In Situ Measurement of the Water Vapor $^{18}O/^{16}O$ Isotope Ratio for Atmospheric and Ecological Applications

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ABSTRACT

In this paper a system for in situ measurement of $H_2^{16}O/H_2^{18}O$ in air based on tunable diode laser (TDL) absorption spectroscopy is described. Laboratory tests showed that its 60-min precision (one standard deviation) was 0.21‰ at a water vapor volume mixing ratio of 2.67 mmol mol^{-1} (dewpoint temperature $-10.8°C$ at sea level) and improved to 0.09 at 15.3 mmol mol^{-1} (dewpoint temperature 13.4°C). The TDL measurement of the vapor generated by a dewpoint generator differed from the equilibrium prediction by $-0.11 \pm 0.43‰$ (mean $\pm$ one standard deviation). Its measurement of the ambient water vapor differed from the cold-trap/mass spectrometer method by $-0.36 \pm 1.43‰$. The larger noise of the latter comparison was caused primarily by the difficulty in extracting vapor from air without altering its isotope content. In a 1-week test in Logan, Utah, in August 2003, the isotope ratio of water vapor in ambient air was positively correlated with the water vapor mixing ratio and also responded to wetting events (rain and irrigation) in an expected manner.

This system has been in continuous operation in New Haven, Connecticut, since December 2003. It is suggested that such uninterrupted measurement may open a new window on the hydrologic cycle, particularly processes involving phase changes of water, and can increase the power of the isotope method in ecological applications.

1. Introduction

An improved understanding of stable water isotopes as tracers of water movement in the atmosphere and as indicators of climate change requires detailed knowledge of the isotope composition in all three phases of water. To date, extensive data exist on the isotope content of the condensed phases [e.g., International Atomic Energy Agency–World Meteorological Organization (IAEA–WMO) Global Precipitation Network; Schotterer et al. (1996)]. In comparison, only a few

studies have reported data on the vapor phase. Such data offer insights into the hydrological cycle that otherwise would not be possible with data on the condensed phases alone. For example, White and Gedzelman (1984) and He et al. (2001) showed that in the northeastern United States the isotope ratio of water vapor is highly correlated with the ambient moisture content, indicating that the vapor isotope ratio bears information on the condensation history of an air mass. The isotope data reported by Jacob and Sonntag (1991) showed that, on seasonal time scales, water vapor in Heidelberg, Germany, seemed to be derived from local precipitation. He and Smith (1999) observed a large difference in the vapor isotope composition, by as much as 200‰ HDO and 30‰ $H_2^{18}O$, between the boundary layer air and the free atmosphere above. Airborne sam-

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pling of the vapor isotope ratio helped to establish that ice lofting was a source of water in the upper troposphere (Smith 1992). Most published studies on water vapor are limited to brief campaigns and discrete sampling. The only exception is Jacob and Sonntag (1991) who measured water vapor isotopes on a nearly continuous basis for over 8 yr, but with a rather coarse time resolution of 24–48 h.

Previous measurement of water vapor isotopes, except for the two studies noted below, usually involves two steps—collection and analysis—both of which are labor intensive. First, water vapor is collected via bags and subsequently condensed to the liquid form (Moreira et al. 1997) or, more commonly, via cold traps made of glass tubes (Jacob and Sonntag 1991; Wang and Yakir 2000; Gat et al. 2003; Riley et al. 2003) or canisters containing metal balls (He and Smith 1999). Collection efficiency depends on the actural design and temperature of the trapping device and on air humidity, and varies from 60% (Yamanaka and Yonetani 1999) to nearly 100% (He and Smith 1999). If the collection efficiency is not perfect, the collected vapor will be heavier than the ambient vapor because heavier isotopes are preferentially condensed out of the airstream. Schoch-Fischer et al. (1983) showed that at a dewpoint temperature of 4.8°C, even a tiny fractional loss of 0.6% could bias the meausurement by 7.5‰ for HDO and 0.64‰ for $H_2^{18}O$. Their analysis also suggests that the bias is more severe when air humidity is lower.

A reduced collection efficiency can also occur if the collection temperature is too low. A trap whose temperature is 40°C lower than the dewpoint temperature of the ambient air is likely to experience homogeneous nucleation where ice crystals form in air and get carried away by the airstream exiting the trap. Unpublished experiments by the third author suggest that the growth rate of these small crystals is diffusion limited. The dominance of diffusion effects over equilibrium effects causes the (lost) particles to be enriched in the lighter isotopes relative to the vapor. Thus, the captured vapor is heavier than the initial vapor. The actual bias is likely to depend on the trap design and flow parameters.

The net result is that both insufficient cooling and excessive cooling can cause the trapped vapor to be too heavy. With the former process, a correction is possible using the Rayleigh fractionation equation based on the measured temperature of the trap. With the latter process, no correction procedure is currently available. The problem of homogenous nucleation is best avoided by maintaining the temperature of the trap in the optimum range (as low as possible but no lower than $t_d - 40°C$, where t_d is the dewpoint temperature).

In the second step, the collected water is analyzed for its isotope ratio on a mass spectrometer. Typical precisions are 0.5–1 and 0.03–0.1‰ for HDO and $H_2^{18}O$, respectively. The overall precision and accuracy of the vapor isotope measurement are limited by both the per-

formance of the analytical instrument and the collection procedure, the latter of which depends on the ambient humidity and the collection temperature.

In this paper we describe a system for in situ measurement of $H_2^{16}O/H_2^{18}O$ (see appendix A for glossary of terms) in air based on tunable diode laser (TDL) absorption spectroscopy. Measurement of the isotope ratio has the advantage of canceling out some of the covarying drifts and noises that may occur in the individual isotopologues. On the other hand, several technical difficulties have been anticipated for the real-time measurement. The first difficulty arises from the need to simultaneously measure both $H_2^{16}O$, a major gas, and $H_2^{18}O$, a minor gas. In observational studies of trace gases that require high measurement accuracy, it is a common practice to remove water vapor before air enters into the detection chamber of an analytical instrument. Obviously, this should not be done in the present study, and the possible dilution and pressure broadening problems associated with the presence of $H_2^{16}O$ must be dealt with by a calibration procedure. Second, unlike many other trace gases in the atmosphere, the abundance of water vapor isotopes can vary over a wide dynamic range, by as much as 10-fold on a diurnal cycle and 30-fold on a seasonal cycle at midlatitudes. Third, high polarity of water molecules results in sticking on walls, damping the instrument's time response and altering the isotope composition due to fractionation effects. Finally, the high precision called for by the isotope ratio measurement requires a calibration gas standard, which is not available commercially.

We suggest that such real-time continuous measurement should open a new window on the hydrological cycle. It may allow us to gain an isotopic view of transient phenomena and phenomena that occur at short time scales, such as frontal passage, boundary layer gusts, boundary layer entrainment, land–sea-breeze circulation, and the exchange of vapor isotopes with raindrops and snowflakes during precipitation events. Examination of the isotope time series may also reveal insights into subtle changes in water vapor condensation and evaporation history of an air mass.

The ecological literature is rich on experimental studies with stable water isotopes as tracers for quantifying water use by plants. A majority of the studies are limited either to single plants in laboratory settings or else to plants growing in natural conditions but with very coarse sampling time resolutions (e.g., Yakir and Sternberg 2000). A few researchers have measured the flux isotope ratio of evapotranspiration using the micrometeorological flux-gradient method (Brunel et al. 1992; Yakir and Wang 1996; He et al. 2001; Riley et al. 2003). That the vapor isotope gradient in the atmospheric surface layer is comparable in magnitude to the precision of the cold-trap method makes such measurement extremely prone to measurement errors. The in situ ap-

proach reported in this study may overcome this problem (Griffis et al. 2004).

Laser absorption spectroscopy has been used by two other groups for water isotope research. The system reported by Kerstel et al. (1999) operates in a batch mode using a single-mode color center laser in the 3-μm spectral region. A liquid water sample is injected into a sample cell and absorption strength is calibrated against that of a standard sample in a reference cell to give the isotope ratio. More recently, they have built a more compact analyzer with much improved performance (Gianfrani et al. 2003; Kerstel et al. 2002). In an aircraft measurement of vertical profiles of water vapor up to the midstratosphere (mixing ratio as low as 5 ppm) reported by Webster and Heymsfield (2003), the isotope ratio measurement was achieved by recording both direct absorption and second harmonic spectra in a wavelength region near 6.7 μm. Their in-flight calibration relied on the measured vibration–rotation line parameters provided by the HITRAN line list, resulting in a measurement uncertainty of 20‰ ($H_2^{18}O$, preflight calibration). Our system differs from these two designs in that we attempt to achieve an accuracy and precision comparable to that of a mass spectrometer and at the same time allow uninterrupted operation.

2. Instrument design

a. Principle of operation

A key component of our measurement system is a Campbell Scientific TDL trace gas analyzer. This analyzer measures volume fraction of a species of interest by comparing the infrared absorption spectra of the sample gas and a known reference gas. The analyzer's sample and reference cells operate at low pressure (typically <75 hPa), reducing the absorption line width to minimize absorption from interfering species. Because volume flow rate is inversely proportional to pressure, the low operating pressure also increases the turnover of the air in the sample cell, thus reducing the instrument time constant. The TDL scanning rate is 500 Hz and the spectra are block averaged to 10 Hz for analysis. The analyzer achieves ppbv-level precision with a 3-Hz frequency response for typical traces gases, such as nitrous oxide, methane, and ammonia.

In our system, a lead-salt diode laser (Specdilas IR-1500.8, Laser Components, GmbH, Olching, Germany) was chosen to scan the $H_2^{16}O$ and $H_2^{18}O$ absorption lines at 1500.546 and 1501.188 cm^{-1}, respectively, in the same way as described in Bowling et al. (2003). These absorption lines were chosen based on the following criteria: 1) strong absorption for the $H_2^{18}O$ line; 2) an $H_2^{16}O$ line within 1 cm^{-1} of the $H_2^{18}O$ line, which gives approximately equal absorbance for natural isotopic abundances, thus avoiding the risk of line saturation; 3) no significant interference from other trace gases in the air; and 4) a suitable HDO absorption line within 1

cm^{-1} (1501.116 cm^{-1}) so that the system can be switched to the HDO/$H_2^{16}O$ mode without hardware modification. The laser is cooled by liquid nitrogen and is controlled at a temperature of 91.2 K. The choice of absorption lines near 1501 cm^{-1} (6.66 μm) required the use of optional liquid nitrogen–cooled mercury–cadmium–telluride (MCT) detectors that respond at longer wavelengths than the standard thermoelectrically cooled MCT detectors, which respond up to 5 μm.

The absorption lines that meet the above criteria have a relatively large difference in ground state energy and, therefore, a significant change in absorbance with temperature. To minimize the effect of temperature, we built the analyzer into an insulated enclosure with active temperature control, calibrated the system by periodically flowing calibration samples through the sample cell, and ensured the air and calibration samples come to a common temperature by flowing them through a sufficient length of tubing inside the enclosure before entering the absorption cell. In this way the change in instrument gain caused by diurnal changes in the ambient temperature was easily corrected. Our experience with CO_2 isotope systems has shown that the analyzer's performance in the field was similar to its performance in the laboratory. McManus et al. (2002) matched the ground state energies and the absorption by using strong lines of each isotopomer and a shorter pathlength for the principal isotopomer (of carbon dioxide), but their results were not as good as the simpler approach used in Bowling et al. (2003) and in this work.

The analyzer is a direction absorption spectrometer. The sample cell was operated at a lower pressure than typical, 12 hPa, to further reduce pressure broadening of the absorption lines and to increase the sample turnover rate. It also allowed the reference gas to be supplied from a closed flask of liquid water (Fig. 1) mounted inside the analyzer enclosure. Pure water vapor was pulled from the top of the flask through a needle valve that limited the flow rate. The low oper-
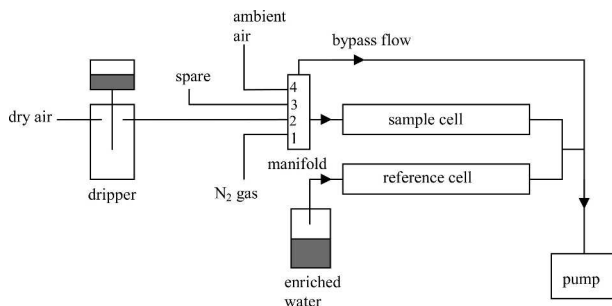

FIG. 1. A schematic diagram of the TDL system for water vapor isotopes. Ultra-high-purity nitrogen gas is used for zero calibration. Flow rate through the four intakes is 0.25 L min^{-1} STP and is controlled by a critical orifice at the inlet. The spare intake 3 can be used to sample ambient air at a different height from intake 4 to give the vertical isotope gradient and therefore the flux isotope ratio.

ating pressured ensured a flow of water vapor through the reference cell even when the analyzer cover was removed and the reference flask cooled to room temperature. With the analyzer cover on, its internal heater controlled the temperature to 40°C, and the reference water flow rate was approximately 0.35 g day^{-1}. Then $H_2^{18}O$ was added to the reference water, enriching it to approximately 4 times the natural abundance to match the reference absorption at the two wavenumbers (10% for $H_2^{16}O$ and 13% for $H_2^{18}O$).

The sample cell length is 153.08 cm and its volume is 400 mL. The reference cell length is 4.53 cm and its volume is 10 mL. A four-intake manifold was mounted inside the analyzer enclosure to connect one of four intake tubes to the sample cell. The unselected intakes were bypassed to the vacuum pump to maintain flow and to minimize pressure transients. Flow through each sampling tube was controlled by a critical orifice (orifice size 0.0178 cm) at a rate of 0.25 L min^{-1} (STP, standard temperature and pressure). The manifold was mounted inside the analyzer enclosure to keep it warm and to minimize the length of tubing between the manifold and the sample cell, reducing the settling time after switching intakes. A typical switching scheme spends 20 s on each port, following the sequence of zero gas, calibration, zero gas, and ambient air. Zero gas is sampled twice in one measurement cycle to account for the fact that the analyzer's zero offset is more variable than its gain and to compensate for a settling time bias, a bias caused by a slightly different speed of response to step changes between the two isotopes. The first 3–7 s of data after each switching are omitted in the calculation described below.

The analyzer's stainless steel sample cell was lined with polyethylene tubing to reduce the problem of water vapor sticking to the surface of the sample cell. The analyzer reached 99.8% of a step change in 3 s, a factor of 5 reduction in step change bias compared to the unlined sample cell. All internal and external sample tubing was a metal–plastic composite (Synflex 1300, Saint-Gobain Performance Plastics, Wayne, NJ). An overlapped aluminum core, protected with a high-density outer jacket and an ethylene copolymer inner coating, gave this tubing very low permeability.

Typical 10-Hz noises were on the order of 2 ppm and 8 ppb at zero concentrations for $H_2^{16}O$ and $H_2^{18}O$, respectively, and increased to 23 ppm and 45 ppb at concentrations of 12 mmol mol^{-1} ($H_2^{16}O$) and 45 μmol mol^{-1} ($H_2^{18}O$).

b. Calibration procedure

The analyzer used ultra-high-purity nitrogen as a zero gas. A dripping device, termed the dripper hereafter, was used to generate a calibration standard. Water of known isotope ratio (−6.66‰) was dripped into a heated evaporating chamber that was fed with dry air (Fig. 1). The dry airflow rate was controlled so that the moist air exiting the chamber had a water vapor mixing ratio that matches the ambient mixing ratio to within 10%. That mixing ratios of the calibration gas and ambient air were nearly matched minimizes possible $H_2^{16}O$ dilution and pressure broadening effects and a nonlinearity problem (section 3a). Care was taken to ensure that water dripping into the chamber evaporated instantly. Thus, the isotope ratio of the moist air exiting the chamber, R_d, was identical to that of the liquid water feed. Tests to date show that the dripper can cope with a large dynamic range of variations, from 0.8 to 30 mmol mol^{-1}.

Let x_i be the TDL output (uncalibrated volume mixing ratio) for intake i ($i = 1$–4). With the intake assignment shown in Fig. 1, correction for zero offset and gain was made according to

$$R = R_d,$$
$$(x_2^{16} - x_1^{16})/(x_2^{18} - x_1^{18}),$$
$$(x_4^{18} - x_4^{16})/(x_4^{16} - x_1^{16}), \tag{1}$$

where R is the isotope molar ratio in ambient air drawn by intake 4, and superscripts 16 and 18 denote molecules H_2O^{16} and H_2O^{18}, respectively. The individual gain factors for the two isotopes were not required for the isotope ratio calibration. [The TDL measurement should be compared with another standard (section 5) to obtain a calibrated water vapor mixing ratio.] Conversion of the isotope molar ratio to the δ convention was made according to

$$\delta = (R/R_{vsmow} - 1) \times 1000‰,$$

where R_{vsmow} = 0.002 005 2 for ^{18}O.

3. Laboratory performance tests

a. Linearity

As a first check on the instrument performance, we used the TDL analyzer to measure mixing ratios of $H_2^{16}O$ and $H_2^{18}O$ in vapor generated by a dewpoint generator (model 610, Licor, Inc., Lincoln, NE). Room air entered into a small water reservoir of known isotope ratio in the generator, whose temperature (t_g) was controlled by a cooler, and rose as bubbles. The resulting moist air contained $H_2^{16}O$ and $H_2^{18}O$ at their respective saturation pressures. The test was done over a temperature range of 1°–20°C, corresponding to $H_2^{16}O$ and $H_2^{18}O$ volume mixing ratio ranges of 6.6–25 mmol mol^{-1} and 13–46 μmol mol^{-1}, respectively. It was found that linear regression accounted for 99.9% of the observed variations in the $H_2^{16}O$ and $H_2^{18}O$ mixing ratios. The residual errors of the regression were, on average, 0.6% and 0.3%, with standard deviations of the residual of 0.21 mmol mol^{-1} and 0.12 μmol mol^{-1} for $H_2^{16}O$ and $H_2^{18}O$, respectively, showing no obvious dependence on the mixing ratios themselves. The residual error was within the accuracy specified for the dewpoint generator (±0.2°C).

Such a linear response, even though sufficient for

mixing ratio measurements, does not guarantee the accuracy desired for the isotope ratio. Since a two-point calibration is used, a 0.1‰ accuracy would require that the nonlinearity, if any, in either isotopes be no greater than 0.005% over the range between the zero and calibration concentrations, a stringent requirement that cannot be verified with the dewpoint generator.

To address this issue, we ran another test. This time the moist air from the dewpoint generator was first mixed with a varying amount of dry air and then fed into the analyzer. A complete measurement cycle, starting with a drying sequence where the proportion of the amount of dry air increased progressively with time, and then a wetting sequence where the amount of dry airflow decreased with time, took 10 min. Because the analyzer's gain and isotope ratio of the moist air from the dewpoint generator were stable enough over this short period, the isotope ratio measurement could provide some gauge of the severity of the nonlinearity problem. A perfectly linear analyzer would give an isotope ratio that should be invariant with the amount of dry air or $H_2^{16}O$ mixing ratio in the mixing test, on the assumption that mixing with dry air did not alter the isotope ratio (but see below). This pattern in fact was not observed. The TDL isotope ratio after correction for a zero offset showed a decreasing trend with decreasing $H_2^{16}O$ mixing ratio, reaching a minimum at $H_2^{16}O$ mixing ratio of 8 mmol mol^{-1} that was 10‰ lower than that at 20 mmol mol^{-1}. A further reduction in $H_2^{16}O$ mixing ratio resulted in an increasing trend in the isotope ratio reading, with a value at the dry end (1.5 mmol mol^{-1}) that was 20‰ higher than the minimum value.

Two approaches can be used to correct the nonlinearity problem. In the first, the TDL analyzer performs its measurement with a calibration gas held at a constant level. Errors due to the nonlinearity problem are corrected in postfield analysis according to the result of the mixing test. In the second approach, the $H_2^{16}O$ mixing ratio of the calibration gas is adjusted in real time to match the ambient mixing ratio, thus avoiding the nonlinearity error. The first approach is not reliable enough because absorption and desorption of water molecules by tube walls could result from the rapidly changing humidity inside the tube, thus altering the isotope composition of the mixed air. Indeed, we suspect that this was the primary cause of the variations in the isotope ratio found in the mixing test. In view of this problem, in this study we have adopted the second approach.

b. Precision

Table 1 summarizes the results of a laboratory test on the precision of the isotope ratio measurement. In the test, the moist air coming out of the dripper was split into two streams with one going into intake 2 (calibration intake) and the other into intake 4 (ambient air intake). Readings for intake 4 were converted to an

TABLE 1. Measurement noise at three levels of $H_2^{16}O$ volume mixing ratio (w^{16}). Results are given as mean ± one standard deviation. The true isotope ratio was −6.66‰.

w^{16} (mmol mol^{-1})	20-s avg (‰)	1-h avg (‰)
2.67	−6.71 ± 1.89	−6.69 ± 0.21
7.38	−6.71 ± 1.41	−6.71 ± 0.13
15.3	−6.70 ± 0.91	−6.70 ± 0.09

isotope ratio following Eq. (1). The test was done at three moisture levels, each lasting 24 h. The result shows that the precision improved as air became more moist and as the averaging interval increased. At an $H_2^{16}O$ mixing ratio of 15.3 mmol mol^{-1} (dewpoint temperature 13.3°C at sea level), the 1-h average isotope ratio had a precision (one standard deviation) of 0.09‰, comparable to that of a mass spectrometer measurement. Table 1 also suggests a small inlet bias of 0.04‰.

Although the primary goal of this work was to measure the $^{18}O/^{16}O$ isotope ratio, some testing was also done to evaluate the performance of HDO measurements. The laser was chosen to be able to use the HDO line at 1501.116 cm^{-1} with the $H_2^{16}O$ line at 1500.546 cm^{-1}. One gram of D_2O was added to 17 g of distilled water to provide the reference water. The D_2O exchanged atoms with H_2O molecules to form a mixture with approximately 11% HDO, with a 0.35% D_2O, and the balance H_2O and minor isotopomers. This enrichment by a factor of approximately 350 gave an absorption of 23% for the HDO line at 1501.116 cm^{-1}. This strong reference absorption prevented the rise in noise with humidity observed for the $H_2^{18}O$ and $H_2^{18}O$ measurements. The 10-Hz noise for HDO was 78 ppbv for dry air or humid air (14.3 mmol mol^{-1}). This HDO line was used with the H_2O line at 1500.546 cm^{-1} to measure isotope ratios in humid air (14.3 mmol mol^{-1}), with a precision of 18‰ at 10 Hz and 3.1‰ for a 1-min cycle including the two-point calibration. Serendipitously, the laser was also able to operate in a nearby region that includes a stronger pair of lines: H_2O at 1501.846 cm^{-1} and HDO at 1501.813 cm^{-1}. This line pair gave a 10-Hz noise of 8‰ and a 1-min noise of 2‰.

c. Tests against the Rayleigh distillation prediction

In this section, we describe a series of tests that used the dewpoint generator as a Rayleigh distillation device. Let $R_{l,o}$ be the initial molar isotope ratio and m_o be the initial $H_2^{16}O$ mass in its water reservoir, respectively. Air with a vapor isotope ratio R_i enters into the reservoir at a $H_2^{16}O$ mass flow rate of Q_i and rises as bubbles, and exits the reservoir flask at a $H_2^{16}O$ mass flow rate of Q_e with a vapor isotope ratio R_v that is related to its liquid counterpart, R_l, as

$$R_v = R_l/\alpha,$$

where α (>1) is a fractionation factor. Consideration of the mass balance yields R_l as a function of time t as

$$R_l = \frac{a}{b} + \left(R_{l,o} - \frac{a}{b}\right)\left(1 + \frac{Q_i - Q_e}{m_o}t\right)^{-b/(Q_i - Q_e)},$$ (2)

where

$$a = Q_i R_i \quad \text{and}$$

$$b = Q_e/\alpha + (Q_i - Q_e),$$

($Q_i \neq Q_e$; appendix B). In the special case where the inflow air is dry ($Q_i = 0$), the above equation reduces to the familiar Rayleigh distillation equation:

$$R_l = R_{l,o}\left(\frac{m}{m_o}\right)^{(1/\alpha)-1},$$ (3)

where $m = m_o - Q_e t$.

Assuming that air in the reservoir flask is saturated, α should equal the equilibrium fractionation factor, as

$$\alpha = \exp[1137/(t_g + 273)^2 - 0.4156/(t_g + 273) - 2.0667$$
$$\times 10^{-3}]$$ (4)

(Jouzel 1986), where t_g (°C) is the temperature of the water reservoir. Once R_l is known, the isotope ratio of the moist air exiting the dewpoint generator is given by

$$\delta_v = \left(\frac{R_l}{\alpha R_{vsmow}} - 1\right) \times 1000.$$ (5)

At the beginning of each test, the dewpoint generator reservoir was flushed several times with water of known isotope ratio (-6.66‰) before being filled with water of the same isotope composition. Its inlet was fed by ultra-zero-grade air and its outlet was connected to intake 4 of the TDL analyzer (Fig. 1). Each test lasted 24–50 h. At the end of the test, water was withdrawn from the reservoir and was sent to an analytical laboratory (Iso-Analytical Limited, Sandbach, Cheshire, United Kingdom) for analysis of its isotope ratio by a mass spectrometer. The airflow was controlled by a

rotameter at a rate of 0.3–0.5 L min^{-1}. The H$_2^{16}$O mass flow rate Q_e was determined by weight loss of the liquid reservoir over the test period.

Three comparisons were made with the data collected. First, the first valid hourly TDL observation was compared with the equilibrium calculation [Eqs. (4) and (5)]. Prior to the calculation, a small adjustment, typically smaller than -0.1‰, was made to the initial isotope ratio (-6.66‰) of the liquid water according to Eq. (3) to account for the change between the start of the test and the first valid TDL measurement. The difference between the measured and calculated isotope ratios was 0.1 ± 0.27‰ (mean $\pm$ one standard deviation; Table 2).

Second, the TDL was compared to the prediction at the end of the test, again using the equilibrium fractionation factor and the measured isotope value for the water. This comparison yielded a bias of -0.29 ± 0.48 (Table 2), which was of opposite sign to the first comparison and was more variable. The reason for this was not clear. The overall bias was -0.11 ± 0.43 if all the data in Table 2 were considered.

The third comparison was between the measured values and the prediction of how the ratio changed over time, using the starting water isotope ratio, initial water mass, its mass flow rate, and the equilibrium fractionation factor [Eqs. (3)–(5)]. An example was given in Fig. 2. Four features are evident in this plot: (i) water vapor from the dewpoint generator became progressively enriched with H$_2^{18}$O as time elapsed; (ii) the TDL measurement followed closely the theoretical prediction, the difference between the measured and predicted values being -0.08 ± 0.30‰ (mean $\pm$ one standard deviation); (iii) the TDL measurement was noisy right after refill of the TDL detectors' liquid nitrogen dewars, causing two outliers at 25 and 45 h; and (iv) excellent agreement existed between the measured and predicted isotope ratios at the beginning of the test, but the former became more negative with time than the latter (Fig. 2 inset).

The trend that the difference between the measured

TABLE 2. Comparison of the measured isotope ratio (δ, ‰) of the water vapor from a dewpoint generator with the isotope ratio (δ_v, ‰) of the water vapor in equilibrium with the liquid water at temperature t_g (°C) at the time of the TDL measurement. Also given is H$_2$O^{16} volume mixing ratio (w^{16}, mmol mol^{-1}). The lowest w^{16} was achieved by mixing dry air with moist air generated by the dewpoint generator at 1°C.

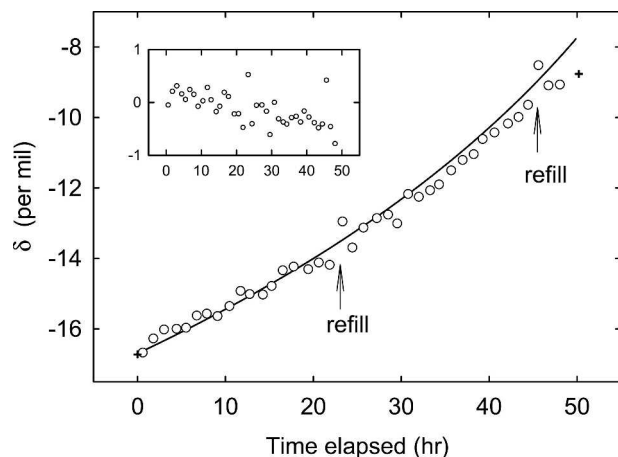| Temperature t_g	w^{16}	Start			End		
		δ	δ_v	$\delta - \delta_v$	δ	δ_v	$\delta - \delta_v$
15	17.1	-16.68	-16.63	-0.05	-9.07	-9.31	0.24
15	17.1	-16.14	-16.62	0.48	-12.85	-12.67	-0.18
12	14.0	-16.99	-16.95	-0.04	-13.61	-13.65	0.04
12	14.0	-17.25	-16.94	-0.31	-13.33	-12.93	-0.40
8	10.7	-17.07	-17.26	0.19	-16.88	-16.14	-0.74
8	10.7	-16.88	-17.32	0.44	-15.50	-14.79	-0.71
1	6.57	-18.06	-17.99	-0.07	-17.89	-16.77	-1.12
1	2.45	-17.83	-17.98	0.15	-16.63	-16.40	-0.23
		Mean $\pm$ 1 std dev		0.10 ± 0.27			-0.29 ± 0.48

FIG. 2. Comparison of the measured isotope ratio of water vapor (circles) generated by a dewpoint generator at a temperature of 15°C with that predicted from the Rayleigh distillation equation (solid line). Crosses indicate isotope ratio of water vapor in equilibrium with the liquid water in the generator. Inset: departure of the measured isotope ratio from the predicted value.

impurity of the ultrazero air was rated to be <5 ppm of water vapor. Using this mixing ratio and an extremely low isotope ratio of −500‰, we estimated that the impurity could introduce a change of −0.2‰ to the liquid water over a 48-h period. Because water vapor in the room was lighter than the reservoir water, the diffusion contamination would also bias the isotope ratio toward more negative values as compared to the theoretical prediction, although its magnitude was not known at this time. In this regard, the dewpoint generator was not a perfect Rayleigh distillation device.

4. Comparison with the cold-trap method

In this comparative study, the TDL system drew ambient air via intake 4 (Fig. 1) from the rooftop of our laboratory in New Haven, Connecticut. Positioned upstream of the intake critical orifice was a 0.67-L bottle to buffer moisture variations. The buffer volume, its inlet filter, and the critical orifice were contained in a heated enclosure, minimizing the possibility of condensation. The TDL measurement was done on a 20-s cycle following the procedure described in section 2a, and data were averaged to hourly intervals for comparison with the cold-trap method.

A total of 12 vapor samples were collected, using the stainless steel canisters described by He and Smith (1999), on 3 days in December 2003, spanning a range of $H_2^{16}O$ volume mixing ratio of 2.98–8.14 mmol mol^{-1} or a dewpoint temperature range of −9.5° to 4.0°C. The canisters were cooled by dry ice. The temperature of the air exiting the canister varied in the range of −45° to −55°C. Each collection lasted 60 min. After the collection was completed, water in the canister was extracted by vacuum distillation and was analyzed for its isotope ratio with a mass spectrometer (Iso-Analytical Limited). The weight of the collected water sample was within 10% of that expected from the ambient mixing ratio, flow rate, air temperature, and pressure.

Table 3 summarizes the data on the isotope measurements. Also given in Table 3 is a correction factor Δ for

and predicted vapor isotope ratios became more negative as time elapsed was observed in all other tests. This is consistent with the isotope content of the liquid water, which was, on average, 0.6‰ more negative at the end of the test than the Rayleigh prediction [Eq. (3)]. We are unable to identify problems with the TDL system that could cause the time-dependent bias. Errors in the fractionation factor will not cause the difference either, as the observed bias in the liquid isotope content would require a fractionation factor to be smaller than the equilibrium factor, which in turn would result in a higher vapor isotope ratio at the beginning of the test and contradict the observation. Instead, we suggest that the problem resulted from contamination due to (a) impurity of the dry air feed to the dewpoint generator and (b) water vapor in room air diffusing through the wall of Bev-a-line tubes used inside the generator. The

TABLE 3. Comparison of the TDL measurement of the isotope ratio (δ, ‰) of the ambient water vapor with the mass spectrometer analysis of water vapor samples collected with cold traps (δ_{trap}, ‰). Here, Δ is a correction factor to account for vapor loss during the cold-trap collection, t_a is air temperature (°C), and w^{16} is the H_2O^{16} volume mixing ratio (mmol mol^{-1}).

Date	Time (LST)	t_a	w^{16}	δ	δ_{trap}	Δ	$\delta - \delta_{trap}$	$\delta - (\delta_{trap} + \Delta)$
10 Dec	1117–1217	11.70	5.75	−23.71	−22.24	−0.50	−1.47	−0.97
	1221–1321	10.30	7.57	−19.57	−20.65	−0.74	1.08	1.82
	1325–1425	10.00	8.14	−18.63	−18.93	−1.10	0.30	1.41
	1428–1528	8.30	8.07	−18.63	−19.91	−1.18	1.28	2.45
19 Dec	1352–1452	6.00	3.08	−29.58	−26.43	−1.67	−3.15	−1.48
	1454–1554	3.70	2.98	−29.83	−26.00	−2.22	−3.83	−1.61
	1603–1703	2.30	2.99	−29.93	−26.89	−1.44	−3.04	−1.60
20 Dec	1018–1118	3.70	3.90	−28.60	−26.79	−1.36	−1.81	−0.45
	1120–1220	5.00	3.75	−29.72	−27.47	−1.40	−2.25	−0.85
	1300–1400	4.70	3.74	−29.61	−27.48	−1.68	−2.13	−0.45
	1404–1504	4.70	3.58	−31.03	−28.25	−1.82	−2.78	−0.96
	1507–1607	2.30	3.47	−30.89	−27.42	−1.88	−3.47	−1.59
					Mean ± 1 std dev		−1.77 ± 1.75	−0.36 ± 1.43

the cold-trap/mass spectrometry data to account for the small amount of water vapor that was lost during the collection. The calculation of Δ was based on the Rayleigh distillation principle (Jacob and Sonntag 1991) and should be viewed as approximate rather than precise because it assumed that the canister temperature was uniform everywhere. The difference between the TDL measurement and the cold-trap method was -1.77 ± 1.75‰ (mean $\pm$ one standard deviation). Correction to the cold-trap data resulted in a much improved agreement (-0.36 ± 1.43‰), underscoring the difficulty in obtaining high-precision measurements with the cold-trap method as discussed in section 1.

5. A field test

a. Experimental setup

A field test was performed in Logan, Utah, from 1 to 6 August 2003. The isotope ratio measurement was calibrated against dry grade air (dewpoint temperature $<-62°C$) for zero offset and the moist air generated by the dripper for calibration. The other two intakes of the manifold were used to sample ambient air and the moist air generated by the dewpoint generator. Both ambient air and the air coming out of the dewpoint generator were buffered, with (unheated) buffer volumes of 0.67 and 4 L, respectively, before entering into the sampling tubes. The manifold spent 15 s on each flow stream, following a switching sequence of zero, dewpoint generator, dripper, and ambient air. The first 3 s after the switching were excluded from the mean computation. The dewpoint generator was fed by room air and had its temperature set at 10°C. At the end of the experiment, water was extracted from the dewpoint generator reservoir and was analyzed for its isotope content. In parallel to the TDL system, an infrared gas analyzer (model 6262, Licor Inc.) was used to measure the water vapor mixing ratio in ambient air.

Weather during this period was dry except for a 3-h storm on day 215 (3 August) that produced 7 mm of rain (isotope ratio -4.5‰). A sprinkler irrigation system would run for about 1 h every other day at the spot where the air intakes were located, generating a cloud of mist that extended 1–2 m beyond the height of these intakes (1.5 m above the grass surface). The isotope ratio of the irrigation water was -17.2‰.

b. Results

Figure 3 compares the ambient water vapor mixing ratios measured with the TDL system and the infrared gas analyzer. Here the TDL $H_2{}^{16}O$ span was calibrated against the dewpoint generator. Excellent agreement was observed on days 214 and 215. On days 216–218, the two measurements agreed well in the late morning and afternoon hours but showed significant discrepan-
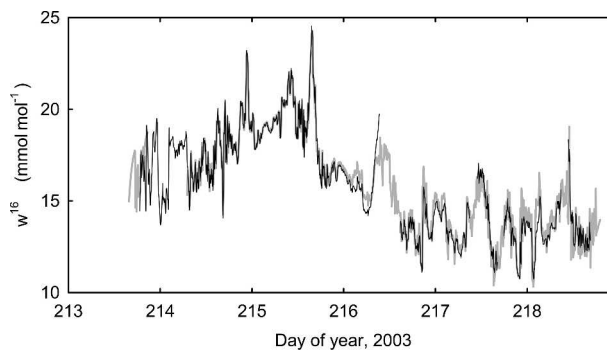
FIG. 3. Time series of 5-min-average water vapor volume mixing ratio measured with the TDL analyzer (solid line) and that measured with an infrared gas analyzer (gray line), at Logan, UT, on 1–6 Aug 2003 (days of year 213–218).

cies in the evening and early morning hours. This was most likely caused by condensation (and the subsequent evaporation) within the buffer volume of the TDL ambient air intake: on those days, the air temperature would drop below the dewpoint temperature early in the morning. The phase change within the sampling stream was obviously undesirable because it would alter the vapor isotope content. This was the reason why the buffer volume was heated in later measurements. (The sampling tube downstream of the critical orifice does not need heating because vapor pressure there is much lower than the ambient vapor pressure.) Excluding these periods suspected of condensation, a 1:1 relationship existed between the two measurements (Fig. 4).

Figure 5 plots all valid 15-s data on the ambient vapor isotope ratio. The measurement noise was on the order of 1‰ (Table 1), adequate to resolve the considerable variation in the time series. The isotope ratio was
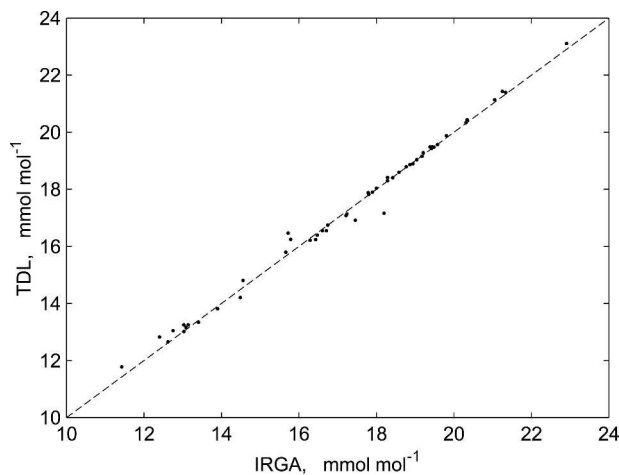
FIG. 4. A scatterplot of 1-h-average water vapor volume mixing ratio measured with the TDL analyzer against that measured with an infrared gas analyzer at Logan, UT. Dashed line represents 1:1.
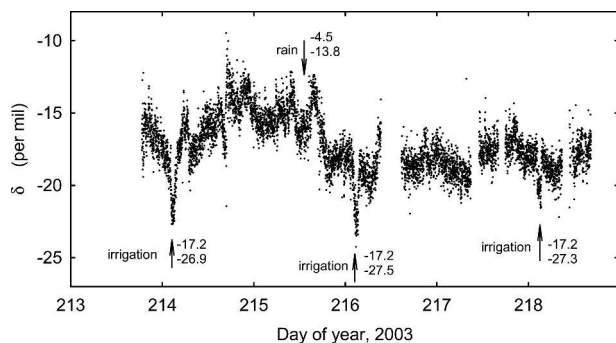
FIG. 5. Time series of 15-s isotope ratio of ambient water vapor measured with TDL, at Logan, UT, on 1–6 Aug 2003 (days of year 213–218). Arrows mark sprinkler irrigation and a rain shower event. Top numbers next to the event arrows are isotope ratios (‰) of the irrigation water/rainwater (measured with a mass spectrometer) and bottom numbers are calculated isotope ratios (‰) of water vapor in equilibrium with the liquid water at the surface temperature.

reduced by 2‰–3‰ in the irrigation events, but did not drop down to the equilibrium value. Similarly, during the rain event, water vapor did not reach the state of equilibrium with the liquid phase. Consistent with other related studies (He et al. 2001; White and Gedzelman 1984; Jacob and Sonntag 1991), the water vapor isotope ratio was positively correlated with the $H_2^{16}O$ mixing ratio (Fig. 6).

The isotope ratio of the liquid water in the dewpoint generator was -8.51‰ at the end of the experiment. The corresponding equilibrium vapor isotope ratio was -19.02‰ according to Eqs. (4) and (5). In comparison, the TDL measurement in the last 6 h of the experiment

gave a reading of -19.35‰. The difference was within the uncertainty range for such a comparison (Table 2).

Figure 7 shows that the vapor isotope ratio of the dewpoint generator increased steadily with time over the experimental period, but at a much slower rate than that of the laboratory test (Fig. 2). The reason for the difference lies in the composition of the inflow air: in the Logan experiment the dewpoint generator was fed with room air whereas in the laboratory test it was fed with dry air.

To check the consistency of the TDL measurement, Fig. 7 also presents a comparison of the TDL measurement of the water vapor of the dewpoint generator with the Rayleigh distillation prediction. Two calculations were performed. First, the isotope ratio of room air entering into the generator water reservoir, R_i, was assumed to be the same as that of the ambient air measured by the TDL analyzer. Similarly, the room air was assumed to have the same mixing ratio of ambient air in order to obtain the mass flow rate of $H_2^{16}O$ entering into the reservoir, Q_i. The equilibrium vapor isotope ratio was computed backward in time according to Eqs. (2), (4), and (5) (Fig. 7, dashed line). Next, the calculation was repeated by adjusting R_i upward by 0.3‰ (solid line). The small change in R_i caused a much larger change of about 1‰ in the predicted vapor isotope ratio when projected 5 days back in time, due to the cumulative nature of the Rayleigh equation. Interestingly, from day 218 back to day 215 the second calculation (Fig. 7, solid line) produced a much better match with the TDL measurement of the dewpoint generator vapor isotope ratio. This suggests a possible -0.3‰ systematic error in the ambient isotope ratio measurement. Projected further back in time (days 213 and 214), the TDL measurement did not agree with either prediction. One possible explanation is that on
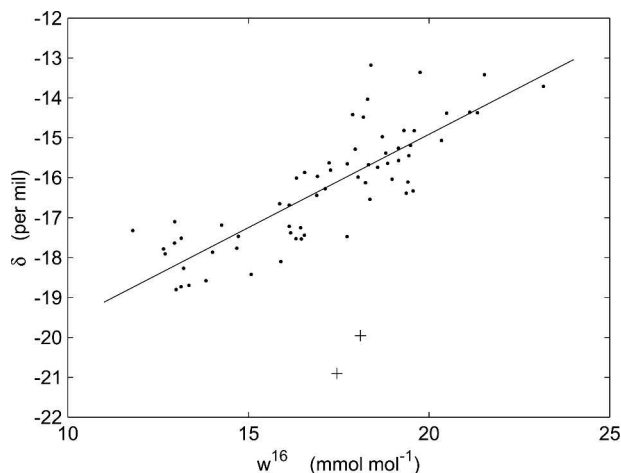

FIG. 6. A scatterplot of 1-h-average isotope ratio of ambient water vapor against $H_2^{16}O$ volume mixing ratio, at Logan, UT. Outliers (crosses) are observations influenced by irrigation. Solid line represents linear regression $\delta = 0.467w^{16} - 24.3$. Data suspected of condensation in the inlet buffer flask are excluded from the plot.
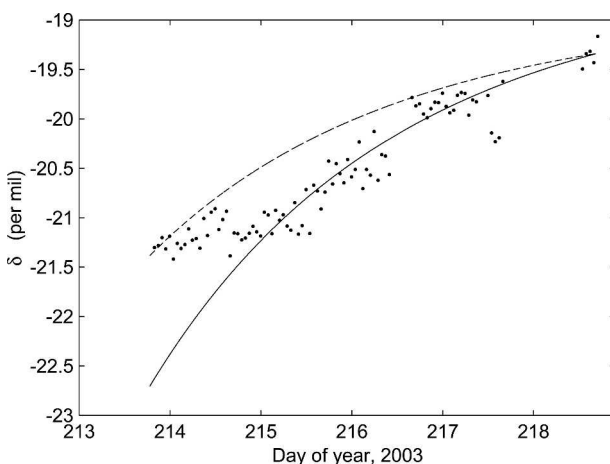

FIG. 7. Time series of 1-h-average isotope ratio of water vapor from a dewpoint generator, at Logan, UT, on 1–6 Aug 2003 (days of year 213–218). Lines represent prediction from the Rayleigh distillation principle with (solid line) and without (dashed line) a bias correction to the TDL measurement.

those humid days (Fig. 3) the air handling system of the laboratory that housed the TDL system had altered the room air mixing ratio and isotope composition to the extent that they could no longer be approximated by the ambient measurement.

One source of bias error had to do with pressure variations in the sample cell. When the TDL sampled the dripper air, its cell pressure was 0.01 mb higher than when it sampled ambient air, because the ambient intake tube was longer and hence more resistant to the flow than the dripper intake tube. Subsequent performance tests revealed that pressure variations had different effects on the two isotopes: a 1-mb increase in the sample cell pressure would increase the $H_2^{16}O$ sensitivity by 13% and $H_2^{18}O$ sensitivity by 10%. So a 0.01-mb imbalance in pressure between the calibration and the ambient measurement could result in a $-0.3‰$ error. This bias can be avoided by adjusting the bypass flow to eliminate the pressure variation (Fig. 1). Alternatively, it can be corrected with a correction factor that is proportional to the pressure difference in postfield data analysis.

Another source of error was impurity of the dry grade air (dewpoint temperature rating $< -62°C$ or <14 ppm at standard pressure) used in the Logan experiment, which could affect the ^{16}O and ^{18}O isotope measurements differently. This problem is minimized by use of ultra-high-purity nitrogen (water content rating <1 ppm) and a switching scheme that samples the zero air twice in one measurement cycle.

6. Discussion and conclusions

We have described a system for in situ measurement of $H_2^{16}O/H_2^{18}O$ in air based on tunable diode laser (TDL) absorption spectroscopy. The TDL analyzer alternates scans between $H_2^{16}O$ and $H_2^{18}O$ absorption lines to provide nearly simultaneous detection of their molar fractions. The scanning rate is 500 Hz and data are block averaged to 10 Hz for archiving and analysis. A typical measurement cycle lasts 60–80 s. Calibration of its isotope ratio is accomplished by a device that drips liquid water of known isotope ratio into dry air in an evaporating flask.

Laboratory tests showed that the instrument precision was dependent on humidity level: its 60-min precision (one standard deviation) was 0.21‰ at a water vapor volume mixing ratio of 2.67 mmol mol^{-1} (dewpoint temperature $-10.8°C$ at sea level) and improved to 0.09 at 15.3 mmol mol^{-1} (dewpoint temperature 13.4°C). The TDL measurement of the vapor generated by a dewpoint generator differed from the equilibrium prediction by $-0.11 \pm 0.43‰$ (mean $\pm$ one standard deviation). Its measurement of the ambient water vapor differed from the cold-trap/mass spectrometer method by $-0.36 \pm 1.43‰$. The larger noise of the latter comparison was caused primarily by the difficulty

in extracting vapor from air without altering its isotope content. In a 1-week test in Logan, Utah, in August 2003, the isotope ratio of water vapor in ambient air was positively correlated with the water vapor mixing ratio and also responded to wetting events (rain and irrigation) in an expected manner.

Settling time bias, instrument nonlinearity, water vapor density and pressure broadening effects, and pressure variations in the sample cell are potential sources of error. Strategies for dealing with these are discussed. It is possible that the instrument performance can be further improved if water for the dripping device is chosen to better match the isotope content expected of the ambient vapor and if the bypass flow is adjusted automatically to eliminate pressure variations associated with the valve switching.

The commercially available dewpoint generator was a useful tool for the TDL performance evaluation. However, it was not a perfect Rayleigh distillation device because the isotope content of its reservoir did not follow precisely the Rayleigh prediction. This problem must be overcome if a similar apparatus, where dry air enters into a liquid water reservoir and rises as bubbles, is to be used instead of the dripper for calibration. For long-term uninterrupted operation, the water reservoir must also be much larger than that in the dewpoint generator.

Our system differs from other published studies on the TDL technology for water isotopes in that we attempt to achieve an accuracy and precision comparable to that of a mass spectrometer and at the same time allow uninterrupted operation. We suggest that such high-frequency continuous measurement may open a new window on the hydrologic cycle, particularly processes involving phase changes of water, and can increase the power of the isotope method in ecological applications.

APPENDIX A

List of Symbols

m	Mass of liquid water in the dewpoint generator reservoir (mol)
Q	Mass flow rate of $H_2^{16}O$
R	Isotope molar ratio ($H_2^{18}O:H_2^{16}O$)
t	Temperature (°C) or time elapsed
x_i	Uncorrected TDL mixing ratio reading for intake i ($i = 1 - 4$)
w	Volume mixing ratio (mmol mol^{-1})
α	Fractionation factor, defined as the ratio of isotope fraction of the liquid to

that of the vapor phase ($\alpha \equiv R_l/R_v$)

δ	Isotope ratio in reference to VSMOW (‰); for $H_2^{18}O$ $\delta = (R/R_{vsmow} - 1) \times 1000$, where $R_{vsmow} = 0.0020052$
Subscript e	Exit flow
d	Dripper
g	Dewpoint generator
i	Inflow
l	Liquid water
o	Initial value
v	Water vapor
Superscript 16	$H_2^{16}O$
Superscript 18	$H_2^{18}O$

APPENDIX B

Derivation of the Rayleigh Distillation Equation for the Dewpoint Generator

To derive Eq. (2), we note that $H_2^{16}O$ and $H_2^{18}O$ masses m and m^{18} in the reservoir follow the rate equations

$$\frac{dm}{dt} = Q_i - Q_e \quad \text{and} \quad \text{(B1)}$$

$$\frac{dm^{18}}{dt} = Q_i R_i - Q_e R_l/\alpha. \quad \text{(B2)}$$

The time rate of change of the liquid isotope molar ratio is given by

$$\frac{dR_l}{dt} \equiv \frac{d(m^{18}/m)}{dt} = \frac{1}{m}\frac{dm^{18}}{dt} - \frac{R_l}{m}\frac{dm}{dt}. \quad \text{(B3)}$$

Substituting Eqs. (B1) and (B2) into Eq. (B3), we have

$$\frac{dR_l}{a - bR_l} = \frac{dt}{m}, \quad \text{(B4)}$$

where $m = m_o + (Q_i - Q_e)\,t$ from Eq. (B1), and a and b are two constants defined in the main text. Integrating Eq. (B4) and making use of the initial condition

$$R_l = R_{l,o} \quad \text{at} \quad t = 0,$$

we obtain Eq. (2).

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