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# Realtime Stable Isotope Monitoring of Natural Waters by Parallel-Flow Laser Spectroscopy

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**S** Supporting Information

**ABSTRACT:** A parallel-flow  $\text{H}_2\text{O}(\text{liquid})\text{--H}_2\text{O}(\text{vapor})$  equilibration and laser spectroscopy method provides a new way to monitor the hydrogen and oxygen stable isotopic composition of water from rivers or lakes or in hydrologic tracer tests in real time. Two custom-built equilibrator devices and one commercial membrane device were tested to determine if they could be used to convert natural water samples (lakes, rivers, groundwater) to a  $\text{H}_2\text{O}$  gas phase for continuous online  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotopic analysis by laser spectroscopy. Both the commercial minimodule device and the marble-filled equilibrator produced water vapor in isotopic equilibrium with the flowing liquid water, suggesting that unattended field measurement using these devices is possible. Oxygen isotope disequilibrium was indicated using the minimodule device at low temperatures.

The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotopic composition of natural waters are important tracers of global hydrological processes.<sup>1</sup> The hydrogen and oxygen stable isotopic compositions of water are frequently used in the study of climatic processes and in surface and groundwater resource evaluations.<sup>2–4</sup> For over 55 years, water stable isotopic assays have been conducted on single (1–25 mL) water samples collected in the field and which are returned to the laboratory for subsequent H and O isotope analyses. Hydrogen and oxygen stable isotopic compositions are usually measured by  $\text{CO}_2$ - or  $\text{H}_2$ -water equilibration, thermochemical reduction to  $\text{H}_2$  by reaction with a hot reductant, or pyrolysis to  $\text{H}_2$  and  $\text{CO}$ , by either dual-inlet or continuous-flow isotope ratio mass spectrometry.<sup>5–9</sup> More recently, laser-based spectrophotometers have enabled liquid, vapor, and pore water isotope analyses directly on the water molecule at sufficient precisions for routine hydrologic applications, with no need for chemical conversions or sample preparation other than complete  $\text{H}_2\text{O}$  vaporization.<sup>10–14</sup> One drawback of these laser spectrophotometers is that they can produce inaccurate or incorrect measurements when dissolved organic carbon (DOC) is present.<sup>15</sup> Laser-based instrumentation is sufficiently portable and inexpensive so that field applications are increasingly feasible.<sup>12,16</sup> However, recent field implementations are still limited by the necessity to do individual water analyses by evaporating liquid water into the cavity using a sampling device.<sup>12,16</sup> While such implementations are field portable, an operator is still required to service the sample input device.

Here, we demonstrate a new method that uses a parallel-flow equilibrator device to isotopically equilibrate flowing liquid water samples with  $\text{H}_2\text{O}$  vapor, followed by wavelength-scanned cavity ring-down laser spectroscopy (WS-CRD) to enable continuous, real-time measurement of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of the water stream. While all of our testing was done in the laboratory, it is our intent that this device will be used in the field to enable continuous hydrogen and oxygen isotopic monitoring of rivers, lakes, groundwater, or pumped water samples at sufficient precision for hydrological research.

Obtaining real-time stable isotopic results are an especially key advantage for surface water and groundwater hydrograph separation tests where the highest possible resolution time series of analyses are needed,<sup>17,18</sup> because it may be difficult to predict ahead of time when and how many samples are required. Real-time isotopic measurement may help to eliminate the need for individual sample vial collections, client analysis wait times, and the comparatively high cost of conventional isotope ratio mass spectrometry (IRMS)-based assays.

## MATERIALS AND METHODS

The basic principles of the  $\text{H}_2\text{O}(\text{liquid})\text{--H}_2\text{O}(\text{vapor})$  pore water equilibration method<sup>14</sup> can be extended to real-time analyses of water through the use of an equilibrator device coupled to a commercial water isotope laser analyzer. There are three linked components: (1) a flowing sample or water source (lake, river, ground, or test water) connected to (2) an  $\text{H}_2\text{O}_\text{v}\text{--H}_2\text{O}_\text{l}$  equilibrator device to equilibrate liquid water with  $\text{H}_2\text{O}$  vapor, connected to (3) a  $\text{H}_2\text{O}$  isotope laser analyzer for real-time H and O isotopic analysis of the water vapor (Figure 1).

With this setup, water was pumped through the equilibrator at a fixed flow rate between 0.2 and 3 L per minute, and the temperature was manually recorded at the inlet with a thermometer. The equilibrator inlet carrier gas was ambient air, connected with stainless steel or Teflon tubing through a polycarbonate commercial laboratory gas drying unit (Drierite NP-303) filled with self-indicating Drierite (4 mesh) to reduce the  $\text{H}_2\text{O}$  volume fraction of the air entering the equilibrator to <100 ppmV  $\text{H}_2\text{O}$ .

The analyzer gas inlet was connected to the equilibrator gas outlet using 1 to 2 m of 1/8 in. copper tubing. Teflon or metal tubing was used for all gas phase connections since many plastics are permeable to  $\text{H}_2\text{O}$  vapor. The carrier gas flow rate through the equilibrator device was controlled by the laser analyzer

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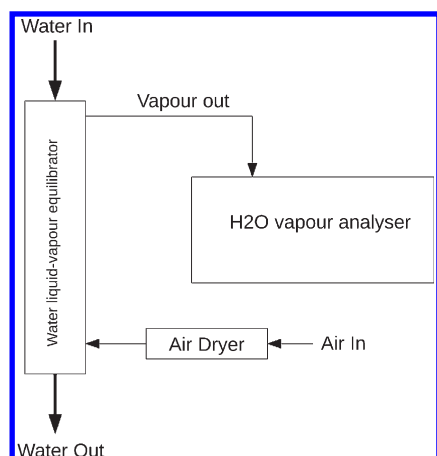


Figure 1. Use of the vapor–liquid equilibrator.

vacuum pump, which drew sample gas through the equilibrator and dryer at a precise and fixed rate of 30 mL/min. The WS-CRD flow rate closely matched the optimal H<sub>2</sub>O removal efficiency of the inlet gas drying unit (2.0 L/h; www.drierite.com). The volume fraction of water of the analysis gas leaving the equilibrator was water temperature dependent, ranging between about 8000 and 7000 ppmV H<sub>2</sub>O (see Results and Discussion). This range covered an appropriate working concentration range for the water isotope laser analyzer specifications.

For most laboratory-based tests, we used a closed system recirculating water chiller (Neslab RTE-210) to flow temperature controlled ( $\pm 0.1$  °C) tap water through the equilibrator test setup. The stable isotopic composition of the water used in all of the experiments was measured independently using a Los Gatos Model 908-0008 liquid water isotope analyzer as described previously.<sup>13</sup>

**Water Liquid–Vapor Equilibrators.** Three equilibrator devices were tested. Two are in-house custom-built liquid–vapor equilibrators based on the “showerhead” design (Figure 2), while the third was a Membrana Minimodule (Model G-542; www.membrana.com), a device normally used to degas N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> from industrial production waters. Similar designs of these showerhead equilibrators are commonly used for measurement of dissolved gases,<sup>19</sup> but we anticipated that they would provide water vapor in isotopic equilibrium with liquid water. Both were constructed from 3 1/2 in. (89 mm) aluminum pipe with O-ring aluminum end-caps (Figure 2). Aluminum was used for the prototype because it is cheaper and easier to machine than stainless steel which would be preferred for the final design. In order to attain a high water surface area to volume ratio, two different interior designs were tried. The first was to fill the equilibrator with common marbles.<sup>20</sup> The second equilibrator was designed primarily for low water flow applications and used a drip screen, whereby the water input was directed onto a coarse aluminum screen so that water droplets descend evenly through the equilibrator. In both cases, the equilibrators are airtight and designed such that the air flow and water flow move in opposite directions to maximize the water–air interaction. The marble-filled equilibrator utilizes a commercial flow-limiting showerhead, which limits the water flow to a maximum of 10 L/min. Both equilibrators were mechanically designed for easy disassembly and cleaning, so that they may ultimately be used in the field and may be used with clear to turbid waters.

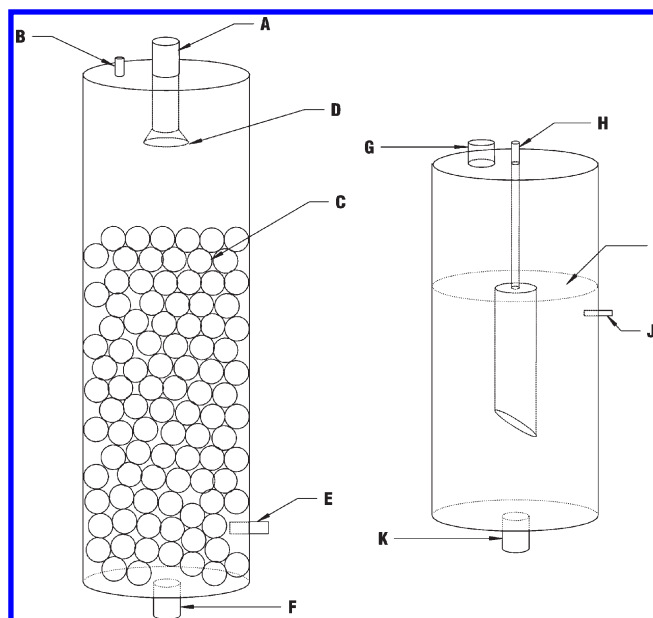


Figure 2. Marble filled equilibrator (left) and the drip-screen equilibrator (right): (A) water inlet; (B) vapor outlet; (C) marbles; (D) constant-flow showerhead; (E) air inlet; (F) water outlet; (G) water inlet; (H) vapor outlet; (I) drip-screen; (J) dry air inlet; (K) water outlet.

While not specified by the manufacturer for H<sub>2</sub>O, our early tests revealed the minimodule produced comparable concentrations of water vapor from liquid water, suggesting that water vapor was in equilibrium with the liquid water (see Results and Discussion). This device contains 7400 Celgard microporous XS0 hollow polytetrafluoroethylene (PTFE) fibers that are connected to the shell-side (gas side) of the parallel device to create a large surface area for H<sub>2</sub>O(liquid) and H<sub>2</sub>O(vapor) to exchange molecules but not permit liquid water to penetrate into the gas side of the device. Although the efficiency of transfer of water vapor through the membrane is not known for this device, the gas transfer efficiency is close to 100% and near instantaneous.<sup>21,22</sup>

**Laser Spectroscopy.** For all H<sub>2</sub>O vapor stable isotopic analyses, we used a Picarro L1115-i isotopic water vapor analyzer based on wavelength-scanned cavity ring down spectroscopy (WS-CRDS; www.picarro.com). This instrument continuously measures H<sub>2</sub>O concentrations (as volume fraction of water in ppm) and the H<sub>2</sub>O isotopic composition of water vapor at 10 s integration intervals. Measured isotopologues of H<sub>2</sub>O were converted to familiar  $\delta$  values within the control software, corrected by internal algorithms for H<sub>2</sub>O amount dependencies.<sup>12,13</sup> All raw data (ppmV H<sub>2</sub>O,  $\delta$ D,  $\delta^{18}$ O, instrument operational parameters) were recorded to ASCII files by onboard software.

Because laser-based vapor isotope measurements do not make use of a calibrated reference isotopic gas and may experience some temporal instrumental drift,<sup>12,13</sup> all our lab tests were conducted using isotopically known waters or by collecting individual water samples during the tests that were analyzed offline for comparison and calibration using established methods.<sup>13</sup> Furthermore, for all laboratory testing, the covariate combinations (temperature, flow) were tested for isotopic stability over sample acquisition periods of 2–9 h, which allowed us to gain an estimate of specific instrumental drift that might occur over relevant field sampling timeframes. We recognize that some of our findings here may be instrument unique; hence,

researchers are encouraged to perform similar tests on their own instrumentation. All isotopic measurement results are normalized against the Vienna standard mean ocean water (VSMOW)-standard light antarctic precipitation (SLAP) scale by assigning  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of  $-55.5$  and  $-428$  per mil, respectively, to SLAP reference water.<sup>23</sup>

We also attempted the minimodule device setup with the Los Gatos Research Model 908-0004 laser-based water vapor isotope analyzer ([www.lgrinc.com](http://www.lgrinc.com)). This analyzer has a comparatively high gas inlet flow rate in order to obtain rapid sample response ( $<100$  mL/min). With this high vapor flow rate, it was unlikely, on the basis of  $\text{H}_2\text{O}$  concentrations, that  $\text{H}_2\text{O}_{\text{l-v}}$  equilibrium was attained. Reduction of the flow rate by partially restricting the sample gas inlet resulted in excessive vacuum in the transfer tubing when the Minimodule was used, resulting in partial liquid water penetration through the membranes with correspondingly highly variable  $\text{H}_2\text{O}$  yields. Hence, no further tests were conducted using the minimodule with the Los Gatos Research instrument; however, we see no reason why the Los Gatos Research instrument could not be used successfully with either the marble-filled equilibrator or the drip screen equilibrator.

## RESULTS AND DISCUSSION

A series of lab-based tests were conducted to determine the impact of several variables and operating parameters relevant to the types of field operation and research objectives required.

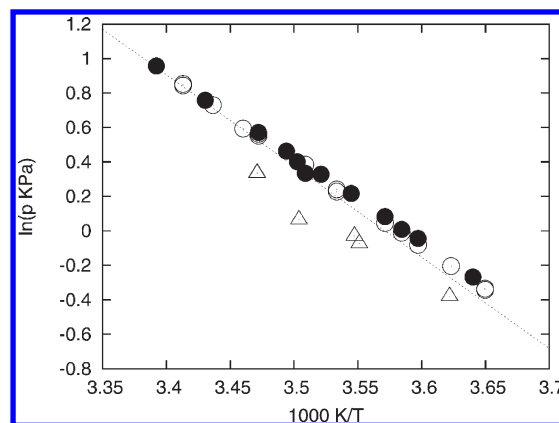
**Water Temperature Effects and Corrections.** The effect of water temperature needed to be considered for two important reasons. First, the vapor pressure of  $\text{H}_2\text{O}$  is nonlinearly correlated with water temperature. Previous studies have shown that, for some laser isotope instrumentation, the amount of water vapor in the laser cavity can have a direct and significant dramatic effect on the isotopic measurements,<sup>13</sup> akin to source nonlinearity in conventional IRMS-based analysis, and therefore, laser cavity water “amount” corrections will need to be applied. Fortunately, the Picarro L1115-i has a proprietary internal algorithm that corrects the isotopic composition for the volume fraction of water in the laser cavity between about 6000 and 26 000 ppm. Second, the hydrogen and oxygen isotopic fractionation between  $\text{H}_2\text{O}$  liquid and  $\text{H}_2\text{O}$  vapor is highly temperature dependent.<sup>24–27</sup> In order to determine the isotopic composition of liquid water based on  $\text{H}_2\text{O}$  vapor isotopic analyses, the temperature dependent H and O isotopic fractionation between  $\text{H}_2\text{O}_{\text{l}}$ – $\text{H}_2\text{O}_{\text{v}}$  using the parallel flow devices needed to be determined.

From thermodynamics, the equilibrium partial pressure of vapor over a liquid may be approximated by the Clausius–Clapeyron equation:

$$\frac{dP}{dT} = \frac{L_v}{T\Delta V} \quad (1)$$

where  $L_v$  is the latent heat of vaporization of water. If we assume that the molar volume of liquid is very small compared to the molar volume of the gas,  $\Delta V$  will reduce to  $V$ , which, assuming an ideal gas, can in turn be substituted with  $(RT)/P$ . The resulting equation can be written

$$\frac{dP}{dT} = \frac{L_v}{T} \frac{P}{RT^2} = \frac{L_v P}{RT^2} \quad (2)$$



**Figure 3.** Pressure of water vapor in the optical cavity as a function of temperature. Closed and open circles are the vapor produced by the marble-filled equilibrator and the minimodule, respectively. Open triangles are vapor pressure using the drip-screen equilibrator. The dashed line is the relationship based on thermodynamic models.<sup>28</sup>

Rearranging and integrating, it can be seen that  $\ln(P)$  should linearly covary as  $1/T$ :

$$\int \frac{dP}{P} = \int \frac{L_v}{RT^2} dT \quad (3)$$

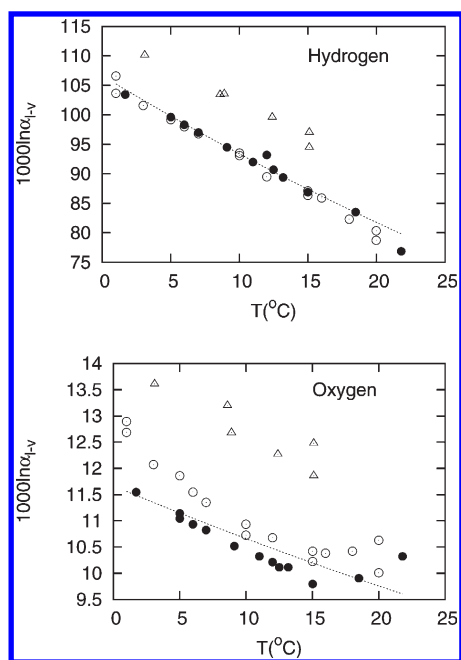
$$\ln(P) = -\frac{L_v}{RT} + C$$

Many rigorous and complicated derivations of the temperature dependence of vapor pressure of water on temperature have been compiled, primarily by curve-fitting of experimental data.<sup>28</sup> However, for this application with the very limited temperature range, it is adequate to treat  $L_v$  as independent of temperature and solve eq 3 by inserting the numerical values of latent heat and vapor pressure of water at an appropriate temperature, in this case  $25^\circ\text{C}$ .

A series of tests conducted to determine the effect of source water temperature ( $2$ – $20^\circ\text{C}$ ) on the measured concentration of  $\text{H}_2\text{O}$  vapor in the analyzer cavity are summarized in Figure 3. The relationship between water temperature and the measured vapor concentrations agree well with the partial pressures of water vapor expected from the theoretical considerations outlined above for both the minimodule device and the marble-filled equilibrator. This temperature dependency of water volume fraction was extremely useful. Not only did it confirm that, at least chemically, the equilibrators were producing expected results, but also it enabled us to exploit the close temperature–vapor pressure  $\text{H}_2\text{O}$  relationship to obtain the water equilibration temperatures at any time during measurement without the need for an external thermometer. This aspect is useful for field deployment.

Measured hydrogen and oxygen isotope fractionations at temperatures ranging from  $0$  to  $20^\circ\text{C}$  between water vapor and liquid water are shown in Figure 4. When measured using the marble-filled equilibrator or the minimodule, the measured  $1000 \ln\alpha$  values compare well with those from previous studies. The fact that we can replicate the hydrogen and oxygen isotopic fractionation and the temperature dependence of this fractionation between liquid water and water vapor is a very important result. This means that both the minimodule and the marble filled equilibrator are producing water vapor in isotopic equilibrium with liquid water and that the internal algorithm to correct vapor isotopic compositions as a function of vapor concentration





**Figure 4.** Measured isotopic fractionations measured between vapor and liquid water for hydrogen and oxygen isotopes using the marble filled equilibrator (●), the minimodule (○), and the drip-screen equilibrator (Δ) as a function of temperature. The dashed lines represent previously measured isotopic fractionations.<sup>27</sup>

is functioning correctly in this particular instrument. The only other possibility is that the equilibrator is generating nonequilibrium vapor which is exactly compensated by an incorrect concentration effect algorithm of the laser analyzer from 0 to 20 °C. We consider this extremely unlikely.

At low temperatures, the oxygen 1000  $\ln \alpha$  values measured using the minimodule deviate slightly from previous measured values and from the values measured with the marble-filled equilibrator (Figure 4). A corresponding deviation in the hydrogen isotope fractionation was not observed. The reason for this discrepancy is unclear, although it may be attributable to membrane effects in the minimodule where slower diffusion through the membranes becomes important at low temperature. Nevertheless, the minimodule or the marble-filled equilibrator at moderate temperatures (i.e., 10–20 °C) will allow the continuous measurement of the isotopic compositions of a flowing water stream at temperatures typical of environmental applications. Isotopic fractionations were not measured above 20 °C because the equilibrator and all of the connecting tubing is kept at ambient temperature and condensation in this apparatus would occur if saturated water vapor at higher temperature was introduced. At any time, the amount of water vapor in the cavity can be used to calculate the flowing water temperature, which in turn can be used to calculate the hydrogen and oxygen isotopic fractionation factors. Application of these to the measured isotopic compositions of the water vapor yields the isotopic compositions of the flowing water stream in real time.

Unfortunately, the small drip-screen equilibrator did not produce water vapor concentrations in equilibrium with liquid water at a given temperature, and 1000  $\ln \alpha$  values for both hydrogen and oxygen isotopes are lower than those expected (Figures 3 and 4). This indicates that the drip screen equilibrator is not producing vapor in equilibrium with the flowing water. For this reason, the

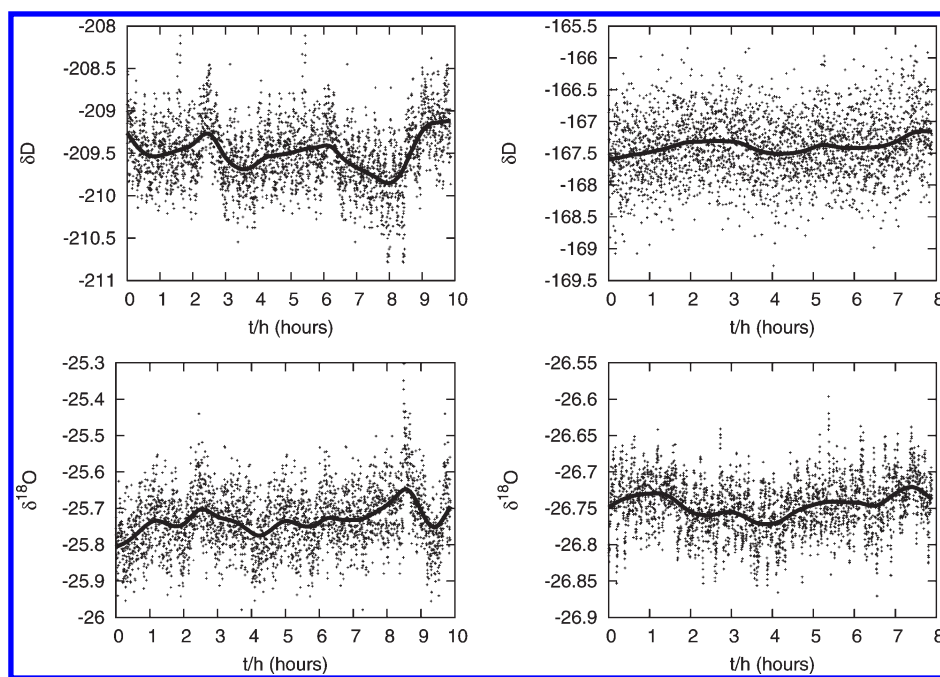
drip screen equilibrator was not used in any subsequent tests, although because of its compact and simple design, it is likely better suited for field use. Different internal designs of this equilibrator are currently under testing in our laboratory.

**Instrumental Drift.** The equilibrator and minimodule devices were set up to test for isotopic drift in the laboratory over periods ranging from 3 to 9 h under isothermal conditions using isotopically known water. Minimodule conditions were set to uniform sample water flow rates ranging between 2 and 3 L/min, while flow rates for the marble filled equilibrator were approximately 5 L/min. For all time trials between 3 and 9 h, the parallel-flow device and laser instrument configuration showed no significant instrumental drift (Figure 5). For the minimodule drift test, the mean standard deviations ( $1\sigma$ ) of  $\delta D$  and  $\delta^{18}O$  values at the default 10 s sampling frequency was 0.5 and 0.11 per mil, respectively. The marble filled equilibrator showed similar precisions with  $\delta D$  and  $\delta^{18}O$   $1\sigma$  values of 0.4 and 0.08 per mil, respectively.

The default Picarro L1115-I isotopic data sampling period was 10 s. However, we found that the 10 s sampling period resulted in a slightly greater range (max/min) of isotopic values, although all data were normally distributed. A more realistic sampling frequency for many field hydrology applications may be on the order of minutes or more, not to mention that a large amount of data is generated at 10 s sampling period. The 9 h test was chosen to correspond to a typical working day in the field. We resampled the entire minimodule 9 h data set with 2.5 min boxcar averaging. With this resampling, the  $\delta D$  and  $\delta^{18}O$  means were comparable and standard deviations were reduced ( $-167.4 \pm 0.2$  and  $-26.8 \pm 0.03$  per mil;  $n = 183$ ). A visual inspection and a least-squares regression of the time series data revealed some minor fluctuations for  $\delta D$  but no meaningful trends over 9 h for either  $\delta D$  or  $\delta^{18}O$  (Figure 5). Additionally, the reported precisions were excellent and comparable to that attained by conventional IRMS analysis. These findings suggested that both the equilibrator and minimodule devices with the laser instrument could be used to accurately monitor the isotopic composition of flowing waters over 9 h or possibly longer time scales without the need to correct for uncontrolled instrumental drift.

**Calibrations.** One of the major drawbacks of isotopic measurement of water vapor by laser molecular spectroscopy is the lack of calibration to in-house references, which can then be used to calibrate the measured values to the VSMOW-SLAP scale. One proposed solution is to periodically inject a reference pulse of isotopically known water vapor, which is produced by entirely evaporating an isotopically known reference water in a separate evaporating device. However, these devices are only recently becoming commercially available and may be too delicate and complex for field measurements. We propose another strategy, which is to periodically sample the liquid water stream. The water can then be analyzed separately and used to correct the continuous water vapor analyses at known intervals. Drift tests (above) indicate that no significant drift occurs over 9 h, at least in the laboratory. In the field, it is possible that the laser instruments may suffer from more rapid or pronounced drift depending on ambient conditions. Therefore, water samples need only be taken three times daily, or more frequently, depending on the application and field conditions.

A surprising result was that the raw delta values determined on water vapor from the equilibrators did not need to be independently normalized. In other words, the internal calibration on this particular instrument produced delta values that were within



**Figure 5.** Stability of the isotopic compositions of water vapor using the marble-filled equilibrator (left) and the minimodule (right) at 12 °C.

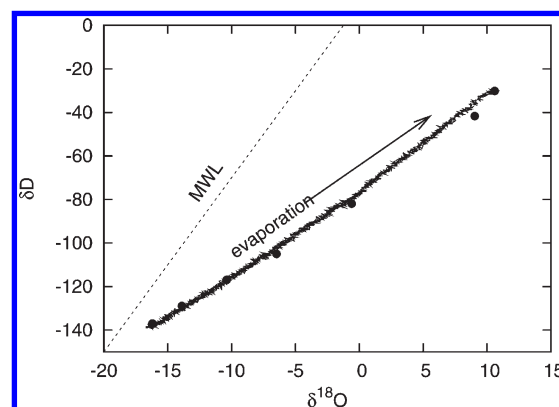
error of the actual delta values on the VSMOW-SLAP scale. This may not be the case for all instruments, however, and researchers will have to determine the calibrated accuracy of their own instruments.

#### Liquid–Vapor Parallel-Flow Device Equilibration Time.

We conducted tests to determine the response time of the parallel-flow device and laser analyzer to rapid changes in the isotopic composition of the source water. An abrupt switch to a water source reservoir of different isotopic composition changed rapidly on the laser analyzer and fully reached the new equilibrium isotopic values in <30 s (data not shown). For the minimodule, this finding supports previous studies that showed the response of gas exchange in parallel-flow device membranes is nearly instantaneous.<sup>22</sup>

**Effect of Water Flow Rate on Isotopic Composition.** One concern with the minimodule was that the flow rate of water through the minimodule device might affect the isotopic composition of the vapor passing across the membranes. A series of isothermal tests at several temperatures (5–20 °C) were performed spanning the sample water flow specifications of the Minimodule (fixed flows between 0.2 and 3 L/min). At each isothermal temperature test, we observed no change in the isotopic composition of the vapor phase H<sub>2</sub>O regardless of the water flow rate (data not shown). These findings indicated that water flow rate, fixed or variable, within the specifications of the parallel-flow device had no effect on the isotope results. A similar result is anticipated for the two shower-type equilibrators. This finding allows for considerable flexibility in field applications and tracer tests where water quantity and flow rate is an issue.

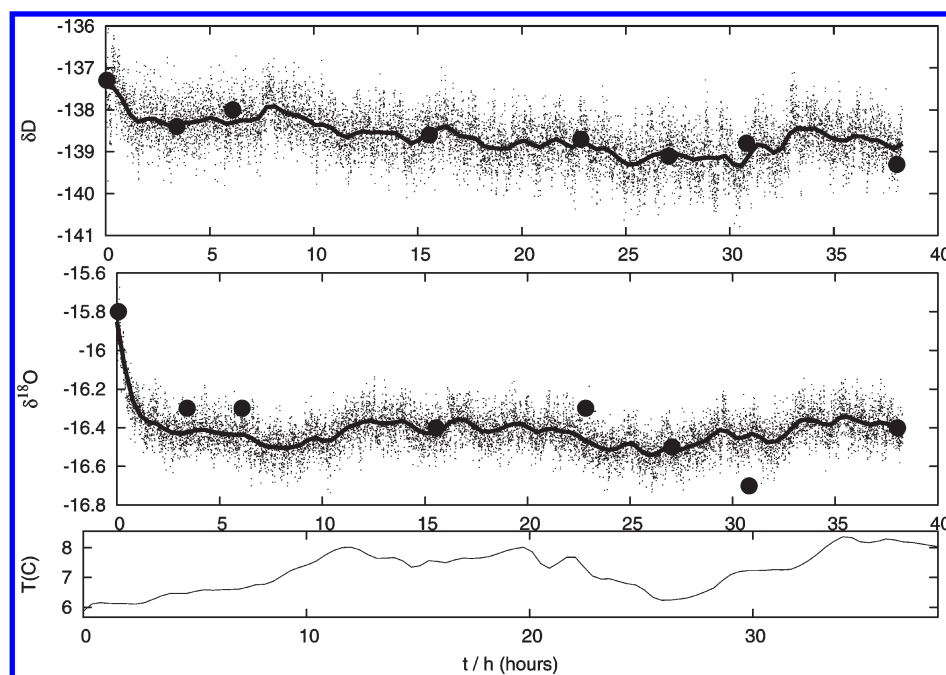
As a final test, we simulated two field situations. One where a source of water would change its isotopic composition significantly over a period of a week, and the other where the isotopic composition may only vary slightly. For the first simulation, an evaporating source of water was continuously pumped through the marble-filled equilibrator. A small aquarium was filled with local tap water ( $\delta D \approx -136$  per mil,  $\delta^{18}O \approx -16.0$  per mil), and a small in-line pump was used to pump the water through the



**Figure 6.** Isotopic composition of water evaporated for approximately 4 days as measured by WS-CRDS using the marble-filled equilibrator.

equilibrator. To aid evaporation, dry air was blown across the surface of the water in the aquarium. In the second simulation, ordinary unregulated tap water was allowed to flow through the same equilibrator over a weekend. Although the laser spectrometer was monitored over the Internet, it was left unattended over the entire weekend. In both cases, the isotopic composition of the flowing water was calculated by applying equilibrium isotopic fractionation factors at temperatures calculated from the concentrations of water vapor in the laser cavity. In both simulations, the water was collected at regular intervals and analyzed independently for its isotopic composition. The sampling period was 10 s for both experiments.

Results of the evaporation experiment are shown in Figure 6. The water started with isotopic compositions typical of tap water in Saskatchewan. As evaporation proceeds, the  $\delta D$  and  $\delta^{18}O$  values of the remaining water increase from values of -137 and -16.2 per mil to -29 and 10.7 per mil, respectively. This trajectory is typical of water evaporation.<sup>29</sup> Periodic water samples, analyzed offline, agree to within analytical error throughout the experiment.



**Figure 7.** Stable isotopic composition and temperature of tap water over a weekend measured by WS-CRDS and the marble filled equilibrator.

The  $\delta D$  values of tap water over a 40 h period are shown in Figure 7.  $\delta D$  values slowly decrease from  $-138$  to about  $-139$  per mil over 30 h. Samples taken periodically throughout the experiment have  $\delta D$  values that are indistinguishable within experimental uncertainty to those measured with the vapor equilibrator. Calculated temperatures show a distinctly diurnal pattern that correspond to day/night cycles in Saskatoon.

## CONCLUSIONS

Pressures and isotopic compositions of water vapor measured by optical methods and using either the minimodule or marble filled equilibrator indicate that these devices both produce vapor in equilibrium with flowing water through the device. Disequilibrium with the minimodule device was indicated at low temperatures. Using the measured vapor pressures to calculate the temperature of the water, the isotopic composition of the parent water can be in turn calculated using known isotopic fractionation factors. Overall stabilities of the laser analyzer–equilibrator setup appear good for periods of at least 9 h; however, it is apparent that an independent strategy will need to be developed to normalize the measured water isotopic compositions to the VSMOW-SLAP reference scale. A principal advantage of the vapor equilibrator is that it continually supplies water vapor so that unattended field use may be possible.

## ASSOCIATED CONTENT

**S Supporting Information.** Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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