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Possible soil tension controls on the isotopic equilibrium fractionation factor for evaporation from soil

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Abstract

The stable isotopes of hydrogen and oxygen (δ^2H and δ^{18}O) are useful conservative tracers for tracking the movement of water in soil. But although the tracking of water infiltrating through the soil profile and its movement as run-off and groundwater recharge are well developed, water movement through the soil can also include evaporative fractionation. Soil water fractionation factors have, until now, been largely empirical. Unlike open water evaporation where temperature, humidity, and vapour pressure gradient define fractionation, soil water evaporation includes fractionation by soil matrix effects. These effects are still poorly characterized. Here, we present preliminary results from a simple laboratory experiment with four soil admixtures with grain sizes that range from sand to silt and clay. Our results show that soil tension seems to control the isotope fractionation of resident soil water. The relationship between soil tension and equilibrium fractionation appears to be independent of soil texture and appears well supported by thermodynamic theory. Although these results are preliminary, they suggest that future work should go after soil tension effects as a possible explanatory factor of soil water and water vapour fractionation.

KEYWORDS

Craig and Gordon model, evaporation, fractionation, soil water, stable isotopes

1 | INTRODUCTION

Evapotranspiration controls the water, energy, and carbon fluxes of the earth surface (Jung, 2010; Trenberth, Fasullo, & Kiehl, 2009). Water fluxes into and out of the earth's surface can be traced by the stable isotopes of hydrogen and oxygen (δ^2H and δ^{18}O) Hoffmann, Jouzel and Masson (2000). Each component of the water cycle has a distinct isotopic signature and meteoric water (e.g., precipitation) and most groundwater and streamflow plot along the global meteoric water line in dual isotope space (Craig (1961)). Flux components of the water cycle cause fractionation and mixing of reservoirs. The soil water storage is a key reservoir to most components of the water cycle within the soil–plant-atmosphere continuum (McHugh, Morrissey, Reed, Hungate, & Schwartz, 2015; Sprenger, Leistert, Gimbel, & Weiler, 2016). Evaporation enriches the resident soil water. Equilibrium and kinetic fractionation processes cause enrichment of ^{2}H and ^{18}O in the remaining soil

water. This enrichment decreases the slope of the regression line of δ^2H and δ^{18}O values. The so-called soil water evaporation line (EL) plots below the global meteoric water line (Barnes & Allison, 1983; Soderberg, Good, Wang, & Caylor, 2012). Preexisting water that has been evaporated can have an effect on new soil water due to mixing with the resident water. The combined processes of soil water evaporation, infiltration, and mixing characterizes the slope of the EL.

We know that soil water equilibrium fractionation occurs between liquid water and the surrounding soil water vapour (Miller, Yakir, White, & Tans, 1999; Stern, Amundson, & Baisden, 2001). Equilibrium fractionation is determined empirically as a function of temperature (Majoube, 1971). Kinetic fractionation also occurs, driven by the transport resistances from the evaporating surface to the atmosphere and the diffusivities of the isotopic species. Although adhesion, cohesion, and the interaction between soil water, soil water vapour, and atmospheric water vapour are well described in the soil physics literature

(Bachmann & van der Ploeg, 2002; Bittelli, Campbell, & Tomei, 2015), we still do not know how these processes combine to control the resulting soil water isotopic environment. This is problematic because much new research is linking the isotopic composition of soil water to that of atmospheric vapour and using these values for predicting the partitioning of the global terrestrial water fluxes (Evaristo, Jasechko, & McDonnell, 2015; Good, Noone, & Bowen, 2015; Jasechko, 2013). Soil water can be apportioned into mobile water and immobile water. The threshold to separate these two water pools can be defined on the basis of soil tension. Soil tension is the suction that has to be applied to remove water from the soil. It can be expressed as the logarithm of the height of the water column (cm) on a pF-scale. The separation of mobile and immobile water can be done in many ways; most commonly defined as the water held at field capacity pF2.4 (=330 hPa; Lal & Shukla, 2004) or more recently as the portion of water that cannot be extracted using suction lysimeters at a pF of 2.8 (=600 hPa; Berry et al., 2017).

Recent work has shown that particle size controls the condensation of water and the formation of water films (Yeşilbaş & Boily, 2016). How the thickness of the water film, interactions between the soil particle surface, mobile, immobile water, and water vapour combine to control the isotopic environment is not yet fully understood. Recent research has shown that soil tension promotes a reduction of the relative humidity and affects the calculations with the Craig and Gordon model (Soderberg et al., 2012). More recently, it has been shown that the equilibrium fractionation factor changes if the vapour pressure controls the quantity of water adsorbed on a surface (Lin & Horita, 2016; Lin, Horita, & Abe, 2018).

Here, we present a simple laboratory experiment with four admixtures of soils with different grain sizes (sand, silt, and clay) and water contents to examine quantitatively the relationship between soil tension (as a quantitative description of the soil system) and the isotope fractionation of resident soil water and water vapour. We test the null hypothesis that soil tension has no control on soil water fractionation.

2 | METHODS

We begin with some definitions of the terms used. We follow Coplen (2011) as a key reference for our nomenclature. The isotope ratio R is the ratio between the abundance N with the number of each isotope ^iE and ^jE, of chemical element E in substance P expressed as

$$R(^iE/^jE) = \frac{N(^iE)_P}{N(^jE)_P}, \tag{1}$$

where the substances in the present study are water vapour (v) and liquid water (w). The presentation of isotope values is done in delta notation (δ) and refers to the measured isotope ratios of the sample R_{sample} relative to an international or laboratory reference standard $R_{reference}$:

$$\delta = \left(\frac{R_{sample}}{R_{reference}} - 1\right). \tag{2}$$

We calculated our tension-based equilibrium fractionation factor $\alpha^{i/j}E_{v/w}$ based on the isotope ratio of the labelled water $R(^iE/^jE)_w$ and the isotope ratio of the measured water vapour $R(^iE/^jE)_v$ as follows:

$$\alpha^{i/j}E_{v/w} = \frac{R(^iE/^jE)_v}{R(^iE/^jE)w} = \frac{1000 + \delta_v}{1000 + \delta_w} = a_{v/w}, \tag{3}$$

where α can be used as simplified notation for the equilibrium fractionation factor. The isotopic ratio of the vapour is used as the reactant here in order to describe the enrichment of the vapour relative to the water.

Our experimental approach is based on the well-known direct equilibration approach used for geological cores (Hendry, Schmeling, Wassenaar, Barbour, & Pratt, 2015; Wassenaar, Hendry, Chostner, & Lis, 2008). Four soil samples were oven dried for 24 hr and subsequently labelled with a water of known isotopic signature (−15.5‰ $\delta^{18}O$ and −125‰ δ^2H). Mixtures of soil (200 g each) and the tracer were prepared at different gravimetric water contents ranging from 0.1% to 30%. These were each prepared in individual Ziploc bags (~1-L volume) and the headspace filled with dry air. The samples in the sealed bags were allowed to equilibrate for 24 hr. We used an equilibration time of 24 hr, consistent with literature values for such samples (Garvelmann, Külls, & Weiler, 2012; Mueller et al., 2014; Gazis & Feng, 2004). No mixing ratio dependencies were found within the range of our measurements (29,901 to 22,840 ppm with a mean of 27,274 ppm ± 1,769 and with one exception, 8,000 ppm). The bag head space (i.e., the vapour) was then measured with a water vapour isotope analyses device (LGR, IWA-45-EP) with a trueness of 0.5‰ for $\delta^{18}O$-values and 3‰ for δ^2H-values determined from the quality check standard. Following the vapour isotope sampling, subsamples of the soil were taken from the bags and placed in a water potential metre (Model WP4C, Decagon Devices) for the determination of soil matric potential (soil tension). The precision of these measurements is ±0.1 *10⁴ hPa for soil tensions between 0 and −10 *10⁴ hPa and ± 1% for soil tensions between −10 and −300 *10⁴ hPa (as per Gubiani, Reichert, Campbell, Reinert, & Gelain, 2013).

3 | RESULTS

Our primary finding is that soil tension affects the equilibrium fractionation factor (hereafter defined as "α") for soil tensions above 1,260 hPa (equivalent to a value of 3.1 on the pF scale; Figure 1). This "effect" at tensions at and beyond >pF 3.1 is a value midway between "field capacity" (pF~2.4) and "wilting point" (pF~4.2) on the moisture release curve (Figure 1a). As indicated by the colour bar on the top of Figure 1, the "dry end" of the moisture release curve reflects the immobile portion of the soil water. The tension effect on the equilibrium fractionation factor increases linearly with increasing soil tension (Figure 1b). Our secondary finding is that the observed relationship between soil tension and the fractionation factor appears to be
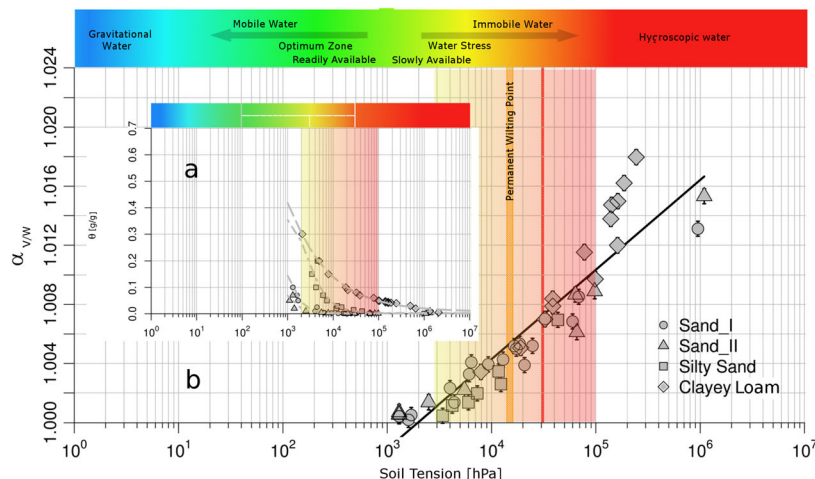
FIGURE 1 The inset in (a) shows the moisture release curves for the four add mixtures of soils. The gravimetric water content of the two quartz sand samples remained below 0. 05 g/g in the range of wilting point to hygroscopic water. But gravimetric water content of the silty sand was higher up to 0. 15 g/g in the same range. Highest gravimetric water content within the range of capillary water was found for the clayey sand with values up to 0.2 g/g. Sand Sample I and Sand Sample II had gravimetric water contents of 0.01 and 0.005, respectively, at soil tension 106 hPa. At the same soil tension, the silty sand had a gravimetric water content of 0. 05 g/g. More data points above 105 hPa were obtained for the clayey loam with gravimetric water content between 0.05 and 0.0 05 g/g. The graph of part (b) shows that the equilibrium fractionation factor (aP/Q) is not related to the soil moisture content or soil type but shows a distinct relationship to matric potential (soil tension). The intersection at αP/Q = 1 defined a threshold for the tension-mediated fractionation effect at ~1,260 hPa (equivalent to a value of 3.1 on pF scale) for both δ18O and δ2H, respectively. Hence, we observe tension-mediated fractionation mainly for the immobile water

independent on soil texture ($\alpha^{18}O$ and α^2H are shown separately in Figure 1b). However, shown in dual isotope space, soil texture seems to control the slope of the EL. Figure 2 shows that the finer the soil texture, the lower the slope of the EL in dual isotope space.
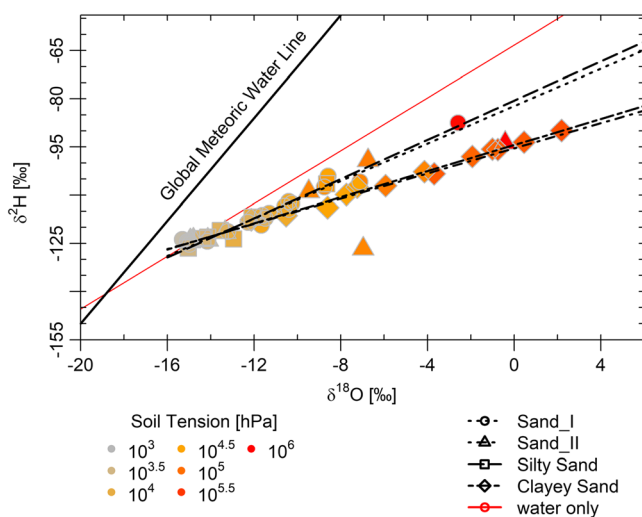

FIGURE 2 Soil tension increases the equilibrium fractionation and causes the isotope values to plot along an evaporation line (EL) in dual isotope space. The colour coding indicates that the higher the soil tension, the farther away the isotope values plot from its origin. The slope of the EL decreases with decreasing grain size. The sandy soil samples plot on an EL with a slope of 3 and R^2=0.96. The soil samples with elevated clay content plot on an EL with slope 2 and R^2=0.98. The red line indicates the EL from our water-only test and has a slope of 4.1

4 | DISCUSSION

Our findings suggest that soil tension affects the equilibrium fractionation factor between soil water and water vapour. This goes beyond what is has been used previously for modelling soil water evaporation, and until now, based on temperature alone. If soil tension as a physical dimension for interfacial forces mediates isotopic equilibrium conditions, then it should be possible to determine the tension mediated equilibrium conditions based on thermodynamics like that shown for pure water system by Criss (1999). Our work suggests that interfacial tension increases the amount of energy required to remove water from the soil matrix. Based on these findings, it can be concluded that the surface free energy (also called the Gibbs-free energy; see Greiner, Neise, & Stöcker, 2012) of the soil particle is satisfied preferably by the stable isotopes with less mass. In this way, the interfacial tension increases the fractionation factor between water and the water vapour. Hence, we hypothesize that adhesion is the cause of the additional fractionation as we explain in further detail below.

4.1 | Adhesive forces

Bachmann and van der Ploeg (2002) have noted that a high ratio of adhesive to cohesive forces within soil is a key control on water spreading on a surface. Following on from this, we argue that the greater the adhesive forces, the stronger the isotopic enrichment in ^2H and ^{18}O of the water vapour under equilibrium conditions. Therefore, soil water and soil vapour fractionation at high soil tension will be driven by the surface properties and the ionic strength of the

remaining soil solution. Recent work showing that particular cations within the interlayer space of clay minerals and mineral surfaces could help explain our findings (Gaj et al., 2017; Oerter et al., 2014). Oerter et al. (2014) performed an experiment where they maintained the amount of water in the soil but increased the amount of mineral-mixture to reduce the actual soil water content. Their results showed that increasing the mineral mix increased the number of hydratable cations. The intense electrostatic attraction of these cations tended to bind preferably to $H_2^{18}O$. They observed a depleted signature in the bulk water with decreasing water content and noted that hydrogen bonds of the outer hydration spheres attracted in a preferred way, the $H_2^{16}O$ isotopologue. In other studies, hydrogen bonds have also been found predominantly at particle surfaces where nonpolar and polar functional groups-controlled wettability (Woche et al., 2017).

Putting these previous findings into perspective, such functional groups attract preferentially the isotopic species with the lower mass. Hence, immobile water at high soil tension will be depleted in the heavy isotopic species and cause the enrichment in the isotopic signatures of the vapour in equilibrium with the soil water atmosphere—leading to the development of a lower slope of the soil water EL in dual isotope space (as shown in Figure 2). Hence, in the context of this previous work, the observed enrichment of the water vapour during our equilibrium experiment is likely related to wettability properties. Further research is needed to understand the linkages between soil tension mediated fractionation and differing mineral and organic surfaces in this regard.

4.2 | Soil-specific soil water ELs

Our finding of soil-specific soil water ELs can possibly place the early benchmark work of Barnes and Allison (1988) into perspective. Commonly, a soil water EL is defined as the linear regression between of $\delta^{18}O$- and δ^2H-values of soil water taken from a depth profile. Barnes and Allison (1988) argued that the change of slope was caused by a change of the diffusive resistance. Their findings suggested that this was controlled by diffusion, meaning that air filled porosity and the tortuosity of the soil were the main drivers of fractionation during soil evaporation. Interactions with the soil particle surface were not considered in their work. However, our results show rather conclusively in this simple experiment that under dry conditions, soil tension and hence adhesion forces are the main driver of such fractionation. This means that diffusive transport of vapour out of and within a soil column appear to be driven by soil tension gradients and cause fractionation during water vapour transport. If our results are supported by others in future experiments, it would have significant implications for recent work on plant water source analysis (a good summary can be found in Rothfuss & Mathieu, 2016). This will be especially relevant under dry conditions where plant root water uptake itself may induce high soil water tensions and therefore cause tension mediated fractionation of the soil water left behind.

The threshold at which the tension-related fractionation effect occurs corresponds well to the soil tension at which water becomes more difficult for plants to take up, that is, above 1,260 hPa
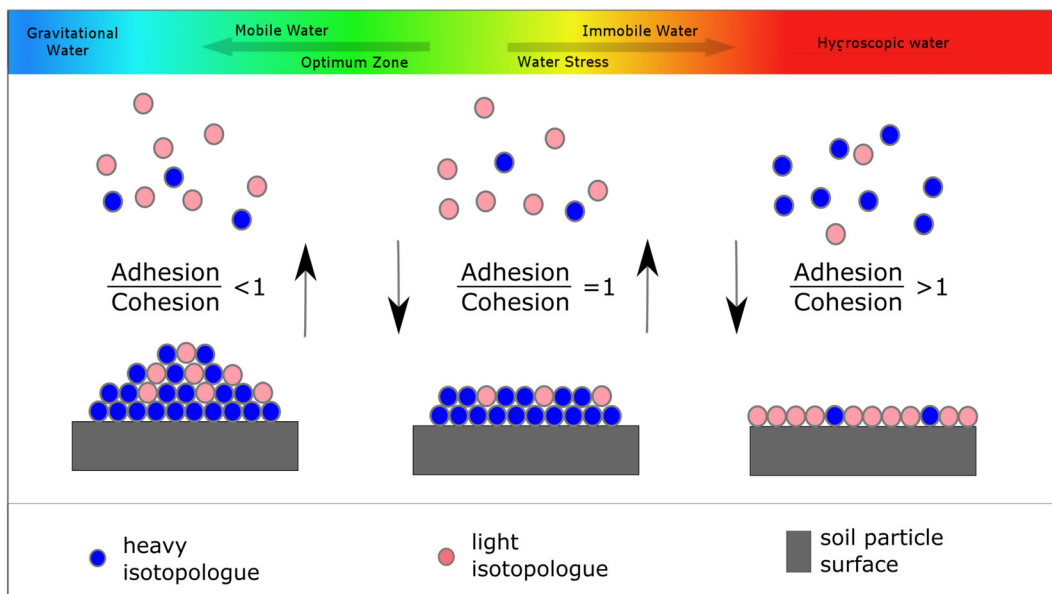

FIGURE 3 A simple conceptual model of tension mediated isotope fractionation in a closed system. The heavy isotopologue is shown in purple, and the light isotopologue is shown in light blue. The water is attached to the soil particle surface (in grey), and the water vapour is in equilibrium with the liquid water. The equilibrium fractionation factor α is defined by temperature alone, if cohesion forces between water molecules dominate (left). This changes with increased tension, whereby the soil particles control the vapour pressure and the equilibrium fractionation when adhesion dominates (right). The ratio of adhesion to cohesion forces increases from left to right. Tension, specifically interfacial tension and the physical controls on soil water adsorption, dominates the associated fractionation effects when adhesion forces dominate. This is the case for the immobile portion of the soil water storage

(equivalent to a value of 3.1 on pF scale; Figure 1). A discrimination of stable isotopes during root water uptake as visible in xylem water isotopic composition has been observed for some xerophytes (plants adapted to arid conditions) and halophytes (plants adapted to saline environments; Lin & Sternberg, 1992; Ellsworth & Williams, 2007). More recently, it was observed that the plant isotopic signatures are more depleted in the heavier isotopes (i.e., $^1H_2^{18}O$) at soil tensions between 700 and 1,000 hPa (Vargas, Schaffer, Yuhong, & Sternberg, 2017). They further concluded that the rate of transpiration is related to an enrichment of the soil water pool, which supports the possibility of tension driven fractionation effects during water uptake.

4.3 | A simple conceptual model

Our simple conceptual model (Figure 3) shows that the smaller the water film thickness, the stronger the influence of the Gibbs-free energy of the soil particle surface binding the water molecules at the solid surface. Generally, in a water-vapour system, temperature controls the saturated vapour pressure in the air. The different saturated vapour pressures of the isotopologues cause the vapour to be saturated with more water molecules of lower mass compared with the liquid source. This is because of an energetic gradient towards the air. In a solid–liquid–vapour system at low water contents, the saturated vapour pressure is a function of temperature and soil tension. Thus, the vapour pressure deficit is no longer controlled by the atmosphere. However, the soil tension promotes the vapour pressure deficit, and the surface free energy of the soil particle surface controls the equilibrium conditions. Soil tension is the measured potential energy required to move a unit of water. Analogous to the saturated vapour pressure, the equilibrium fractionation factor becomes a function of soil tension in addition to temperature. As in the case of evaporation, the lighter isotopic species will tend to satisfy the vapour pressure deficit preferably. Consequently, the remaining water vapour in the headspace of the experimental bags is more enriched with the heavier isotopic species.

5 | CONCLUSIONS

This briefing has presented preliminary results from a simple laboratory experiment with four different soil admixtures. Our results have shown that soil tension appears to control the isotope fractionation of resident soil water. And that the relationship between soil tension and equilibrium fractionation appears to be independent of soil texture and the effect supported by thermodynamic theory. Clearly, more work needs to be done. Although these results are preliminary, we hope that they stimulate others to examine these processes and to explore soil tension effects of soil water fractionation further. Indeed, several questions remain, including does tension mediated fractionation of stable isotopes matter on a larger scale? Do tension effects control the kinetic fractionation factor? Can the equilibration bag method reliably be used over the whole moisture range? Is the

isotopic signature of water taken up by plants affected by soil tension effects? We hope that this short note stimulates much needed new research in these areas.

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