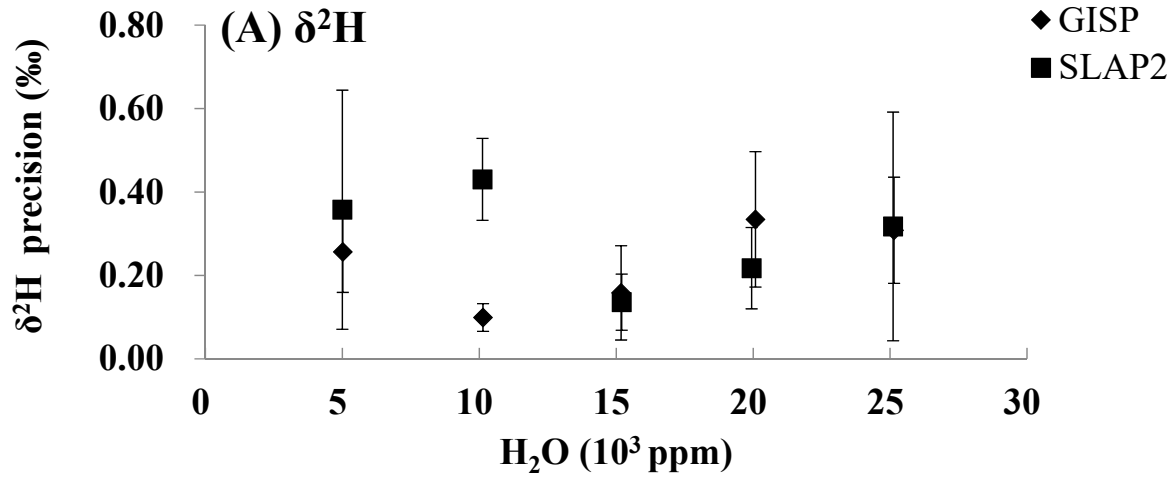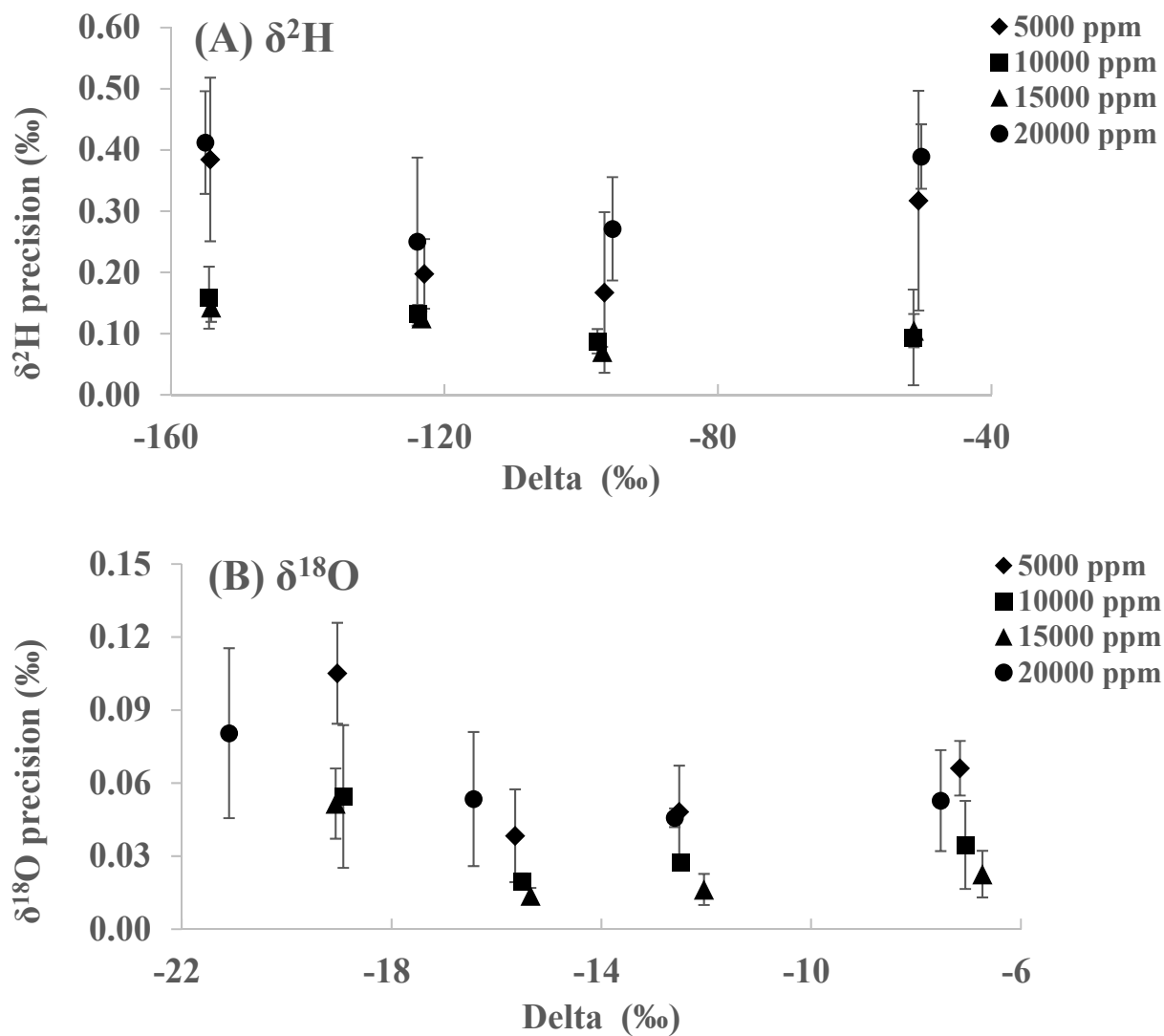Figure 2. The precision dependence of δ^2H (A), $\delta^{18}O$ (B) and $\delta^{17}O$ (C) on water vapor concentrations for GISP and SLAP2 (‰). Each data point represents an average of three repeated experiments. Error bars indicate one standard deviation (1σ) of the average (n=3).

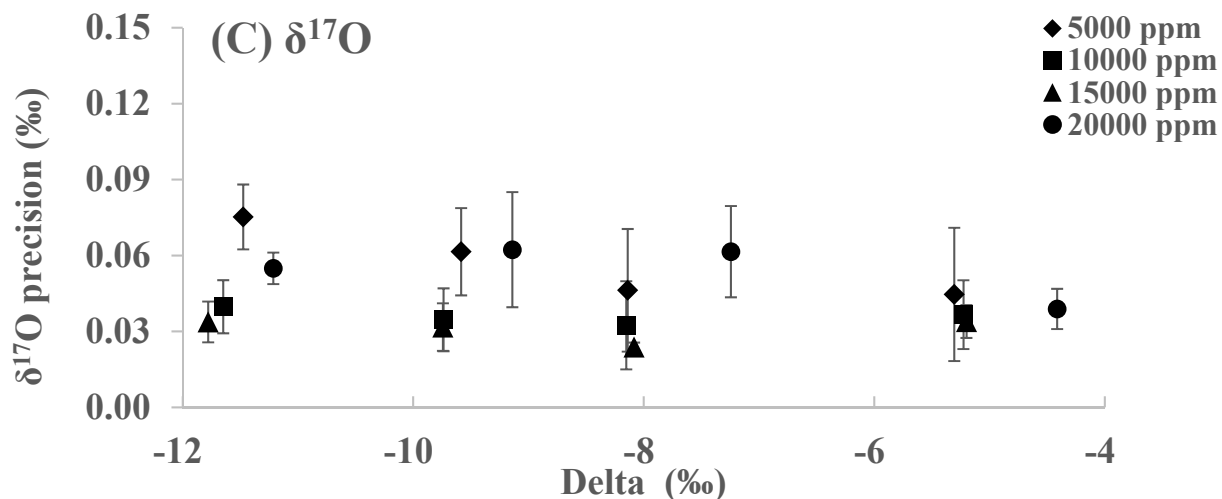Figure 3. The precision dependence of δ^2H (A), $\delta^{18}O$ (B) and $\delta^{17}O$ (C) on the delta ranges (‰). Each data point represents an average of three repeated experiments. Error bars indicate one standard deviation (1σ) of the average (n=3). The δ^2H true values of four working standards from LGR are -154.00‰, -123.70‰, -97.30‰ and -51.60‰, respectively. The $\delta^{18}O$ true values are -19.49‰, -8.56‰, -13.39‰ and -7.94‰, respectively. The $\delta^{17}O$ true values are -10.30‰, -16.24‰, -7.06‰ and -4.17‰, respectively.

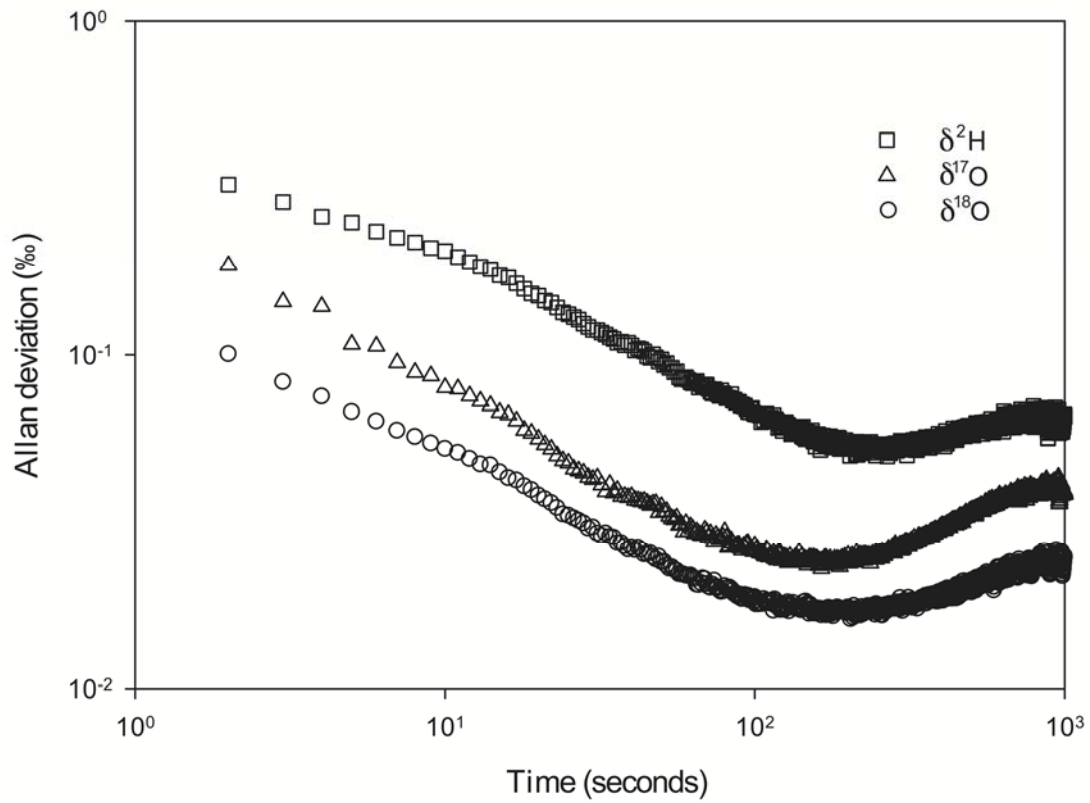Figure 4. Allan deviation curves of δ^2H (square signs), $\delta^{18}O$ (circles) and $\delta^{17}O$ (triangle) as a measurement of time-dependent stability under 15000 ppm water vapor concentration.