

Short communication

A simple, accurate, field-portable mixing ratio generator and Rayleigh distillation device

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ABSTRACT

Routine field calibration of water vapor analyzers has always been a challenging problem for those making long-term flux measurements at remote sites. Automated sampling of standard gases from compressed tanks, the method of choice for CO₂ calibration, cannot be used for H₂O. Calibrations are typically done manually with a dew point generator, and as a consequence are done less frequently, degrading the accuracy and utility of H₂O flux data. To remedy this, we have designed, built and tested a field-portable mixing ratio generator, also including features that facilitate its use in water vapor isotope research. It consists of an aluminum cell, with a usable capacity of 80 cm³, that is coupled to a Peltier heater/cooler and encased in insulation. The temperature of water in the cell is monitored with a thermocouple and a pressure transducer is used to measure the cell pressure. A data logger uses this information to compute the mixing ratio in the cell and control the polarity and duty cycle of the power input to the Peltier block in order to drive the system toward the desired mixing ratio and to maintain it. Incoming air enters through a bubbler and the exiting air is directed to the gas analyzer. A separate fitting mates to a syringe, allowing easy filling and draining of the cell. The cost of the components, exclusive of the data logger, is approximately 1100 USD. Power consumption is low, on the order of 10 W, facilitating use at remote sites. As a consequence, the response time of the instrument is relatively slow, but could be substantially improved for situations where dynamic response is more important than power consumption. Testing has shown that the unit is accurate over a broad range of mixing ratios, able to compensate for changes in ambient pressure, and stable for long periods of time. In addition, it has been used to generate Rayleigh distillation plots, demonstrating its utility for routinely checking the performance of water vapor isotope lasers.

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1. Introduction

1.1. Background

Evapotranspiration (ET) is a primary conduit for energy transfer between the biosphere and the atmosphere, in the process providing the return flow that completes the hydrologic cycle. In the atmosphere, ET affects boundary layer growth and cloud development. On the ground, it can be a key determinant of ecosystem function, since biomass accumulation is directly proportional to transpiration when normalized by the vapor pressure deficit (Tanner and Sinclair, 1983). Crop models, hydrologic models, and coupled climate models all must be concerned with properly parameterizing and predicting ET. Thus it is not surprising that scientists from a broad variety of disciplines have long had an interest

in collecting data sets of accurate ET measurements from diverse environments.

The explosive increase in CO₂ flux measurement sites around the globe (e.g., Ameriflux, AsiaFlux, CarboEurope, Fluxnet Canada),¹ primarily driven by carbon cycle and climate change concerns, potentially offers the ancillary benefit of a rich bed of ET data, since latent heat flux is concurrently measured at virtually all of the more than 500 CO₂ flux sites. In fact it could be argued that these data may ultimately be at least as valuable as the CO₂ flux data, both for validation of climate models and for tracking the impact of a changing climate. To this point however, the ET data from these flux networks have not been widely used. One reason may be a lack of confidence in its accuracy, relative to the CO₂ data. Nearly all sites use the eddy covariance method for their gas exchange measurements, and the most trusted CO₂ data seem to be those from sites using closed-path infrared gas analyzers (IRGAs), because calibration gas tanks can

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¹ <http://public.ornl.gov/ameriflux/>, <https://db.cger.nies.go.jp/asiafluxdb/>, <http://www.carboeurope.org/> and <http://www.fluxnet-canada.ca/>.

be readily plumbed into such systems, permitting frequent, routine recalibration of the analyzers. This, however, is not possible for water vapor due to condensation upon compression. Consequently, water vapor calibrations are generally either done manually on an infrequent basis with a dew point generator, or indirectly by comparing mean concentrations against co-located humidity sensors (e.g. Berger et al., 2001). The need for better water vapor calibration procedures has been clearly stated by Loescher et al. (2009). Further, with the recent development of field-portable laser spectroscopy systems that can measure the stable isotopologues of water vapor (Lee et al., 2005; Wang et al., 2009; Sturm and Knohl, 2009), there is also a role for devices that can provide a source of air with a known, controlled mixing ratio and isotope composition.

1.2. Theory

The mixing ratio of water vapor in air is given by:

$$\chi = 1000 \frac{e}{P - e} \quad (1)$$

where e is the vapor pressure and P is the total pressure, and the quotient is multiplied by 1000 as a convenience so that χ is expressed in mmol mol^{-1} . If a moving stream of air is saturated at a particular pressure P^* and temperature, T^* , its vapor pressure at that point, e_s^* , is primarily a function of temperature, with a very slight dependence on pressure, expressed in the following equation (Buck, 1981; Ham, 2005), with e_s^* and P^* in kPa and T^* in $^{\circ}\text{C}$:

$$e_s^* = (1.0007 + 3.46 \times 10^{-5} P^*) 0.61121 \exp \left(\frac{17.502 T^*}{T^* + 240.97} \right) \quad (2)$$

The mixing ratio at the point of saturation can thus be computed from P^* and e_s^* , using Eq. (1). Downstream, the mixing ratio will be conserved regardless of changes in P and T , provided that there is no point at which the local combination of P and T causes the vapor pressure in the air stream to reach the local saturation vapor pressure, which would induce condensation. A mixing ratio generator can be envisioned as a chamber in which flowing air equilibrates with water at a known (measured) temperature and pressure. The capability of generating a specific desired mixing ratio requires that at least one of the measured variables be controlled; if it is necessary to produce air at a specified mixing ratio and dew point, then both temperature and pressure must be controlled. Cortes et al. (1991) described a vapor pressure generator, in which they controlled chamber gauge pressure with a two-stage regulator and stabilized the chamber temperature by immersing it in a water bath, limiting its use to the laboratory. A widely used dew point generator (LI-610, Licor Inc., Lincoln, NE) controls temperature in a bubbling chamber to produce a desired dew point. It is quite accurate, but its cost (>7000 USD) and power consumption (up to 60 W) preclude its routine use at multiple remote field sites. Our goal was to develop a rugged, inexpensive, yet accurate mixing ratio generator that operates on 12 VDC with minimal power draw, to function as a virtual calibration tank for water vapor analyzers at field sites. To facilitate its use for Rayleigh distillation tests of H_2O isotope lasers, an additional criterion was imposed – easy filling and draining of the water in the generator.

The isotope composition of the generated water vapor can be predicted based on the Rayleigh distillation principle (Lee et al., 2005; Wen et al., 2008):

$$R_v = \frac{R_{l,0}}{\alpha} \left(\frac{m}{m_0} \right)^{(1/\alpha)-1} \quad (3)$$

where R_v is the molar isotope ratio of the water vapor (D/H or $^{18}\text{O}/^{16}\text{O}$), and $R_{l,0}$ is the initial molar isotope ratio of the liquid water used to fill the mixing ratio generator, m_0 and m are the initial mass of water and the residual mass of water, respectively. Assum-

ing that the air in the mixing ratio generator is saturated, then α is equal to the temperature-dependent equilibrium fractionation factors for D/H or $^{18}\text{O}/^{16}\text{O}$ (Majoube, 1971). The residual mass can be predicted with high accuracy knowing the dry air flow rate and the difference in mixing ratios between the incoming and outgoing air streams, so that R_v can be predicted forward in time.

2. Materials and methods

The components of the mixing ratio generator include an aluminum chamber, a thermoelectric cooler, a porous frit, a temperature sensor, a pressure transducer, and a data logger (Fig. 1). The chamber was milled from a solid block of aluminum, 10 cm \times 9 cm \times 6 cm. The internal chamber is cylindrical, 50 mm in diameter and 75 mm deep, with a rounded bottom surface to eliminate any areas where water might stagnate. At the bottom of the chamber there are two holes. One is tapped to accept a 1/16" NPT stainless steel luer fitting, to which a syringe can be attached for accurate quantitative filling and draining of the chamber with deionized water. The other hole is tapped for a 1/8" NPT to Swagelok union. The center of this fitting is drilled to accept a frit, punched from a sheet of porous stainless steel with an effective pore size of 25 μm . This fitting is connected to a tank of dry air. At the top of the chamber there is a tee fitting, with one leg connected to an absolute pressure transducer (Vaisala PTB101B or similar). The other leg provides the output air stream and is connected to a needle

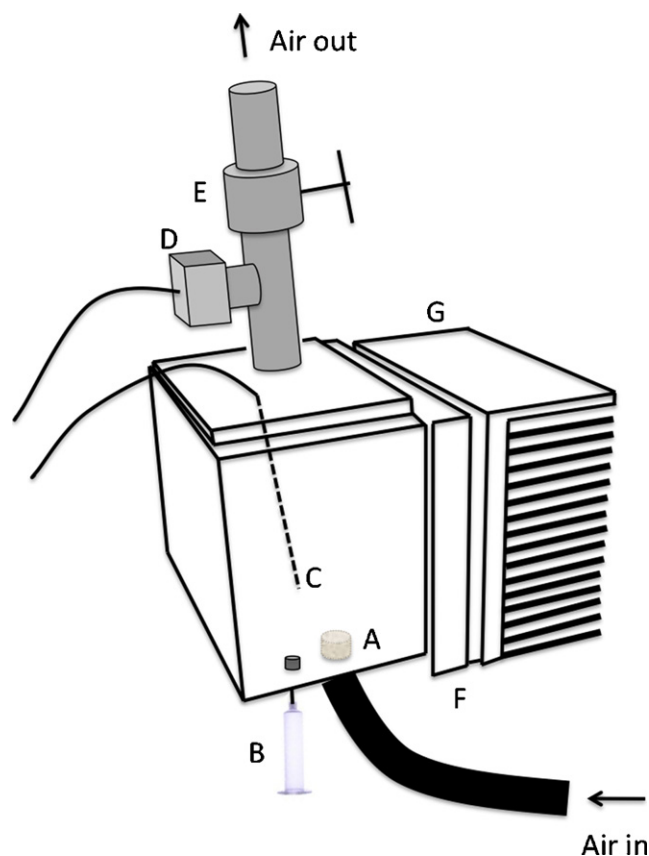


Fig. 1. Schematic of the mixing ratio generator. Incoming air passes through a stainless steel frit (A) creating bubbles in the water within the aluminum cell. Water is added to and removed from the cell with a syringe (B). Cell temperature is measured with a chromel-constantan thermocouple (C), and cell pressure is measured with pressure transducer (D). A needle valve (E) is used to restrict flow. It can be replaced with a back-pressure regulator if it is desirable to control both pressure and temperature. Temperature of the cell is controlled with a Peltier block (F) that is coupled to a fan-cooled heat sink (G). The water-filled cell is encased in rigid foam insulation.

valve. A copper bulb that extends down into the chamber contains a chromel-constantan thermocouple, made from wire that had been previously calibrated against a secondary standard platinum resistance thermometer (Baker et al., 2001). The chamber is attached by screws to a fan-cooled thermoelectric device (model CP-031, TE Technology, Traverse City, MI) and encased in 5 cm rigid styrofoam insulation. A mass flow controller that can be configured as a back-pressure regulator (Alicat MC Series, Alicat Scientific, Tucson, AZ) can be plumbed into the output side of the cell if it is necessary to control both pressure and temperature. We have verified that this works, but the results that are presented were all obtained without the pressure regulator in place, to simplify operation and minimize power consumption.

In operation, dry air from a tank is saturated at the water temperature as it bubbles up through it. A data logger (model 23X, Campbell Scientific, Logan, UT) records the water temperature and the cell pressure every 2 s, computes the mixing ratio, then specifies the polarity and duty cycle (between 0 and 1.8 s) of a DC power input to the Peltier device to drive the mixing ratio to the set point specified in the logger program by heating or cooling the cell. This is accomplished with a proportional-integral-difference (PID) control algorithm and two double-pole, double-throw relays (Baker et al., 2001). The mixing ratio set point is chosen with consideration of downstream pressures and temperatures to avoid subsequent condensation. The Ziegler–Nichols method (1942) was used to tune the PID coefficients. If a Rayleigh distillation test is to be performed, a molecular sieve must be attached to the outlet from the gas cylinder to remove residual water vapor, which can be present in tank air at concentrations as high as several hundred ppm. If the objective is simply calibration of a gas analyzer for mixing ratio the sieve is not necessary, nor is the air tank; instead a small pump can be used to supply filtered ambient air to the mixing ratio generator.

3. Results

3.1. Stability and accuracy

The absolute accuracy of this device depends upon the accuracy of the pressure and temperature measurements. An earlier exercise with infrared thermometry (Baker et al., 2001) indicated that this temperature measurement system has an absolute accuracy of approximately $\pm 0.2^\circ\text{C}$, and the specified accuracy of the pressure transducer is $\pm 0.15\text{ kPa}$. This translates to an uncertainty in χ of approximately $0.04\text{ mmol mol}^{-1}$ at a set point of 14 mmol mol^{-1} . The precision, or noise, of the unit was estimated by maintaining a set point of 14 mmol mol^{-1} over an 18 h period in which T , P , and χ were measured every 2 s, with means and standard deviations computed every 5 min. Fig. 2a shows how cell pressure (left axis) changed during the test due to changes in atmospheric pressure, and how the controlled cell temperature (right axis) changed in response to maintain the set point mixing ratio, which is plotted in Fig. 2b. The average value of the 5 min means was $13.9998 \pm 0.002\text{ mmol mol}^{-1}$, while the average value of the 5 min standard deviations was $0.0035\text{ mmol mol}^{-1}$.

Accuracy of the unit was assessed by routing the exit air to an infrared gas analyzer (LI-6262, Licor, Lincoln, NE) that was independently calibrated against a commercially available dew point generator (LI-610, Licor Biosciences, Lincoln, NE). The IRGA was calibrated prior to exposing it to each of six set point mixing ratios by first zeroing it with tank air that had been passed through a molecular sieve, then spanning it against the dew point generator, with a dew point chosen to generate a mixing ratio close to the current set point of the mixing ratio generator. The results, shown in Fig. 3, indicate that the mixing ratio generator and the dew point generator produce virtually identical air streams.

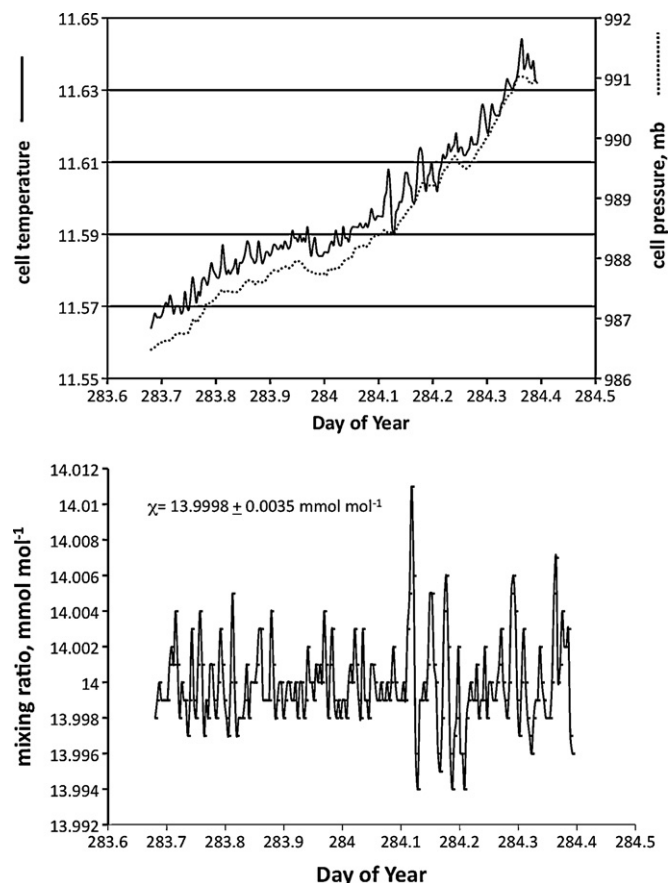


Fig. 2. (A) Cell temperature (solid line) and cell pressure (dashed line) during a 16-h period when the set point was maintained at 14 mmol mol^{-1} . Pressure was changing in response to ambient pressure changes, and the unit adjusted the temperature accordingly to maintain a stable mixing ratio, shown in (B).

3.2. Rayleigh distillation test

Fig. 4 shows an example of a Rayleigh test conducted under laboratory conditions for a period of about 18 h with a mixing ratio set to 18 mmol mol^{-1} (dew point temperature of 15.2°C). In this test, a tunable diode laser (TDL, TGA200, Campbell Scientific Inc, Logan, Utah, USA) was used to measure the isotope ratio of the water vapor in the air stream from the mixing ratio generator. Hourly average

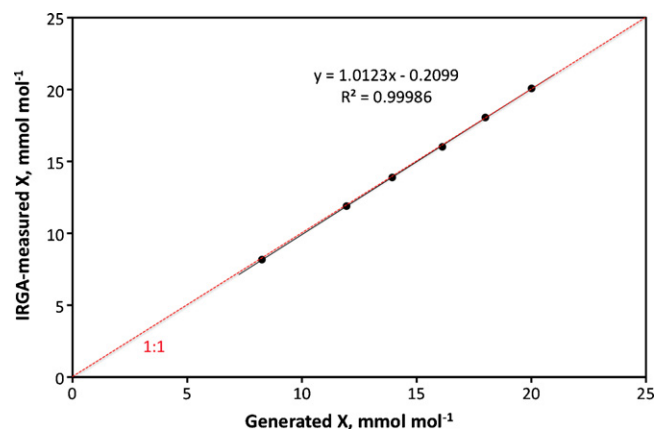


Fig. 3. Mixing ratio produced by the mixing ratio generator, as measured by an infrared gas analyzer that was calibrated before each measurement with the LI-610 dew point generator.

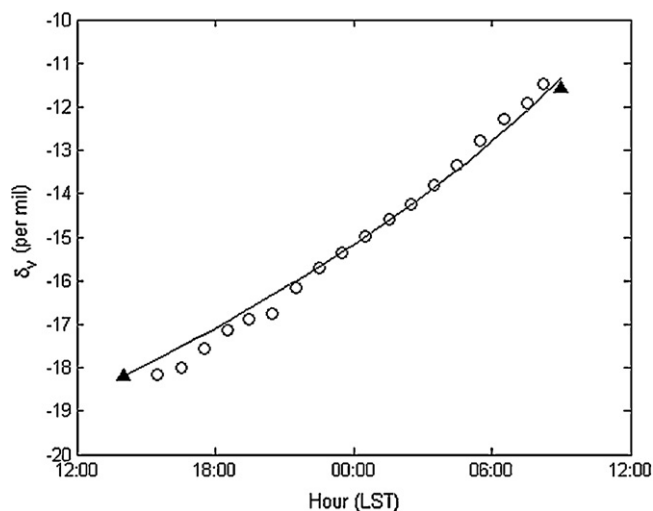


Fig. 4. A comparison of the tunable diode laser water vapor isotope measurements versus the values predicted/generated using the mixing ratio generator with the Rayleigh distillation theory. The data shown are for laboratory conditions measured over a period of about 18 h. In this case the mixing ratio was 18 mmol mol^{-1} (dew point = 15.1°C). The triangles indicate the calculated isotope ratio of the vapor in equilibrium with the liquid water at the beginning and end of the experiments and were measured with distributed feedback TDL with off-axis integrated-cavity-output spectroscopy. In this example, the isotope composition of the water vapor at the end of the experiment was estimated to be -11.5 , -11.6 , and -11.4‰ , for the TDL, vapor in equilibrium with the liquid water, and Rayleigh prediction, respectively.

values from the TDL are shown as symbols and the predicted isotope ratio of the vapor is shown as a solid line. Further, we measured the isotope ratio of the residual water at the end of the experiment using a liquid water isotope analyzer (DLT-100, Los Gatos Research Inc., Mountain View, California). In general, we observed excellent agreement among the methods. The differences observed at the end of the experiment were within about 0.1‰ and within the uncertainty of the various measurement techniques (Griffis et al., 2010).

We note from many experiments and modifications that the predicted isotope ratio is very sensitive to changes in residual mass (m in Eq. (3)) and contamination from small amounts of residual water vapor that might be present in the compressed air cylinders or introduced via leakage of room air into the system. The design of the mixing ratio generator evolved over time and we attempted to reduce errors associated with residual water sticking to walls and dead spaces. Further, in this design there is no internal tubing that might allow water vapor diffusion, which is an issue with the Bevaline tubing in the LI-610.

3.3. Operational details

The major costs in building the mixing ratio generator were the Peltier cooler (160 USD) and the shop time to mill the aluminum block and attach it to the Peltier device, for which the charges were approximately 300 USD. We scavenged a spare pressure transducer; had it not been available, a new one of similar quality would have cost 600 USD, bringing the total cost of the unit to about 1100 USD.

Power consumption of the system, including Peltier cooler, fan, and data logger, varies from approximately 15 W immediately after a change in set point to approximately 10 W when the unit is controlling at a given set point. This can likely be reduced with better insulation of the cell and fine tuning of the PID control algorithm. As currently configured, the dynamic response of the unit to a step change in set point is rather slow, but this could

be substantially improved by increasing the power to the Peltier controller.

Maximum air flow rate through the unit is approximately 2 slpm; at higher flows mixing in the cell is sufficiently chaotic that liquid droplets are ejected into the exiting air line. The minimum set point mixing ratio is determined by the lowest liquid water temperature and highest cell pressure that can be controlled and measured. With adequate insulation the cell can be maintained just above the freezing point; with a back-pressure regulator capable of controlling at 200 kPa, the resulting mixing ratio given by Eqs. (1) and (2) is $3.09 \text{ mmol mol}^{-1}$, equivalent to a dew point of approximately -8°C . Lower mixing ratios would require a correspondingly higher controlled cell pressure. The maximum possible mixing ratio is primarily determined by downstream conditions. The cell temperature can be controlled at a set point many degrees above ambient to produce a mixing ratio that corresponds to a dew point much higher than the ambient air temperature, but this will result in condensation downstream unless the plumbing is maintained at a higher temperature than the cell. Useful fluid capacity of the current system is approximately 80 cm^3 . At an air flow rate of 1 slpm and a set point mixing ratio of 15 mmol mol^{-1} , this provides 110 h of operation. Assuming 10 min of calibration per day, this would last nearly 2 years, indicating that the unit could be made smaller, which would improve its dynamic response and decrease its power requirement. Alternatively, the mixing ratio generator could be used to provide a continuous stream of known mixing ratio that could either be permanently routed through a reference cell in a differential analyzer, or sequentially switched into the sample cell for applications where frequent, near-continuous calibration is deemed necessary. In such a configuration, a lower flow rate and/or a lower mixing ratio could be employed, or pumped ambient air could be used instead of dry tank air to extend the time between refills of the generator.

4. Conclusions

A mixing ratio generator was built for less than 1100 USD that has sufficient accuracy to serve as a virtual calibration tank for open or closed-path water vapor analyzers. It also can be used to conduct Rayleigh distillation tests to confirm the performance of water vapor isotope analyzers. The unit operates on battery power and has the capacity to run for long periods of time without attention, so it should be suitable as a water vapor calibration source for gas analyzers at remote locations, where more frequent calibration should lead to increased confidence in the flux data produced.

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