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A rapid and precise method for sampling and determining the oxygen isotope ratio of atmospheric water vapor

Brent R. Helliker[1]*, John S. Roden[2], Craig Cook[1] and James R. Ehleringer[1]

[1]SIRFER, 257 S. 1400 E., Department of Biology, University of Utah, Salt Lake City, UT 84112, USA
[2]Department of Biology, Southern Oregon University, Ashland, OR 97520, USA

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A quantitative method for cryogenically sampling atmospheric water vapor on the temporal scale of 10 to 15 min in the field or laboratory is described. The sample apparatus is lightweight, affordable, and easy to assemble. The method allows for H_2O:CO_2 equilibration within the same sampling tubes and hence increases turnaround time for $\delta^{18}O$ analysis. Quantitative analysis in the laboratory showed recovery of a vaporized, known, ^{18}O water standard to 0.2‰ precision. Copyright © 2002 John Wiley & Sons, Ltd.

In biosphere-atmosphere exchange and atmospheric micrometeorology studies, accurate measurement of the $\delta^{18}O$ of water vapor in air is an integral component.[1–7] Water vapor $\delta^{18}O$ has large feedback effects on leaf water and soil water enrichment of ^{18}O.[1,4,6,7] Plant and soil fluxes of water vapor can differentially affect both the concentration and isotope ratio of atmospheric water vapor.[5,8,9] Measurements of atmospheric water vapor concentration and isotope ratios, coupled with isotope measurements of liquid water (e.g. soil water), allow for determinations of whole ecosystem water fluxes.[5] Lastly, studies of atmospheric water vapor $\delta^{18}O$ have determined that plant evapotranspiration can be the primary contributor to precipitation over areas as vast as the Amazon basin.[2]

Previous methods of sampling atmospheric water vapor required long sampling periods, extensive field apparatus and/or extensive laboratory preparation before mass spectrometric analysis.[3–6] A modification of a method for atmospheric water vapor sampling that works well in leaf-level gas-exchange systems[7] and in field collections (data presented in this synthesis) is described here. This method allows for quick sampling and fast preparatory times for isotope analysis, reduces the possibility of evaporative enrichment during sampling, yet produces reliable, high precision values.

System description, sampling procedure and mass spectrometric analysis

Assembly 1 was composed of (see Fig. 1(A)): (a) 6 mm (o.d.; 1/4 in.) Cajon Ultra-Torr adapter bored through, (b) 9 mm (o.d.; 3/8 in.) Swagelok Union Tee, (c) 6 mm (1/4 in.) Cajon Ultra-Torr adapter, (d) 9 mm (3/8 in.) Cajon Ultra-Torr adapter. A 200 mm long, 9 mm diameter, closed-bottom glass tube was attached to the 9 mm end of assembly 1 (part d). A 300 mm long, 6 mm diameter open-ended glass tube was fitted through assembly 1, which rested about 20 mm above the bottom of the outer 9 mm tube. The sampling apparatus was then attached to collection tubing (via c on assembly 1). The tubing leading to the pump was attached to the upper portion of the 6 mm tubing. The glass tubing was then placed in a dewar of crushed dry ice or dry ice/ethanol slush, so that the freezing line was 30 mm below assembly 1. Air was pulled through the apparatus such that water vapor condensed on the external portion of the 6 mm tube and the internal portion of the 9 mm tube. After the sampling period, the pump was turned off and the apparatus was removed from the dewar and was allowed to approach ambient temperature to avoid any condensation of outside air within the sampling apparatus. After this time, both tubes were removed from assembly 1, the 6 mm tube was scored and broken so that the broken portion, the portion where water had condensed, resided entirely inside the 9 mm tube. The 9 mm sample tube was then covered with a rubber stopper/septum and wrapped in Parafilm. At this point the samples could be transported back to the laboratory for CO_2:H_2O equilibration.

Pure CO_2 was injected into the 9 mm sample tube through the rubber stopper/septum to bring the [CO_2] to 10% within the tubes. 50 μL of two laboratory water standards (SHOW, −3.2‰ and BSLC, −15.5‰, on the SMOW scale) were injected through septa into separate 9 mm, standard tubes. All samples were then allowed to equilibrate for 48 h[10] at room temperature. A subsample (400 μL) of air from each 9 mm glass tube was then injected into the helium carrier stream of an elemental analyzer (EA) that was upstream and in series with the isotope ratio mass spectrometer in continuous flow mode (CF-IRMS). This EA-CF-IRMS meth-

*Correspondence to: B. R. Helliker, Carnegie Institution of Washington, Dept. of Plant Biology, 260 Panama St., Stanford, CA 94305, USA.

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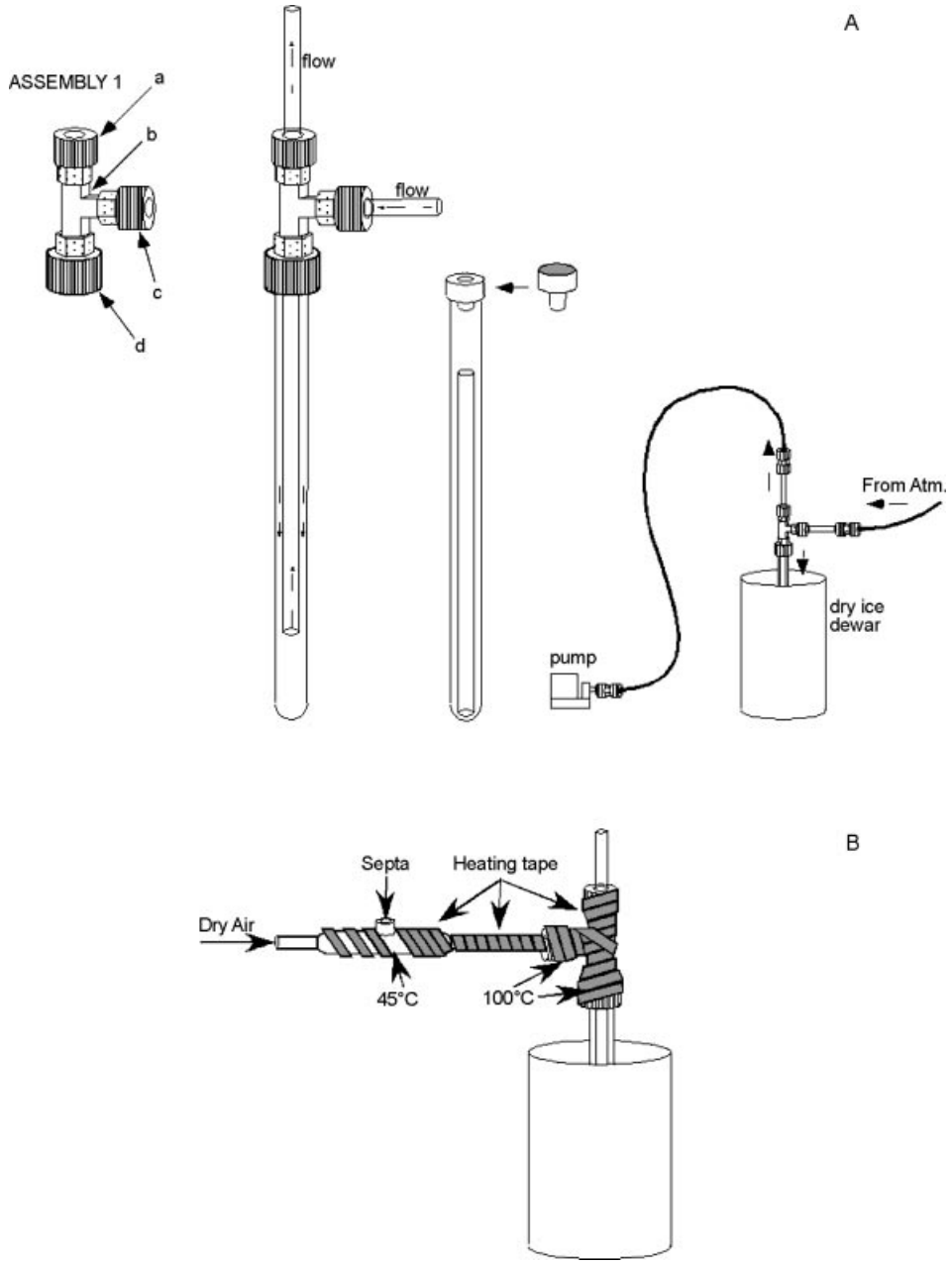

Figure 1. Diagram of the water vapor sampling apparatus. Details are explained in the text.

od, and the necessary operational modifications, are detailed in full in Helliker and Ehleringer.[11] For every 10 samples injected, one of each of the laboratory standards was injected. The isotope ratios of the samples were then corrected by a linear function of the offset of the two known standard values.

Table 1. $\delta^{18}O$ of water vapor extracted in the laboratory quantification. The $\delta^{18}O$ of water injected was -15.5‰ (SMOW scale)

	Flow rate		
	100 cc m^{-1}	250 cc m^{-1}	850 cc m^{-1}
$\delta^{18}O$ vapor (‰)	-15.5 ± 0.2	-15.5 ± 0.2	-15.6 ± 0.2

Laboratory performance

A laboratory method was developed to quantitatively test the efficacy of the water vapor collection apparatus. The line inlet was connected to a drying tube containing magnesium perchlorate [$Mg(ClO_4)_2$] which led to a stainless steel loop (three iterations) which was placed in a dry-ice/ethanol slush. The purpose of this portion of the line was to extract all lab water vapor from the incoming air. The line then led to a 190 mm long glass tube with a septum port situated as a T-junction about midway along the tube (Fig. 1(B)). The water vapor apparatus was connected to the septated glass tube at the end opposite the dry air inlet such that air flow through the apparatus was as detailed in Fig. 1, and a water sample could be injected into the air stream via the septa. Heating tape was wrapped variably from the septum to the sampling apparatus to develop a temperature gradient from the

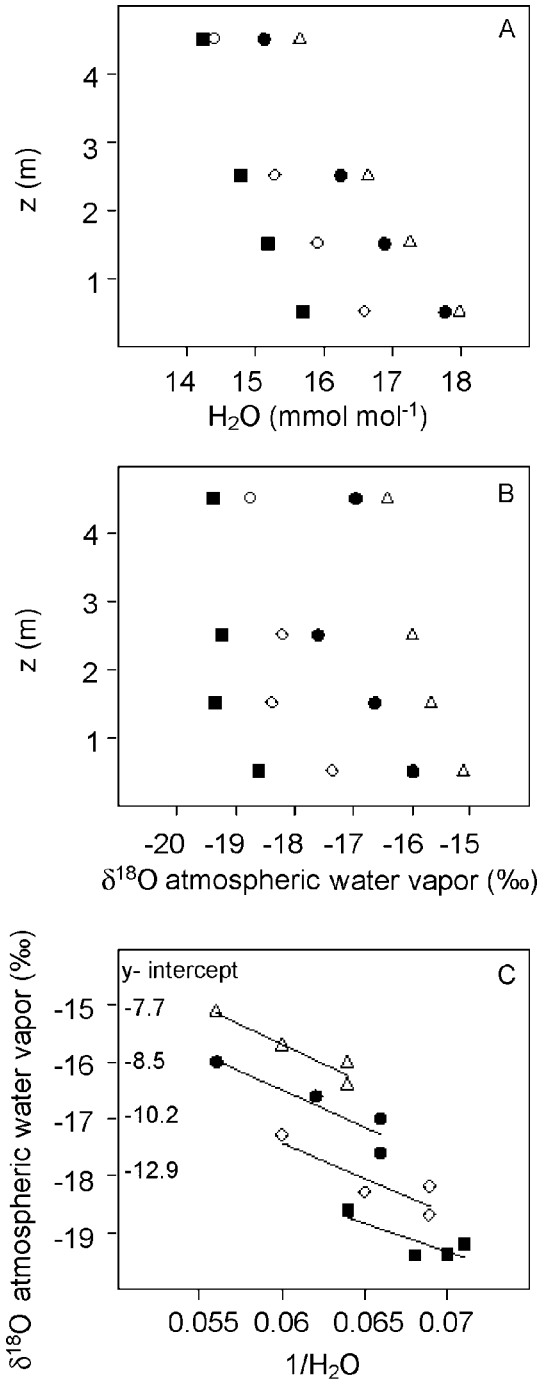

Figure 2. Atmospheric measurements of water vapor [H_2O] and $\delta^{18}O$ at a tall-grass prairie site in Oklahoma. (A) Height profile of [H_2O]. (B) Height profile of water vapor $\delta^{18}O$. (C) Diurnal Keeling plots of $\delta^{18}O$ versus 1/[H_2O]. Symbols for all plots and line equations for (C) are as follows: (■) 10:00; $-92.4x - 12.9$ $r^2 = 0.70$; (◊) 12:00; $-120.6x - 10.2$ $r^2 = 0.80$; (●) 14:00; $-133.8x - 8.5$ $r^2 = 0.81$; (△) 16:00; $-134.0x - 7.7$ $r^2 = 0.91$.

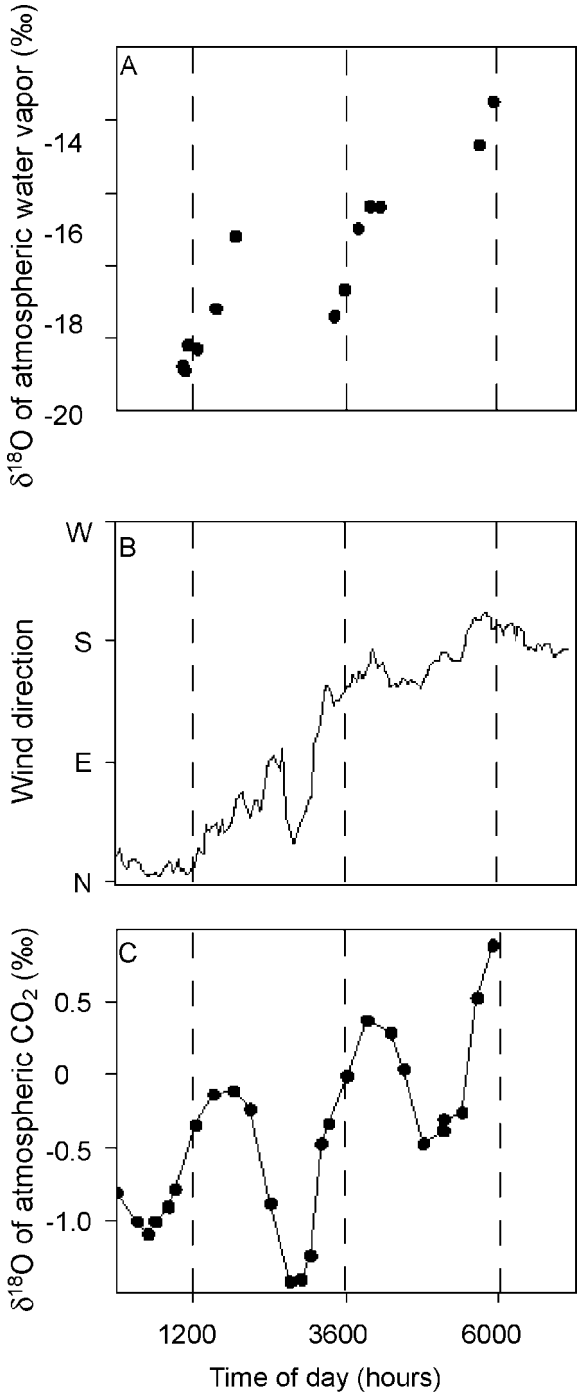

Figure 3. Diurnal measurements of (A) the $\delta^{18}O$ of atmospheric water vapor, (B) wind direction, and (C) the $\delta^{18}O$ of atmospheric CO_2 at 4.5 m above a tall-grass prairie in Oklahoma. Dashed lines represent midday.

septum to the sampling apparatus. The temperature of the septated glass tube, at the septum, was approximately 45 °C and the temperature at the base of assembly 1, where the 9 mm tube attached, was approximately 100 °C. After the tubes of the sampling apparatus had equilibrated with the dry-ice/ethanol slush, 50 μL of the BSLC working standard were injected into the septum.

Water vapor collections were made in this manner at three flow rates (n = 5 at each flow rate) and the results are presented in Table 1. The isotope ratios of the water vapor collected at each flow rate were not significantly different from the known standard (−15.5‰) and statistically indistinguishable from each other. Precision of these measurements was 0.2‰. Crushed dry ice and dry ice/ethanol

maintained temperatures of −79 and −78 °C, respectively, in the sampling tube. At these temperatures, and considering the flow rates and absolute humidity in this sampling system (maximum relative humidity of 36% at a flow of 850 cc m^{-1}), the fraction of vapor lost would be no greater than 0.013%, resulting in an isotopic offset from the standard of approximately 0.03‰ (calculations from Ref. 3), which is less than the precision of the mass spectrometer for the equilibration method.

Field performance

The sampling apparatus was tested in the field and proved to work well in picking up small differences in the $\delta^{18}O$ of water vapor at various heights above a tall-grass prairie canopy in north-central Oklahoma. By measuring water vapor concentration and isotope ratios at increasing height (z) from the plant canopy, one can determine the overall effect that the canopy is having on the background atmospheric water vapor and isotope ratios.[5,12] Figures 2(A) and 2(B) show a height versus water concentration profile and the corresponding height versus $\delta^{18}O$ of the water vapor profile. The gradual increase in whole-profile $\delta^{18}O$ and $[H_2O]$ suggest the increasing contribution of plant transpiration (assumed approximately equal to source water, −3.6‰ if plants were at isotopic steady-state) to the atmosphere. Figure 2(C) shows Keeling-type plots[5,12] of $\delta^{18}O$ versus $1/[H_2O]$. The y-intercepts became increasingly positive throughout the day, from −12.9 at 10:00 to −7.7 at 16:00. The diurnal trend of increasing intercepts could imply that either the proportion of total flux that came from the plant transpiration increased during the day, or that the plant evapotranspiration was slowly approaching isotopic steady-state conditions through the day. If the former is assumed, then the final intercept of −7.7‰ would suggest that plant transpiration accounted for nearly 80% of the ecosystem derived water vapor signal (assuming soil water vapor flux equals the modeled value of −21.7‰). If the latter is assumed, then separating the ecosystem water flux becomes more difficult without direct soil and leaf water vapor flux measurements.

Figure 3(A) shows three consecutive diurnal course measurements of atmospheric water vapor measured at one height (4.5 m) over the tall-grass prairie site.[13] The same daily pattern is observed over all 3 days, presumably due to the buildup of plant evapotranspired water causing the water vapor signal to become more positive throughout the day. While the daily pattern was similar across days, the midday value (represented by dashed lines) became progressively more ^{18}O enriched over the course of the 3 days. Figure 3(B) shows a 180° shift in wind direction that corresponds to the shift in midday water vapor $\delta^{18}O$. Figure 3(C) shows a diel course of $\delta^{18}O$ of atmospheric CO_2 collected at the same height as the water vapor samples (CO_2 flask samples were always taken a few minutes before water vapor measurements to avoid isotope and concentration errors associated with dry ice sublimation). The CO_2 diel march showed the same trend as the water vapor diel march, which has two possible explanations: (1) with a change of wind direction the background signal of both water vapor and CO_2 changed, or (2) with a change in wind direction the water vapor signal changed and caused feedback effects on the $\delta^{18}O$ of CO_2 fluxing from the ecosystem. Regardless of the mechanism, Fig. 3 shows the importance of sampling the $\delta^{18}O$ of atmospheric water vapor in ecosystem plant-atmosphere gas-exchange studies.

For water vapor $\delta^{18}O$ data presented in Figs 2 and 3, sampling flow rates were 250 cc m^{-1}, which was effective at relative humidity ranging from 53 to 75%. Collection times never exceeded 12 min. Early field trials, where flow rates exceeded 600 cc m^{-1} and relative humidity was above 60%, showed obvious signs of incomplete water vapor collection. For example, several Keeling plot intercepts were in the order of −50 to −77‰ in $\delta^{18}O$. It is suspected that flow rate was not a problem in the laboratory quantification (Table 1) because absolute humidity was never very high due to the small volume (50 μL) of water injected into the system.

The water vapor trapping method presented here is a highly compatible system that can be used in a wide range of applications. These applications include, but are not limited to, plant gas-exchange experiments, ecosystem-level CO_2 and H_2O exchange studies, frontal airmass modification by (and feedback to) underlying vegetation, and variable scale hydrological studies. The quick sampling times and the rapid preparatory times from sampling to mass spectrometric analysis allow for a large number of samples to be processed, which represents a significant improvement over previous methods and should help further our understanding of biosphere-hydrosphere interactions on a multitude of scales.

Acknowledgements

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