10.12 IN-SITU MEASUREMENT OF WATER VAPOR ISOTOPES FOR ATMOSPHERIC AND ECOLOGICAL APPLICATIONS

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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., IAEA/WMO Global Precipitation Network). 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. 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 years, but with a rather coarse time resolution of 24-48 hr.

Prior 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 or more commonly, via cold traps made of glass tubes or canisters containing metal balls. Collection efficiency depends on the actual design and temperature of the trapping device and on air humidity, and varies from 60% to nearly 100%. If collection efficiency is not perfect, the collected vapor will be heavier than the ambient vapor because heavier isotopes are preferentially condensed out of the air stream. It has been showed that even a tiny fractional loss of 0.6% could bias the measurement by 7.5 per mil for HDO and 0.64 per mil for $H_2{}^{18}O$.

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 ambient air is likely to experience homogeneous nucleation where ice crystals form in air and get carried away by the air stream 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 Unpublished experiments by the third author suggest that the growth rate of these small crystals is diffusion limited.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 net result is that both insufficient cooling and excess 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.

In the second step, the collected water is analyzed for its isotope ratio on a mass spectrometer. A typical precision is 1 and 0.1 per mil for HDO and $H_2{}^{18}O$, respectively. The overall precision and accuracy of the vapor isotope measurement are limited by both the performance of the analytical instrument and the collection procedure, the later of which depends on the ambient humidity and the collection temperature.

In this paper we describe a system for in-situ measurement of $H_2{}^{16}O$ / $H_2{}^{18}O$ in air based on tunable diode laser (TDL) absorption spectroscopy. The system is designed to overcome several technical difficulties we have anticipated for the realtime 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. Secondly, 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 mid-latitudes. Thirdly, high polarity of water molecules results in sticking on walls, damping the instrument's time response. Finally, the high precision called for by the

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isotope ratio measurement requires a calibration gas standard, which is not available commercially.

We suggest that such realtime 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 gust, boundary layer entrainment, land/sea breeze circulation, and 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 airmass.

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. A few researchers have measured the flux isotope ratio of evapotranspiration using the micrometeorological flux-gradient method. 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 approach reported in this study may overcome this problem.

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 to a sample cell and absorption strength is calibrated against that of a standard sample in a reference cell to give the isotope ratio. In an aircraft campaign 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 per mil ($H_2^{18}O$). 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

2.1 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.

The analyzer software has recently been modified to alternate its spectral scans between two nearby absorption lines, allowing it to measure isotopic ratios in carbon dioxide (Bowling et al. 2003), and has been used to measure isotopic CO_2 fluxes (Griffis et al. 2004). In our system the lead-salt diode laser was chosen to scan the $H_2^{16}O$ and $H_2^{18}O$ absorption lines at 1500.546 cm^{-1} and 1501.188 cm^{-1}, respectively. The laser is cooled by liquid nitrogen and is controlled at a temperature of 91.2 K. The operating pressure is 12 hPa.

2.2 Calibration

The analyzer used ultra high purity nitrogen as a zero gas. A dripping device, termed dripper hereafter, was used to generate a span calibration standard. Water of known isotope ratio was dripped into an evaporating chamber that was fed with dry air. The dry air flow rate was controlled so that the moist air exiting the chamber had an $H_2^{16}O$ 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. Care was taken to ensure that water dripping into the chamber evaporated instantly. Thus, the isotope ratio of the moist air exiting the chamber was identical to that of the liquid water feed.

3 LABORATORY PERFORMANCE TESTS

3.1 Precision

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

3.2 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. At the beginning of each test, the dewpoint generator reservoir was flushed several times with water of known isotope ratio before being filled with the water of the same isotope composition. Its inlet was fed by ultra zero-grade air and outlet was connected to intake 4 of the TDL analyzer. Each test lasted 24-50 hrs. At the end of the test, water was withdrawn from the reservoir and was analyzed for its isotope ratio by a mass spectrometer.

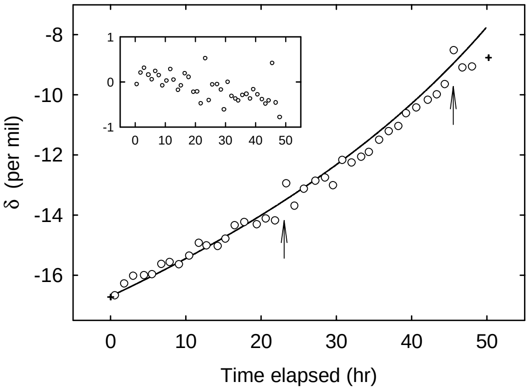

Figure 1: Comparison of the measured isotope ratio of water vapor (circles) generated by a dewpoint generator at a temperature of 15°C with that predicted from the Rayleigh distillation equation (solid line). Crosses indicate isotope ratio of water vapor in equilibrium with the liquid water in the generator. Inset: Departure of the measured isotope ratio from the predicted value.

Three comparisons were made with the data collected. First, the first valid hourly TDL observation was compared with the equilibrium calculation. The difference between the measured and calculated isotope ratios was 0.10±.27 (mean ± one standard deviation).

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 per mil, 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 per mil if all the data 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. An example was given in Fig. 1. 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 per mil; (iii) The TDL measurement was noisy right after refill of the TDL detectors' liquid nitrogen dewars, causing two outliers at 25 and 45 hr; (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. 1 inset).

3.3 Comparison with the cold-trap method

In this comparative study, the TDL system drew ambient air via intake 4 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 averaged to hourly intervals for comparison with the cold trap method.

A total of 12 vapor samples were collected, using the canisters described by He et al. (2001), on three days in December 2003, spanning a range of $H_2^{16}O$ volume mixing ratio of 2.98 to 8.14 mmol mol^{-1}. The canisters were cooled by dry ice. 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. The weight of the collected water sample was within 10% of that expected from the ambient mixing ratio, flow rate, air temperature and pressure.

The difference between the TDL measurement and the cold trap method was -1.77 ±1.75 per mil. Correction to the cold trap data for water vapor loss resulted in a much improved agreement (-0.36±1.43 per mil), underscoring the difficulty in obtaining high-precision measurements with the cold trap method as discussed in section 1.

4 A FIELD TEST

4.1 Experimental setup

A field test was performed in Logan, Utah from August 1-6, 2003. The isotope ratio measurement was calibrated against dry grade air for zero offset and the moist air generated by the dripper for span. 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 dewpoint generator was fed by room air and had its temperature set at 10^{o}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., Lincoln, NE) was used to measure the water vapor mixing ratio in ambient air.

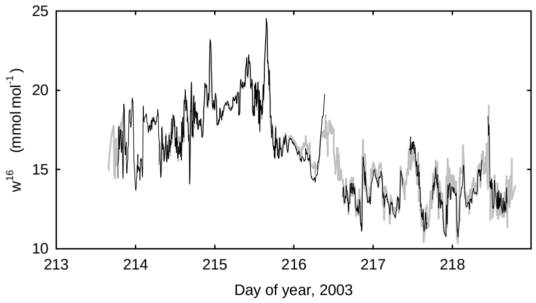

Figure 2: Time series of 5-min average water vapor volume mixing ratio measured with the TDL analyzer (solid line) and that measured with an infrared gas analyzer (gray line), Logan, Utah, August 1--6 (day of year 213-218), 2003.

Weather during this period was dry except for a 3 hr storm on day 215 (August 3) that produced 7 mm of rain (isotope ratio -4.5 per mil). A sprinkler irrigation system would run for about 1 hr 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 per mil.

4.2 Results

Fig. 2 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 discrepancy 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, 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.

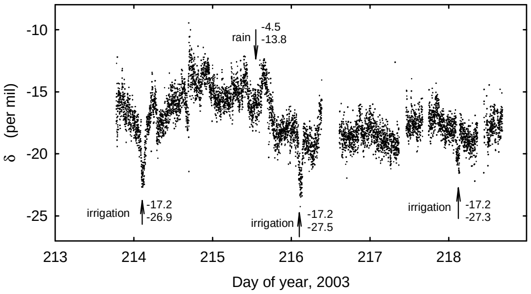

Figure 3: Time series of 15-s isotope ratio of ambient water vapor, Logan Utah, August 1--6 (day of year 213-218), 2003. Arrows mark sprinkler irrigation and a rain shower event. Top numbers next to the event arrows are isotope ratios (per mil) of the irrigation water/rainwater and bottom numbers are isotope ratios (per mil) of water vapor in equilibrium with the liquid water at surface temperature.

Fig. 3 plots all valid 15-s data on the ambient vapor isotope ratio. The measurement noise was on the order of 1 per mil, adequate to resolve the considerable variation in the time series. The isotope ratio was reduced by 2-3 per mil 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 the published studies, the water vapor isotope ratio was positively correlated with the water vapor mixing ratio (data not shown).

The isotope ratio of the liquid water in the dewpoint generator was -8.51 per mil at the end of the experiment. The corresponding equilibrium vapor isotope ratio was -19.02 per mil. For comparison, the TDL measurement in the last 6 hours of the experiment gave a reading of -19.35 per mil. The difference was within the uncertainty range for such a comparison.

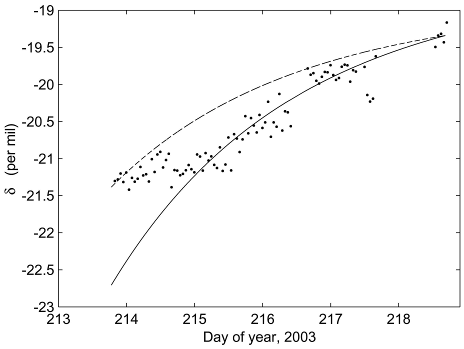

Figure 4: Time series of 1-hr average isotope ratio of water vapor from a dewpoint generator, Logan, Utah, August 1-6 (day of year 213-218), 2003. Lines represent two predictions from the Rayleigh distillation principle.

Fig. 4 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. 1). 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.

5 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 is 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 per mil at a water vapor volume mixing ratio of 2.67 mmol mol^{-1} and improved to 0.09 at 15.3 mmol mol^{-1}. The TDL measurement of the vapor generated by a dewpoint generator differed from the equilibrium prediction by -0.11±0.43 per mil. Its measurement of the ambient water vapor differed from the cold-trap/mass spectrometer method by -0.36±1.43 per mil. 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 one-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.

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.

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