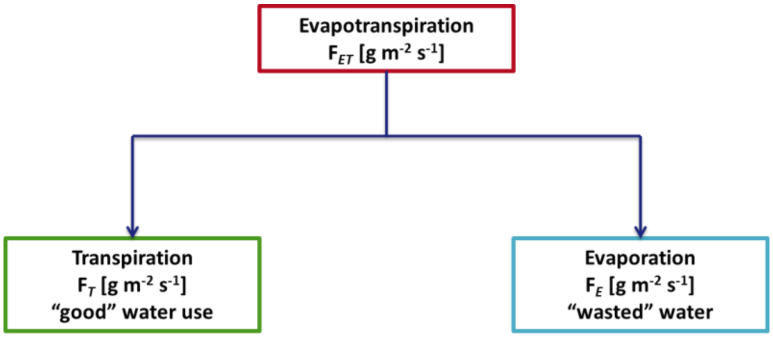
AN036: Water Stable Isotope Technique to Determine Evapotranspiration Partitioning

August 2015

In agriculture, evapotranspiration (ET), or the flux of water from a vegetated surface via both evaporation (E) and transpiration (T) by plants, is an important component of the water budget. Water loss via transpiration can be considered “good” water use, while water loss via evaporation can be considered “wasted” water use. Transpiration occurs through stomatal pores which are the same pores through which the plants uptake CO_2 for building carbon compounds and ultimately gaining biomass. Stomata are tightly controlled by physiological signals to optimize carbon gain per water lost. Water-use efficiency of a plant species or crop type is related to both plant genetics, as well as acclimation to irrigation regime.

Figure 1: Evapotranspiration Model Diagram



The characterization of those plant processes was historically performed through cumbersome and inaccurate water flux measurements. However, with the recent advancement of laser-based water vapor isotope analyzers, various calculation models have been developed to correlate real-time, spatial, and temporal isotopic measurements with evaporation and transpiration fluxes (F_{ET} and F_T).

According to Yakir and Sternberg (2000), the ratio of these fluxes is calculated as:

$$f_{T/ET} = \frac{F_T}{F_{ET}} = \frac{\delta_{ET} - \delta_E}{\delta_T - \delta_E}$$

Equation 1

Where δ_{ET} is the isotopic composition of the bulk evapotranspiration, δ_E is the isotopic composition of evaporated water, and δ_T is the isotopic composition of transpired water.

In these guidelines, we demonstrate how laser-based absorption spectroscopy, and in particular, Cavity Ring-Down Spectroscopy (CRDS), can be applied to many steps of ET analyses, including *(i)* characterization of partial pressure and the isotopic composition of the vertical water vapor profiles to determine the bulk ET signal through a Keeling mixing model, *(ii)* the use of soil water isotopic composition, in combination with the Craig-Gordon model, to determine the evaporation flux signature, *(iii)* direct measurement of isotopic signature of transpiration in leaf chambers to differentiate the isotope signature of this source.

Determining δ_{ET} using the Keeling mixing model

Theory

The isotopic composition of an evapotranspiration flux can be determined by using the Keeling mixing model (1958) that correlates water concentrations (C) and the isotopic composition (δ) of the mixed air above the surface (A), the background air (B), and the evapotranspiration flux (ET).

Keeling Mixing Model:

$$C_A.\delta_A = C_B.\delta_B + C_{ET}.\delta_{ET}$$

Equation 2

Assuming the concentration and the isotopic composition of the background air (C_B, δ_B) and evapotranspiration (C_{ET}, δ_{ET}) are constant over a short period of time, Equation 2 can be rearranged so that δ_A is a function of $1/C_A$. In this case, the intercept of a plot of $1/C_A$ (x-axis) versus δ_A (y-axis) will yield δ_{ET}.

$$\delta_A = (\delta_B - \delta_{ET})\frac{C_B}{C_A} + \delta_{ET}$$

Equation 3

Experimental Approach

Experimentally, one can measure the isotopic composition of the mixed air, δ_A, at various concentrations, C_A, by sampling the air at different elevations above the studied surface. The vertical profile provides the water concentration gradient required to determine δ_{ET}.

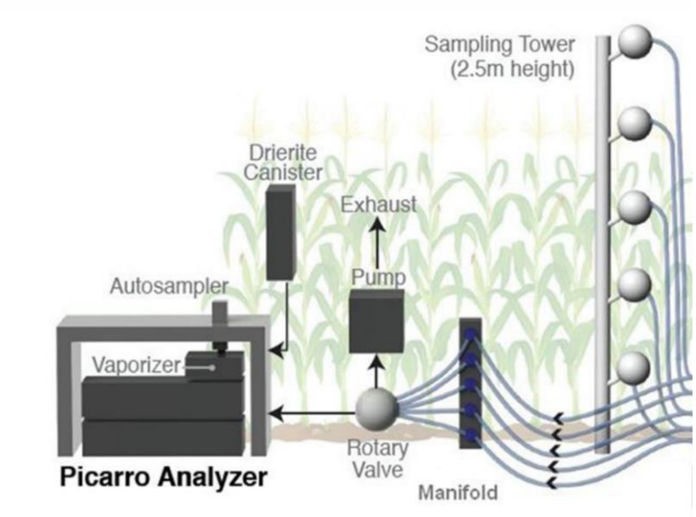


Figure 2: Example of experimental setup for sampling water vapor at different heights.

- Sample air above the studied surface at different heights. The heights at which you sample will be dependent on the specifics of the ecosystem being studied.
- Connect the sample lines to a manifold with a rotary valve selector.
- Use a rotary valve, which can be controlled via a Picarro water isotope analyzer, for example a Picarro L2130-*i* or L2140-*i*, to select the sample line to be sent to the analyzer.
- Run the analyzer in dual mode: vapor and liquid measurement allows the analyzer to calibrate itself with liquid standard while the vapor mode analyzes the sampled water vapor to provide isotopic composition and concentration.
- Using the analyzer's Dual Mode Coordinator, set the system to measure from each sample port for 10 minutes (total of 50 min for one cycle) measuring at a frequency of 1 Hz.
- Picarro recommends that the analyzer be calibrated with liquid water standards of a known isotopic composition every 8 hours. The Autosampler injects the liquid standard sample into the Vaporizer. Each injection measurement take 9 minutes and a minimum of 6 injections per standard is required.

After the analyzer measurements are collected and post-processed (averaging and normalizing per calibration), δ_A and $1/C_A$ are plotted on a graph as shown in the figure below. δ_{ET} is the y-intercept of the regression line between δ_A and $1/C_A$.

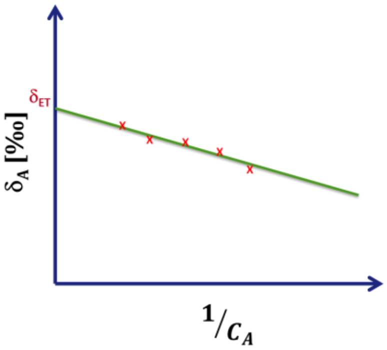


Figure 3: Example of a Keeling plot derived from a vertical profile of water vapor measurements.

Determining δ_E using the Craig-Gordon model

Theory

The Craig-Gordon model (1965) is used to estimate the isotopic composition of soil evaporation. The model takes into account the effect of equilibrium and kinetic fractionations during the phase change between liquid to vapor.

$$\delta_E = \frac{(\delta_L \alpha_e h_s - h'_A \delta_A) - (h_s - h_s \alpha_e) - (\varepsilon_k)}{(h_s - h'_A) + \varepsilon_k}$$

Equation 4

- α_e is the equilibrium vapor-liquid fractionation factor and can be calculated as a function of soil temperature, T_s, [K] following Majoube (1971):

For ^{2}H:

$$\ln \alpha_e = -52.612.10^{-3} + \frac{76.248}{T_s} - \frac{24.844.10^3}{T_s^2}$$

Equation 5

For ^{18}O:

$$\ln \alpha_e = 2.0667.10^{-3} + \frac{0.4156}{T_s} - \frac{1.137.10^3}{T_s^2}$$

Equation 6

- δ_L is the soil liquid water isotopic composition [‰]
- δ_A is the ambient air water isotopic composition [‰]
- h_s is the soil vapor saturation defined by Mathieu and Bariac (1996) as

$$h_s = e^{M\varphi_s/RT_s}$$

Equation 7

- M is the molecular weight of water (18.0148 g/mol)
- φ_s is the soil potential of the evaporating surface [kPa]
- R is the ideal gas constant (8.3145 mL MPa/mol/K)
- T_s is the soil temperature of evaporating surface [K]
- ε_k is the kinetic isotopic fractionation factor

$$\varepsilon_k = n(h_s - h'_A)\left(1 - \frac{D_i}{D}\right)$$

Equation 8

- D_i/D, the ratio of molecular diffusion coefficients of water vapor in dry air is taken as 0.9757 from Merlivat (1978)

$$h'_A = \frac{h_A e_{sA}}{a_w e_{s0}}$$

Equation 9

- h_A' is the humidity of the atmosphere normalized to the evaporating surface
- h_A is the humidity of the atmosphere
- e_{sA} and e_{s0} are the saturation vapor pressures at the atmosphere air temperature and the temperature of the evaporation surface
- a_w is the thermodynamic activity of water
- n is related to the volumetric soil moisture (θ_S), the moisture of the residual (θ_{res}) and the saturated moisture (θ_{sat}), as proposed by Mathieu and Bariac (1996):

$$n = 1 - \frac{1}{2}\left(\frac{\theta_S - \theta_{res}}{\theta_{sat} - \theta_{res}}\right)$$

Equation 10

Experimental Approach

Measuring δ_L

The isotopic composition of soil water can be measured using a Picarro water isotope analyzer. Several water extraction method are available:

Figure 4: Picarro Induction Module and Isotopic Water Analyzer

- *Cryogenic Distillation:* Cryogenic distillation is an established technique for extracting liquid water from soil samples, for example soils and leaves. Once extracted, the liquid water can be analyzed for its isotopic composition using a High Precision Vaporizer and Picarro water isotope analyzer.
- *Picarro Induction Module (IM):* The Picarro IM extracts water from soil samples by inductively heating the sample and directly sending the evaporated water vapor to the CRDS analyzer. Prior to analysis on the CRDS, the water vapor is passed through a Micro Combustion cartridge to destructively remove potential interfering organics. For more information about Picarro's Induction Module, please visit http://www.picarro.com/isotope_analyzers/im_crds.

When extracting water from soils using either method, caution should be applied to ensure that water extraction is complete. If this is not the case, it is possible to fractionation the sample and have inaccurate data during isotopic analysis. Care should also be taken during the storage of soil samples.

Measuring δ_A and C_A and determining h_A

The isotopic composition of water vapor in the background ambient air can be measured with the CRDS water analyzer in the vapor mode.

Sample the ambient air away from the studied system to ensure that no water vapor contamination from evapotranspiration affects the ambient air measurement. Either place the CRDS analyzer input port away from the system or connect tubing to the inlet port of the CRDS to collect the air from well-above the canopy. The specific height will be dependent on the ecosystem being studied.

Ensure that the CRDS analyzer is calibrated for isotopic composition and concentration dependence of the isotopic composition. For information on how to calibration a Picarro Water Isotope Analyzer refer to the User's Manual. A recent version is available at: https://picarro.box.com/s/0nh2wvm4n4ojf8jlmj7v.

Run the CRDS analyzer in dual mode: vapor and liquid. The liquid measurement allows the analyzer to calibrate itself with liquid standards while the vapor mode analyzes the sampled water vapor in ambient air to provide isotopic composition δ_A and concentration C_A.

Calculate h_A using C_A.

Determining δ_T via direct measurement at the leaf

Theory

When re-arranging the mass balance established in equation 2, we get (Wang, 2012):

$$\delta_T = \frac{C_M \delta_M - C_A \delta_A}{C_M - C_A}$$

Equation 11

Where δ_A and C_A are the isotopic composition and water concentration of the ambient air; δ_M and C_M are the isotopic composition and water concentration measured from the leaf chamber where transpiration water vapor mixes with ambient air.

Experimental Approach

Measuring δ_A and C_A

Follow the same procedure outlined on the previous page.

Measuring δ_M and C_M

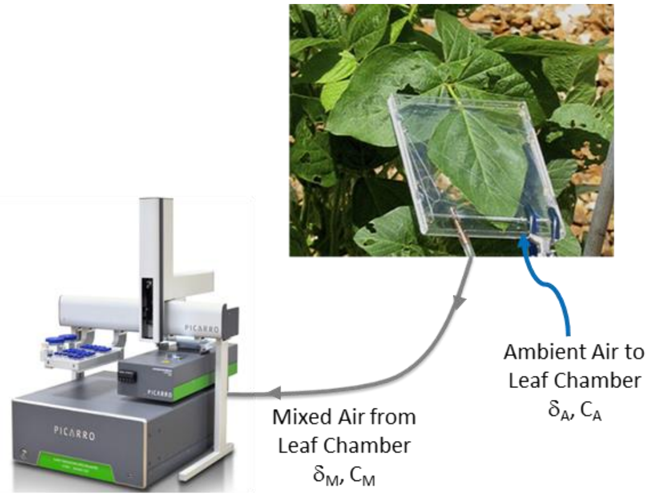


Figure 5: Experimental setup for measuring δ_M and C_m

One can directly measure the isotopic composition of the mixed air, δ_M and water concentration, C_M, in a leaf chamber. Figure 5 depicts the experiment setup:

- A leaf chamber is typically made of transparent plastic with variable volume dependent on the leave size. The chamber has two small air vents to allow ambient air to mix flow in the chamber with the water vapor generated by the leaf.
- A 1/8-inch ID Teflon tubing connects the leaf chamber to the analyzer.
- Place a leaf into the leaf chamber.
- Ensure that the CRDS analyzer is calibrated for isotopic composition and concentration dependence of the isotopic composition. For information on how to calibration a Picarro Water Isotope Analyzer refer to the User's Manual. A recent version is available at: https://picarro.box.com/s/0nh2wvm4n4ojf8jlmj7v.
- Run the analyzer in dual measurement mode: liquid and vapor. The liquid measurement allows the analyzer to calibrate itself with liquid standard while the vapor mode analyzes the sampled water vapor to provide isotopic composition and concentration.

References:

Craig H., Gordon L. (1965), "Deuterium and oxygen-18 variations in the ocean and the marine atmosphere, in Stable Isotopoes in Oceanographic Studies and Paleotemperatures", pg. 9-130, Laboratorio Di Geologica Nucleare, Pisa, Italy.

Majoube, M. (1971), "Fractionnement en oxygene-18 et en deuterium entre l'eau et sa vapeur", J. Chim. Phys. Biol., 68, pg. 1423-1436.

Mathieu, R., Bariac, T. (1996), "A numerical model for the simulation of stable isotope profiles in drying soils", J. Geophys. Res, 101(D7), pg. 12,685-12,696.

Merlivat, L. (1978), "Molecular diffusivities of H216O, HD16O, and H218O in gases", J. Chem. Phys., 69, pg. 2864-2871.

Keeling, C. (1958), "The concentration and isotopic abundances of atmospheric carbon dioxide in rurals", GeoChim. Cosmochim. Acta, 13(4), pg. 322-324.

Wang,L., Good, S., Caylor K.,Cernusak L. (2012), "Direct quantification of leaf transpiration isotopic composition", Agricultural and Forest Meteorology, 154-155, pg. 127-134.

Yakir, D, and L. Sternberg (2000), "The use of stable isotopes to study ecosystem gas exchange", Oecologica, 123(3), pg. 297-311.