



Partitioning evapotranspiration – Testing the Craig and Gordon model with field measurements of oxygen isotope ratios of evaporative fluxes



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SUMMARY

Stable oxygen isotopes of water provide a valuable tracer for water movements within ecosystems and are used to estimate the contribution of transpiration to total ecosystem evapotranspiration (f_t). We tested the Craig and Gordon equation against continuous field measurements of isotopic composition of evaporation and assessed the impact for partitioning evapotranspiration. Therefore, evaporation (E) and its isotopic signature ($\delta^{18}O_E$) on bare soil plots, as well as evapotranspiration (ET) and its corresponding isotopic composition of ($\delta^{18}O_{ET}$) of an herbaceous layer was measured with a cavity ring-down spectrometer connected to a soil chamber on a field site in central Portugal. We quantified the variation in $\delta^{18}O_E$ arising from uncertainties in the determination of environmental input variables to the Craig and Gordon equation: the isotope signature ($\delta^{18}O_e$) and the temperature at the evaporating site (T_e), and the kinetic fractionation factor (α_k). We could hence quantify f_t based on measured $\delta^{18}O_{ET}$, modeled $\delta^{18}O_E$ from observed soil water isotopic composition at the evaporating site ($\delta^{18}O_e$), and modeled $\delta^{18}O$ of transpiration ($\delta^{18}O_T$) from observed total soil water isotopic composition.

Our results demonstrate that predicting $\delta^{18}O_E$ using the Craig and Gordon equation leads to good agreement with measured $\delta^{18}O_E$ given that the temperature and ^{18}O isotope profiles of the soil are thoroughly characterized. However, modeled $\delta^{18}O_E$ is highly sensitive to changes in T_e and $\delta^{18}O_e$ as well as α_k . This markedly affected the partition results of transpiration and evaporation from the total ET flux: the fraction of transpiration (f_t) varied strongly using different formulations for α_k and assuming steady or non-steady state transpiration. These findings provide a first comparison of laser-based and modeled isotopic compositions of evaporation based on the Craig and Gordon equation under field conditions. This is of special interest for studies using stable isotopes to separate soil evaporation and plant transpiration fluxes and highlights the need for a thorough characterization of the micrometeorological and isotopic constitution of the upper soil layer to locate the evaporating front with a resolution of a few cm soil depths. We also call on a better characterization of the kinetic fractionation factor of soil evaporation.

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1. Introduction

Oxygen isotope signatures are valuable tracers for water movements within the ecosystem because of the distinct isotopic compositions of water in the soil and vegetation (Yakir and Sternberg, 2000). Evaporation from the soil modifies the isotopic composition of source water and was first described by Craig and Gordon (1965). Evaporated water vapor is strongly depleted in relation to the evaporating water source based on isotope fractionation associated with equilibrium isotope effects at the vapor–liquid interface (equilibrium fractionation, α^*) and

diffusion-controlled isotope effects (kinetic fractionation, α_k). The evaporation model proposed by Craig and Gordon is widely used in ecological and modeling studies to determine the oxygen isotopic composition of soil evaporation and plant leaf water enrichment. It has been used to achieve better understanding of the dynamics of hydrological processes (Barbour, 2007; Braud et al., 2005a,b; Cuntz et al., 2007; Haverd and Cuntz, 2010), and to partition ecosystem water fluxes into their components: soil evaporation and plant transpiration (e.g. Haverd et al., 2011; Williams et al., 2004; Yezpe et al., 2005, 2007).

Evaporation from the soil occurs at the vapor–liquid interface (the evaporating front) below which liquid transport and above which vapor transport is dominant (Braud et al., 2005a). It has been shown for unsaturated soils that this front is related to a strong enrichment in soil water isotopic composition relative to the rest

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Nomenclature

α_k	kinetic fractionation factor	g_t	total leaf conductance to water vapor (mol m ⁻² s ⁻¹)
α^*	equilibrium fractionation factor	V	water volume (mol m ⁻²)
$\delta^{18}\text{O}$	oxygen stable isotope signature (‰)	T	temperature
θ	volumetric water content	<i>Subscripts</i>	
R	isotope ratio of [¹⁸ O]/[¹⁶ O]	s	soil
E	soil evaporation	e	evaporating surface
T	plant transpiration	v	ambient water vapor
ET	evapotranspiration	m	liquid mesophyll water
ft	T/ET	r	residual
w	H ₂ O concentration	sat	saturation
h	relative humidity	$surf$	surface
nk	exponent relating $\alpha_{k,diff} = (D_v/D_v^i)$ to α_k	lw	leaf water
D_v^i	diffusivity of H ₂ ¹⁸ O in air		
D_v	diffusivity of H ₂ O in air		
ns/na	constants used in the definition of the nk exponent related to soil and atmosphere controlled diffusivity (1 and 0.5, respectively)		

of the soil column and an exponential depletion in isotopic signature within few cm of the underlying soil due to evaporative enrichment of the remaining liquid water (Zimmermann et al., 1967). A precise determination of the evaporating front is therefore very important for a correct estimation of $\delta^{18}\text{O}_E$ but its precise determination remains a challenge in most field studies due to the requirement of large sample sizes (see Lai et al., 2006; Wang et al., 2010; Williams et al., 2004; Yepez et al., 2005, 2007).

While soil evaporation is seldom in the steady state, plant transpiration reaches steady state at certain times of the day. During steady state transpiration the $\delta^{18}\text{O}$ of the transpiration flux is equal to the isotope signature of xylem/source water (Dawson, 1993). The large differences between evaporative non-steady state $\delta^{18}\text{O}$ (depleted compared to source water) and transpirational steady state $\delta^{18}\text{O}$ (equal to source water) then provide the basis using stable isotopes to separate soil evaporation and plant transpiration fluxes (e.g. Lai et al., 2006; Wang et al., 2010; Williams et al., 2004; Yepez et al., 2007). However, it has to be taken into account that steady state conditions are not always found due to the transient changes in atmospheric conditions (Yakir and Sternberg, 2000). Thus, non-steady state transpiration is depleted in $\delta^{18}\text{O}$ relative to xylem/source water during parts of the day (Cuntz et al., 2007; Dongmann et al., 1974; Farquhar and Cernusak, 2005).

Recent developments in laser spectroscopy enable the measurement of $\delta^{18}\text{O}$ of atmospheric water vapor ($\delta^{18}\text{O}_v$), and evapotranspiration ($\delta^{18}\text{O}_{ET}$) and its components with a high temporal resolution in the field (Werner et al., 2012). In the past, however, precise determinations of $\delta^{18}\text{O}_{ET}$, $\delta^{18}\text{O}_E$ and $\delta^{18}\text{O}_T$ have been a challenge since measurements of water vapor were difficult to obtain using cold-trapping methods (e.g. Helliker et al., 2002; Williams et al., 2004; Yepez et al., 2005). Several studies have conducted experiments on isotopic evaporation (Cappa et al., 2003; Craig et al., 1963; Merlivat, 1978; Rozanski and Chmura, 2006; Stewart, 1975), but only few studies (i.e. Braud et al., 2009a,b; Kim and Lee, 2011) used continuous measurements of $\delta^{18}\text{O}$ of evaporation or ambient water vapor. Field studies comparing modeled with directly measured isotope signatures of evaporation are even scarcer (but see Haverd and Cuntz, 2010 and for controlled conditions Rothfuss et al., 2010, 2012). To close this research gap we measured the isotopic composition of evaporation ($\delta^{18}\text{O}_E$) obtained with a cavity ring-down spectrometer connected to a soil chamber on experimental plots in a herbaceous community of an open oak woodland in central Portugal. We tested the Craig and Gordon equation against directly measured $\delta^{18}\text{O}_E$. Specifically, we quanti-

fied the variation in $\delta^{18}\text{O}_E$ arising from uncertainties in the determination of important environmental input variables to the Craig and Gordon equation: the isotope signature at the evaporating site ($\delta^{18}\text{O}_e$), the temperature at the evaporating site (T_e), and the kinetic fractionation factor (α_k). Finally, we measured the isotopic composition ($\delta^{18}\text{O}_{ET}$) and fluxes of evapotranspiration of an herbaceous understory layer and quantified the contribution of transpiration to evapotranspiration (ft) based on measured $\delta^{18}\text{O}_{ET}$ and modeled $\delta^{18}\text{O}_E$ and $\delta^{18}\text{O}_T$ on vegetation plots.

2. The Craig and Gordon equation

Craig and Gordon (1965) developed an equation describing the isotopic composition of evaporation from an open water body:

$$R_E = \frac{1}{\alpha_k \alpha^+ (1-h)} (R_e - \alpha^+ h R_v) \quad (1)$$

where R_E is the isotope ratio (¹⁸O/¹⁶O) of evaporated vapor, R_e is the isotope ratio at the evaporating sites and R_v is the isotope ratio of ambient water vapor, α_k is the kinetic fractionation factor, α^+ is the water vapor equilibrium fractionation factor (Majoube, 1971; α_k and $\alpha^+ > 1$), and h is the relative humidity normalized to the temperature at the evaporating sites (T_e). Most of the environmental input (T_e , h , and R_v , R_e) need to be determined and a thorough estimation with respect to spatial (e.g. conditions at different soil depths) and temporal variation remains challenging.

The evaporation of water in air is characterized by a fractionation effect that derives from two fractionating processes: equilibrium fractionation and kinetic fractionation. Equilibrium isotope effects (α^+) occur because the lighter isotopologue (H₂¹⁶O) evaporates more easily compared to the heavier isotopologue (H₂¹⁸O). This is a rather well characterized, temperature dependent process (Majoube, 1971). In contrast, a determination of the kinetic fractionation (α_k) and an agreement on the correct formulation remains controversial (Braud et al., 2005a,b; Braud et al., 2009a,b; Cappa et al., 2003; Horita et al., 2008; Luz et al., 2009; Rothfuss et al., 2012). Kinetic fractionation occurs because the lighter isotopologue diffuses faster compared to the heavier isotopologue. It involves molecular diffusion through the soil and resistance to water vapor transport in a laminar boundary layer as well as turbulent conditions above the boundary layer. Previous studies determined experimentally the molecular diffusion coefficient (D_v/D_v^i). Cappa et al. (2003) recommended a value of $D_v/D_v^i = 1.032$ according to

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