

Investigation into the Hydrologic Separation of Bound and Mobile Water in Forest Soil
Using Isotopic Analysis

by
Dustin DeGeorge

A PROJECT

submitted to
Oregon State University
University Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Ecological Engineering
(Honors Scholar)

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Kate Lajtha

How water moves through soils is of importance to studies of stream hydrology and biogeochemistry. Although translatory flow, which states how soil water is displaced by additional precipitation into streams, is a widely accepted model, Brooks et al. (2010) found evidence that challenged this model. They suggested that there are two “water worlds” in forest soils in Mediterranean climates that rarely interact: tightly bound water in very small pores that comes from initial rain after a dry summer, and more mobile water in larger pores that moves freely and is displaced by precipitation into streams. This project tests this hypothesis by using a centrifuge paired with a ceramic rod to separate soil water samples into mobile and immobile portions for isotopic analysis to detect differences. Soil cores were taken at six points throughout the year at five depths. Results indicate a critical error during storage causing significant evaporation of the data making comparison of the water pools ineffective. However, the temporal and depth trends are consistent with Brooks’ et al. (2010) conclusions. Characterization of the separation method shows the importance of choosing rods with air-

entry values higher than the desired extraction pressure. This project recommends study repetition with improved methods.

Key Words: water isotopes, centrifuge, translatory flow, forest hydrology,

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I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

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Introduction

Forest Hydrology is tasked with studying and understanding a complex and heterogeneous system involving the physical, biological, and biogeochemical processes that govern how water interacts with the environment. One of the crucial pieces of the hydrological puzzle is how water interacts with and moves through soil media. The mechanisms that affect how water is conducted and stored within forest soils have important implications on stream hydrology, forest slope stability, geophysical mechanics, and seasonal water availability in increasingly arid Mediterranean summers in the Pacific Northwest.

An early and still popular flow model in forest hydrology is the concept of translatory flow, which was pioneered by Hewlett and Hibbard (1967) (McDonnell 2009). This model states that the majority of rainfall is temporarily stored within soil pores before being displaced by further rainfall through the soil into the streams. Therefore, water already present in the soil will be the majority of water added to stream flow, with precipitation repeatedly replacing and displacing the existing soil water.

This assumption over direct and total displacement has been challenged recently by Brooks et al. (2010). They suggest that there are two “water worlds” in the soil, one that is tightly bound to the mineral element of soil and accessible to plants, and one that is loosely held that displaces out of the soil as additional water flows in. Brooks et al. (2010) documented an approximately bimodal distribution of very small (<0.03 mm) and larger (>0.3 mm) soil pore sizes that would explain this phenomenon of segregated water.

In Mediterranean climates like the forests of Western Oregon, Brooks et al. (2010) suggests that the smaller pores are initially filled by the first Autumnal rains. This pool of tightly bound water is then essentially isolated from the cycle of translatory displacement, evaporation, and recharge because of its very high matric potential. This tightly bound water remains relatively unchanged in the smaller pores until the dry Mediterranean summers spur vegetation to create adequate suction to access it, allowing recharge during the next Autumnal rains. The main difference between the accepted model of translatory flow and the mechanism suggested by Brooks et al. (2010) is that if translatory flow is true, then water flowing through soil media is part of a single connected pool of water that mixes; if what Brooks suggests is true, there are at least two distinct and segregated pools of water that flow at different speeds and rarely mix.

The Brooks et al. (2010) paper showed the difference between the water worlds by comparing the isotopic signatures of precipitation, streamflow, bulk soil water samples, and water taken up by vegetation. Isotopic analysis in forest hydrology and biogeochemistry is widely used to track and identify the many cycles occurring within forest watersheds. When used on water, it is based on the proportion of deuterium and ^{18}O within a sample of water, represented by $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Differences in isotopic ratios of different pools of water in a forest water cycle are both a product of the input precipitation isotopic ratios, and the degree of evaporation, since water becomes enriched in heavier isotopes because lighter isotopes evaporate more easily. The different ways that watershed processes affect isotopic ratios are well documented and can be used to track and identify pools of water and how they interact. For example, precipitation that interacts with forest canopies are often isotopically enriched in the process and deeper soil water is generally less enriched because it has less exposure to evaporation (Levia & Carlyle-Moses 2011).

While Brooks et al. (2010) presents evidence that shows a difference in isotopic ratios between bulk soil water and streamflow, the loosely bound water described in the study is not directly isolated from the same bulk soil water samples as the immobile water. This study aimed to separate and directly compare isotopic ratios of the mobile and immobile water from the same soil samples to verify that they are actually segregated. This is done by utilizing and further developing a method introduced by Madrigal (2010), which uses centrifugal force to capture soil water held below a certain matric potential within a ceramic rod without causing isotopic fractionation.

I hypothesized that the isotopic ratios of mobile water within the soil would resemble the ratios of the recent rainfall. However, the immobile soil water would differ significantly from both, and would resemble the isotopically depleted water from the ends of initial Autumnal storms that fill the deep micropores, with deeper soils remaining the most depleted because of their lower exposure to evaporation. If this is found to be true, then the challenge to translatory flow introduced by Brooks et al. can be corroborated.

Design Approach

This project approached the separation of mobile and tightly bound water by using centrifugation to extract mobile water from a soil column. This has the advantage of creating paired samples of mobile and bound water that were extracted from the same sample, allowing direct comparison. Pairing centrifugation with porous ceramic rods has been an established method for creating and analyzing matric potentials in soils for more than a decade (Khanzode et al. 2000, Dane and Topp 2002, Reatto et al. 2008). Khanzode et al. (2000) used a small scale centrifuge to reliably create pressures up to 863 kPa with a 6 cm ceramic rod within silt, till and clay soils and found that spin times ranged from 2 to 12 hours to reach equilibrium. Reatto et al. (2008) conducted a study that compared the matric potentials created using pressure plates with those created with the centrifuge method for potentials between -1 and -1500 kPa. They found that the centrifuge method performed as well as the more traditional pressure plate method but only took a fraction of the time.

The novel approach that was initially conceived in Madrigal (2010) and was further developed in this project is to use the ceramic rod to capture and later extract soil water, instead of just creating a pressure profile within the soil. A simplified illustration of the proposed apparatus is given below in Figure 1, where: r_0 is the distance from the axis to the end of the ceramic rod, r_{min} is the distance from the axis to the beginning of the soil column, and r_{max} is the distance from the axis to the interface of the rod and soil column. F represents the direction of the centrifugal forces.

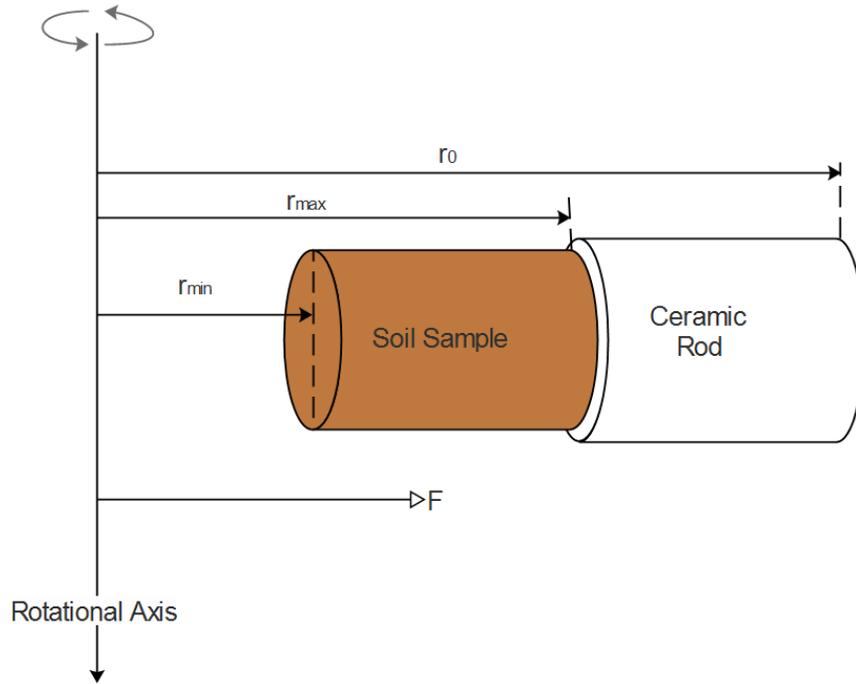


Figure 1: Diagrammatic Illustration of Centrifugal Separation Design

The force per unit volume applied to the water by the centrifuge, F_{cv} , is a product of the fluid density ρ_w , the angular velocity of the rotor ω , and the radial distance from the rotational axis r . This is shown below in Equation 1

$$F_{cv} = \rho_w * \omega^2 * r \quad (1)$$

Assuming a steady state centrifugation force, the centrifugal force per unit volume can be related to Darcy's equation for flow through an unsaturated media. Equation 2 shows the result of this derivation, where q is water flux in the radial direction, K is the hydraulic conductivity, and ϕ is the matric potential in the soil column (Dane and Topp, 2002).

$$q = K * \left(\frac{d\phi}{dr} - \rho_w * \omega^2 * r \right) \quad (2)$$

Assuming that water would be allowed to exit freely from the end of the ceramic rod, r_0 , hydrostatic equilibrium will eventually be reached where the pressure created by the pressure gradient is equal and opposing to the forces created by the centrifugal force. At hydrostatic equilibrium, $q = 0$ and Equation 2 can be rearranged into Equation 3 (Dane and Topp, 2002). Integrating Equation 3 with respect to radial distance r yields Equation 4, which allows the matric potential to be calculated at every point within the soil column.

$$\frac{d\varphi}{dr} = \rho_w * \omega^2 * r \quad (3)$$

$$\varphi(r) = \rho_w * \frac{\omega^2}{2} * (r^2 - r_0^2) \quad (4)$$

The average value theorem can be applied to Equation 4 by integrating it with respect to r and dividing it by the length of the soil column to yield the average matric potential within a soil column at any rotational velocity, $\bar{\varphi}(\omega)$. This is shown below in Equation 6, where r_{min} is the radial distance to the beginning of the soil column and r_{max} is the radial distance from the rotational axis to the end of the soil column.

$$\bar{\varphi}(\omega) = \frac{1}{r_{min} - r_{max}} * \int_{r_{max}}^{r_{min}} \rho_w * \frac{\omega^2}{2} * (r^2 - r_0^2) \quad (5)$$

$$\bar{\varphi}(\omega) = \frac{1}{r_{min} - r_{max}} * \rho_w * \frac{\omega^2}{6} * ((r_{min}^3 - 3 * r_0^2 * r_{min}) - (r_{max}^3 - 3 * r_0^2 * r_{max})) \quad (6)$$

Because the pressure gradient within the soil varies along its length, the precision of this method to extract water at very specific matric potentials is limited. However, the equation for the average matric potential (Equation 6) should be useful for approximating the matric potential at which the water is extracted. An important thing to note with Equation 6 is that it is most useful when the length of the ceramic rod is much shorter than the length of the soil column, making the average matric potential more representative of the range.

Once mobile water is captured by the porous ceramic rod it then needs to be extracted for analysis without significant fractionation occurring and also extracted from the soil, post-extraction. A current popular method for extracting water from soil and plant samples for isotopic analysis is cryogenic vacuum distillation (Orlowski et al. 2013). Madrigal (2010) determined that this method would also work for ceramic rods, achieving full re-extraction without any significant fractionation.

Methodology

Site Description

All soil samples used for this study were taken from H.J. Andrews Research Forest located in the Western Cascades Range of Oregon, USA. It has a Mediterranean climate with wet winters and very dry summers. The specific sampling location is from a soil pit on a south facing slope of 41 degrees within Watershed 01 of the research forest. The soil type is Frissell, which is a fine-loamy Regosol developed in unconsolidated parent materials with many cobbles (Dyrness 1969). Its bulk density is approximately 0.82 g-cm^{-3} with a field capacity of 290 mm/m. Any precipitation data presented in this paper was collected from the H.J. Andrews Research Station PriMet collectors.

Proof of Concept

The method of using a centrifuge to capture soil water within porous ceramic rods was already initially investigated in Madrigal (2010). He proved that water could be successfully captured within the ceramic rods and subsequently extracted via cryogenic vacuum distillation. It was also experimentally shown that extraction with cryogenic vacuum distillation can essentially fully recover the water without causing significant fractionation. One of the objectives of this paper is to further characterize the effectiveness of the method that Madrigal developed.

The centrifuge used in the method characterization and experimental methodology is an Avanti J-HC centrifuge using a JS-4.2A rotor. Its speed is between 1000 and 4200 rpm, with a

rotor radius of approximately 10 in or 25.4 cm. The method uses a series of PVC plumbing parts to position the soil core against the ceramic rod and hold it within the 500 ml vial holders provided with the machine. The specific PVC parts used are two 2" by 1" Spigot and Socket Bushings, one ¾" pipe coupler, and a 1" End Cap, machined lightly to improve fitting. The soil samplers/holders are simply a 5 cm length of PVC pipe with the last centimeter of one end beveled at 15 degrees to improve sampling and allow the sampler to extend to the face of the ceramic rod. The ceramic rods used are the 1 bar 630 series manufactured and purchased by Soilmoisture Equipment Corporation. They are 2" by 1" rods made of high-fired Alumina, with a maximum pore size of 1.7 µm, a porosity of 45%, and a hydraulic conductivity of 86 nanometers per second. The configuration of the device is shown in Figure 2 below.



Figure 2: 1 shows the ceramic rod sitting in the end cap within the first bushing. 2 Shows the addition of the coupler onto the ceramic rod. 3 Shows the addition of the second bushing as well as the soil holder/sampler inserted into the bushing. The entire assembly is then loaded into a 500 ml centrifuge vial holder.

The experiment in Madrigal, 2010 used a river soil with extremely high clay content and only extracted to -1.0 MPa. Because this study uses a significantly different soil type and higher

target matric potential, mass transfer trials were conducted to verify that the method still works. Soil from watershed 01 was dried for 12 hours at 105 degrees C to remove all existing moisture then added into the soil samplers in divisions of 12 to 15 grams. Distilled water was then added to the top of the sampler until the soil samples reached between 29 to 30 percent gravimetric water content, with the samples left untouched for approximately an hour to allow the water to uniformly wet the soil column.

The samples were covered with parafilm to prevent evaporation, then spun within the centrifuge and weighed over time until the ceramic rod no longer gained mass. Initially, three sets of four replicates were spun at 1300, 2600, and 4200 rpm. After reaching equilibrium each replicate was analyzed for matric potential using the WP4C Dewpoint Potentiometer, by Decagon Devices, Inc. Calibration of the Dewpoint Potentiometer was verified against pre-made samples of 0.5 KCl solutions after each measurement. After the initial results were analyzed, another trial using a custom ceramic rod with a 15-bar air entry value was conducted at 4200 rpm and similarly analyzed for matric potential. The mass transfer curves are shown in Figure 5 and the matric potential results are shown in Figures 3 and 4.

Experimental Procedures

Soil samples were taken using the machined soil holders of the device to minimize the amount of handling each sample experienced. At each sampling event, three cores were taken at depths of 10, 20, 30, 50, and 100 cm, securely wrapped in parafilm to prevent evaporation, then kept in refrigeration until centrifugation. Six sampling events were conducted at 09-14-2013, 09-25-2013, 11-11-2013, 02-25-2014, 04-19-2014, and 06-07-2014. Because of resource constraints and sampling complications, the November and February samples only had two replicates of each depth and the June samples only had 1 replicate.

The soil cores were spun in the centrifuge using the previously described device for approximately 14 hours at 4200 rpm. Parafilm was used to cover the top of the sampler and where the bushings meet to help prevent evaporation and fractionation. The duration was chosen based on the mass transfer curve in Madrigal (2010) and the speed was chosen to maximize the amount of water extracted into the ceramic rod. After spinning, the soil and ceramic rod were sealed in Whirl-Paks[®], produced by Nasco, and stored in refrigerators to minimize evaporation. It is worth noting that there were six samples of mobile water from the 09-25-2013 sampling set that were stored in 2 ml vials and sealed with parafilm before Whirl-Paks[®] started being used.

After being spun in the centrifuge, the water in each rod and soil sample was extracted using cryogenic vacuum distillation. The process of cryogenic vacuum distillation begins with samples being completely frozen using liquid nitrogen within a glass apparatus connected to a powerful vacuum. After the sample is frozen to prevent loss of water into the vacuum, the apparatus is evacuated to at least 200 millitorr then closed off. The sample is then heated using boiling water while a separate bulb is exposed to the liquid nitrogen. Over the course of 4 hours the water is completely removed from the sample through a combination of heat and low pressure, and condensed and frozen at the bottom of the collection bulb being cooled by liquid nitrogen. After 4 hours of exposure to the vacuum, a valve is closed to check if water vapor condenses above the heated bulb. If no condensation occurs then that confirms that the sample water is fully extracted and the process is complete (Shimabaku 2012). The collected water was then transferred via pipette into Whirl-Paks[®] for storage.

After final extraction the rod and soil water samples, along with the precipitation samples from the PriMet station at HJ Andrews Research Station, were shipped off-site to the Hillslope and Watershed Hydrology Lab, Global Institute for Water Security at University of

Saskatchewan to determine hydrogen and oxygen isotopic ratios using a Los Gatos Research DLT- 100 Liquid Water Isotope Analyzer. Isotopic ratios $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are reported relative to Vienna Standard Mean Ocean Water (VSMOW) in per million (‰). Equation 7 below represents how $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are determined, where R is the ratio of ^{18}O to ^{16}O atoms or deuterium to hydrogen atoms of the sample and the VSMOW. The 2 sigma uncertainties of the measurements made by the Liquid Water Isotope Analyzer is 0.2 and 2 parts per million for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively.

$$\delta^2H \text{ or } \delta^{18}O = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000 \quad (7)$$

Before shipping off-site for isotopic analysis samples were transferred to 2 ml vials with conical caps and inserts to prevent evaporation via fractionation. Samples which had visible particulates were filtered through a syringe filter beforehand, provided there was enough volume. A limitation of the method used to analyze isotopes is that samples of less than 0.2 ml cannot be measured so many samples of mobile water from very dry periods had to be discarded.

Results and Discussion

Centrifugal Extraction Characterization

The initial results of the mass transfer trials produced a lower matric potential within the soil samples than the theoretically derived Equations 4 and 6 predicted. It was hypothesized that this discrepancy was due to the lower air entry value of the 1 – bar ceramic rods allowing air to disrupt the water column within the ceramic rod. To test this hypothesis the mass transfer trial was repeated with a custom-made ceramic rod with an air entry value of 15 bars at 4200 rpm. It was only tested at 4200 rpm because of time and resource restraints.

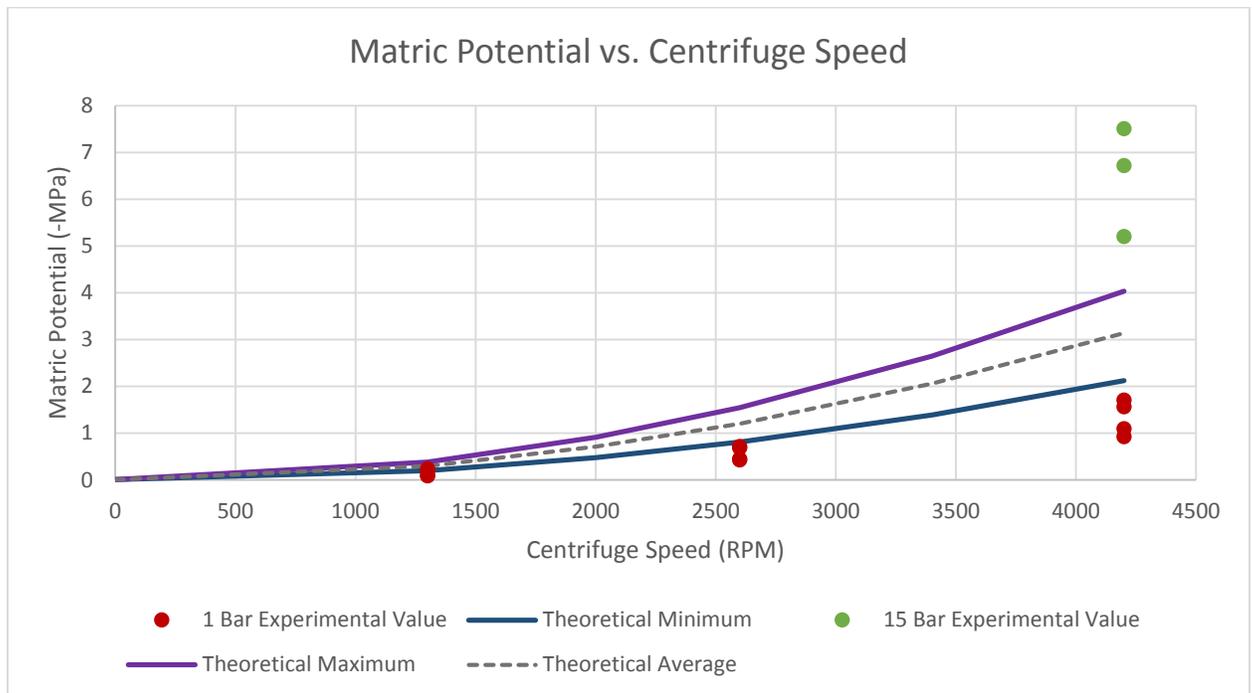


Figure 3: This graph shows the results of the dewpoint potentiometer measurements of the samples spun at 1300, 2600, and 4200 rpm with the theoretical range of matric potentials. It also includes the trials spun with the 15- bar ceramic rod.

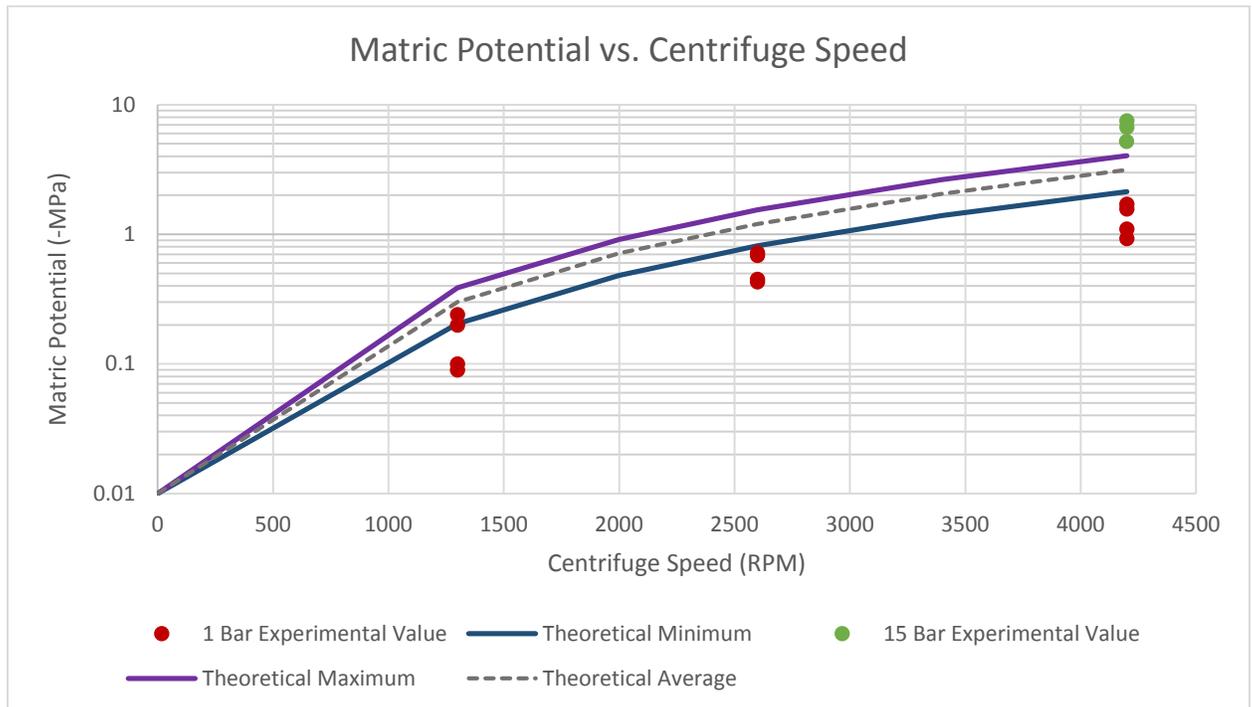


Figure 4: A graph of the dewpoint potentiometer results plotted with a logarithmic scale to increase the visibility of data points.

Figure 3 and Figure 4 plot the theoretical matric potentials achieved in the soil column by centrifuging the device, as well as the experimentally obtained matric potentials as measured via dewpoint potentiometer. The discrepancy between the theoretical minimum, maximum, and average matric potential is due to the variation of centrifugal force along the length of the soil sample. Because this variation expands with the speed of the centrifuge and the length of the soil column, more precision can be obtained either by reducing the initial height of the soil column, or extracting at a lower matric potential. The 1 bar ceramic rods do much better at approximating the theoretical matric potential at lower speeds because at centrifuge speeds that create more than 1 bar of suction, air can begin to enter the rod, disrupting the water column within the rod that allows water to be pulled out of the soil. The trials with the 15 bar ceramic rod corroborates this conclusion, tripling and almost quadrupling the matric potentials

of the 1 bar rods. The magnitude of this result was unexpected, as it substantially exceeds the calculated theoretical maximum potentials. A likely explanation for this surprising exceedance is very slight evaporation experienced during and after centrifugation before analysis by dewpoint potentiometer. When soil gets very dry, even small changes in moisture content can drastically change matric potentials. Some evidence supporting this explanation is the measured matric potential of the soil samples correlated with the time stored between extraction and analysis. Figure 5 below is a conceptual soil water retention curve that illustrates this point, as water content drops below a certain threshold, in this case approximately 0.2, the rate of increase in matric potential rises dramatically.

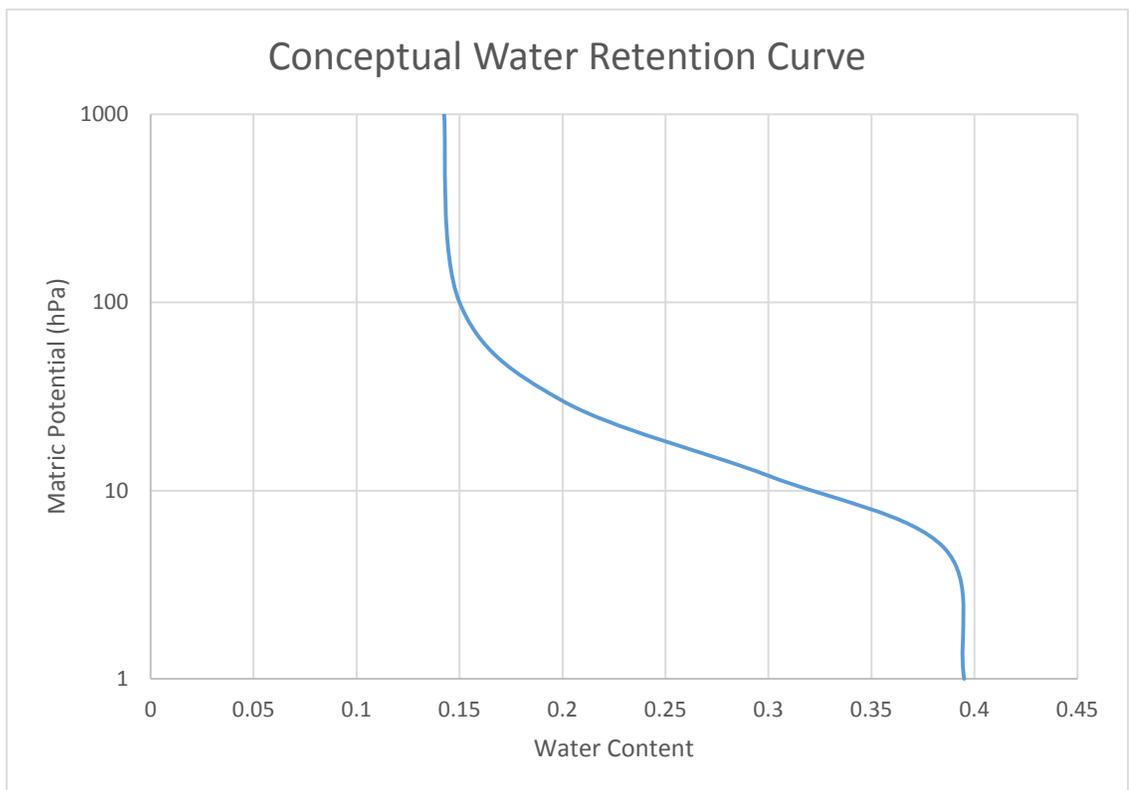


Figure 5: Conceptual graph showing the changes in matric potential in soils with respect to its water content

To better quantify the extraction of water from the soil sample, a mass transfer study was conducted (Figure 6). The trial was very similar to those done in Madrigal (2010) but uses the same Frissell soil as the rest of this experiment and included higher centrifuge speeds. After measuring both the mass of soil, water, and ceramic rods the change in mass was recorded periodically throughout centrifugation until the rate of water transfer dropped below 0.01 grams per hour, which was the precision of our lab scale. One result of note is that the time required to fully extract water from the soil is significantly less than that shown by Madrigal (2010), approximately two to three times shorter. The discrepancy can be explained by Madrigal (2010)'s choice of soils, a very high clay content river soil which would have much lower hydraulic conductivity.

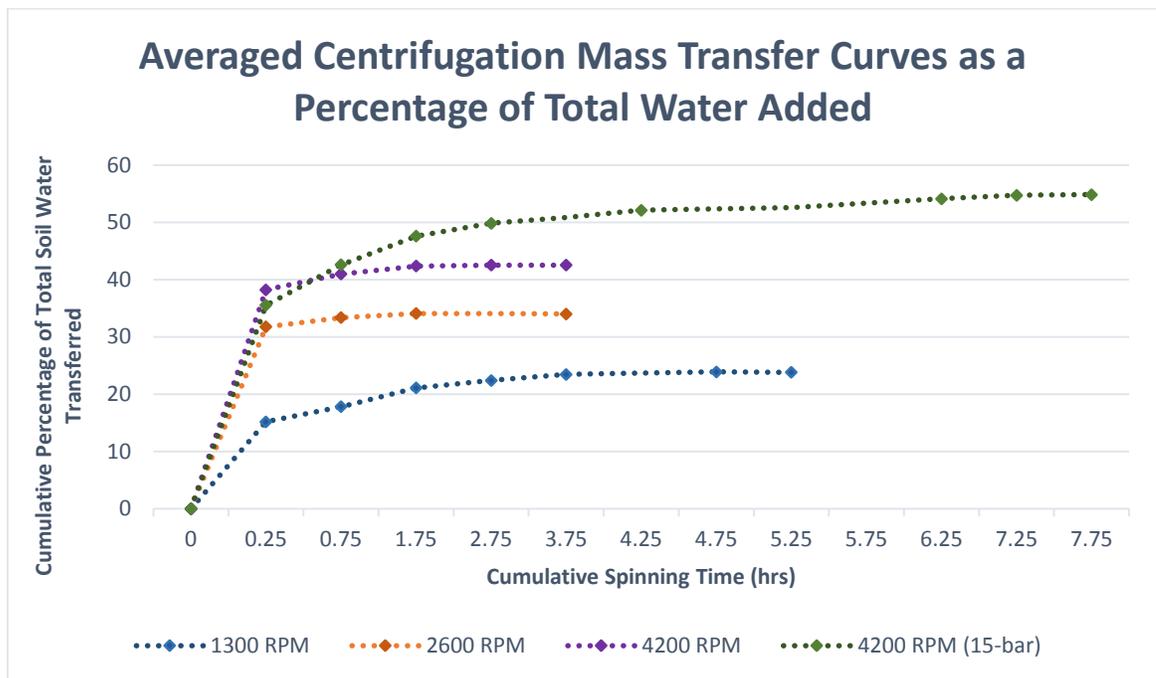


Figure 6: Mass of water gained by the ceramic rods as a percentage of the total water within the soil at each centrifugal speed. The replicates of each trial are averaged for clarity.

The rate of water extraction into the ceramic rod is expected to decrease exponentially as the soil moisture in the soil column decreases, increasing matric potential and decreasing the hydraulic conductivity of the soil until the pressure profile in the soil exerts equal and opposite suction to the centrifugal force resulting in hydrostatic equilibrium. This sort of behavior is exhibited in both the 1300 rpm trial and the 4200 rpm trial using the 15 bar ceramic rods but the shape of the higher pressure trials with the 1 bar ceramic rods exhibit a much less gradual transfer. An explanation is that the lower air entry values combined with the higher suctions quickly extract the water from the larger pores and allow air into the ceramic rod that disrupts the continuity of the water column before more tightly bound water can begin to flow into the rod. The theoretical minimum suctions created within all three speeds (-2, -8.2, and -21.3 bars for 1300, 2600, and 4200 rpm, respectively) are all actually higher than the air entry value of the 1 bar rods, which explains why even the 1300 rpm trials had unexpectedly low matric potentials as shown in Figure 6, despite the shape of its graph.

It is worth noting that all of the trials extracted at least 50% of the mass within the first 15 minutes, with the 2600 rpm and 4200 rpm 1 bar trials extracting more than 90%. In fact, the 15 bar rod trial took slightly longer, on average, to extract the same amount of water as the 1 bar rod. This indicates that for applications that are more concerned with extracting enough mobile water to analyze isotopically than creating very high and precise matric potentials, using the less expensive ceramic rods with 1 bar air entry values could be the better choice.

Isotopic Study

When studying the isotopic data of forest water, the data are generally displayed and analyzed with respect to a Global Meteoric Water Line (GMWL) which describes a linear correlation of water vapor above oceans representing water that has experienced no additional

evaporative enrichment. The GMWL approximates the equation $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 10\text{‰}$. The source of the water vapor can affect the intercept slightly, with arid regions increasing it and more humid regions lowering it but the slope remains near 8. The slopes of all but the most humid surface waters are usually significantly lower than the GMWL with more arid regions having slopes approaching 4 and moderately humid areas having slopes between 5 and 7 (Clark and Fritz, 1997). The difference is due to evaporative fractionation. The local meteoric line as calculated by Brooks et al. (2010) for the HJ Andrews site is $\delta^2\text{H} = 7.8 * \delta^{18}\text{O} + 10.3\text{‰}$, which is remarkably close to the GMWL. Local precipitation data from the 11-2009 to 12-2013 have a slope of 7.6 and an offset of 3.2‰ excluding the arid summer months which have very little precipitation.

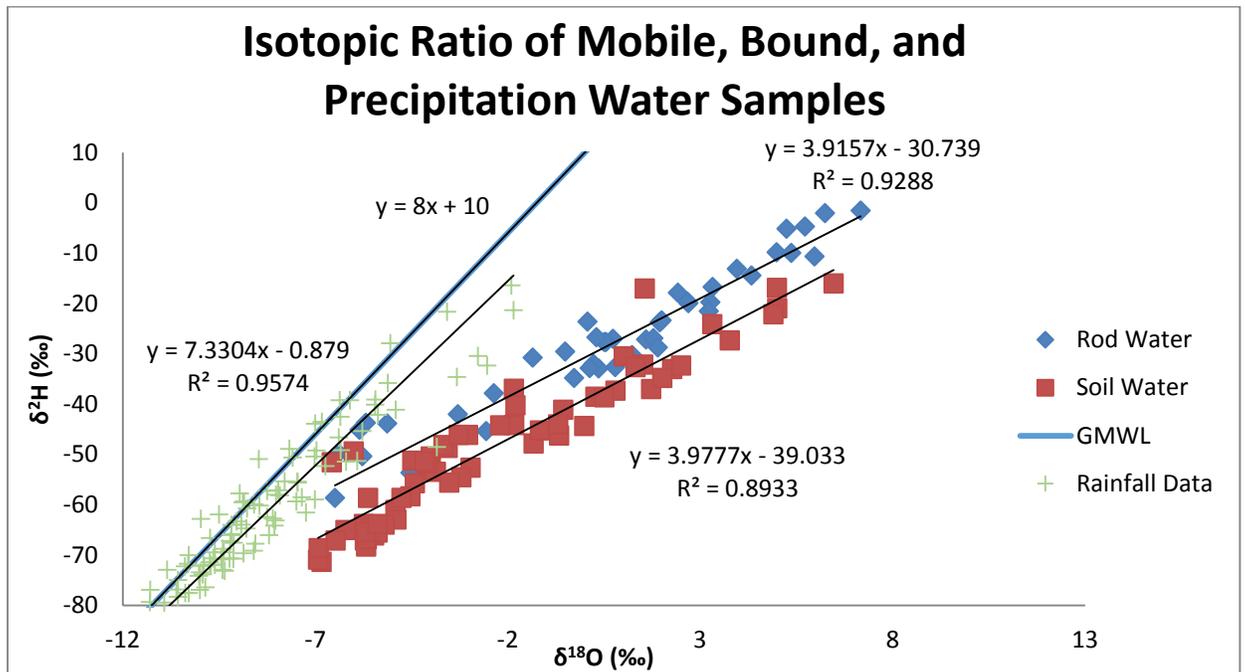


Figure 7: $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ of mobile (rod) water, immobile (soil) water, and precipitation data plotted next to the GMWL with trend lines and correlations.

Mobile water and tightly bound water differ in evaporative enrichment, with the mobile water showing more deuterium enrichment (Figure 7). Both mobile and soil water trend lines deviate very strongly from the local meteoric water line, while the precipitation samples follow it fairly closely except for slight $\delta^{18}\text{O}$ enrichment. The very low slopes of the rod and soil data are indicative of evaporation that would occur in desert environments (Clark and Fritz 1997). Considering that our site location has a fairly high humidity during most of the year, it is likely that substantial evaporation occurred somewhere during our handling.

A useful metric when analyzing water isotopic data is the deuterium excess (d-excess) which is the deviation from the GMWL, calculated as $\delta^2\text{H} - 8*\delta^{18}\text{O}$. Values near 10 represent no evaporation, while lower values represent more and more evaporative enrichment because evaporation affects hydrogen ions more strongly. Deuterium excess is a valuable tool for analysis because $\delta^2\text{H}$ or $\delta^{18}\text{O}$ alone can be identical to precipitation data even if significant evaporation occurred. Deuterium excess incorporates both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ into a ratio which allows it to be plotted against a separate metric, such as space or time (Levia and Carlyle-Moses 2011).

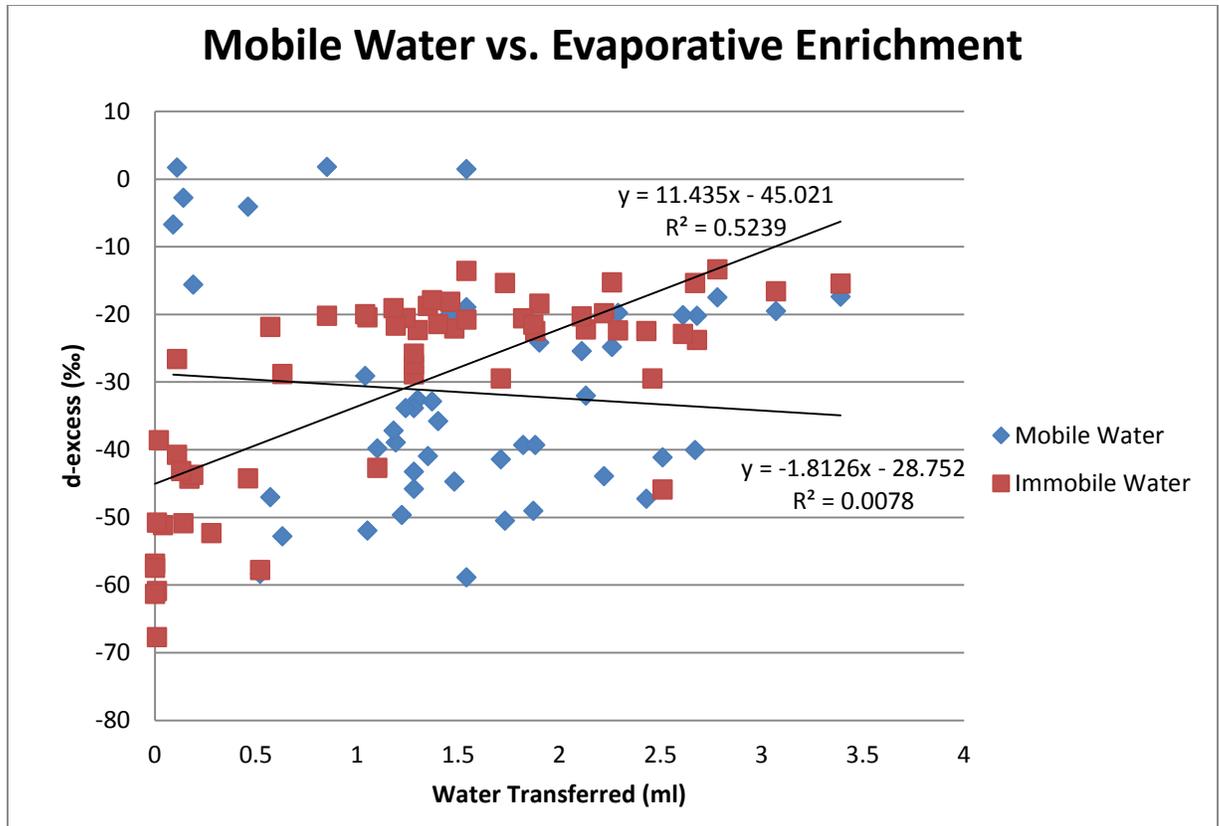


Figure 8: The d-excess of both mobile (rod) and immobile (soil) vs. total water captured by the ceramic rods during centrifugation.

Figure 8 represents how evaporated (d-excess) the samples are vs. the amount of mobile water transferred into the ceramic rod during centrifugation. There is an appreciable R^2 value (0.5239) for the tightly bound water but the mobile water in the rods shows almost no correlation between evaporative enrichment and the amount of mobile water captured. If evaporation was occurring during centrifugation, it would be expected that the less water the rod received, the more evaporative enrichment would occur because a higher proportion of the water would have evaporated. The positive trend that is seen within the soil water samples could partially be explained by evaporation in the field, as there would be more pores exposed with less mobile water in the soil. Based on these results it is unlikely that centrifugation represents the majority of the evaporative enrichment.

The proposed explanation for the lack of correlation between d-excess and amount of water is that the Whirl-Paks® do not seal as effectively as was thought. Fortunately a few of the early samples were collected and stored within 2 ml vials with parafilm around the lid, almost entirely composed of mobile (rod) samples. Figure 9 is identical to the one above but doesn't include the vial samples or any samples that were frozen.

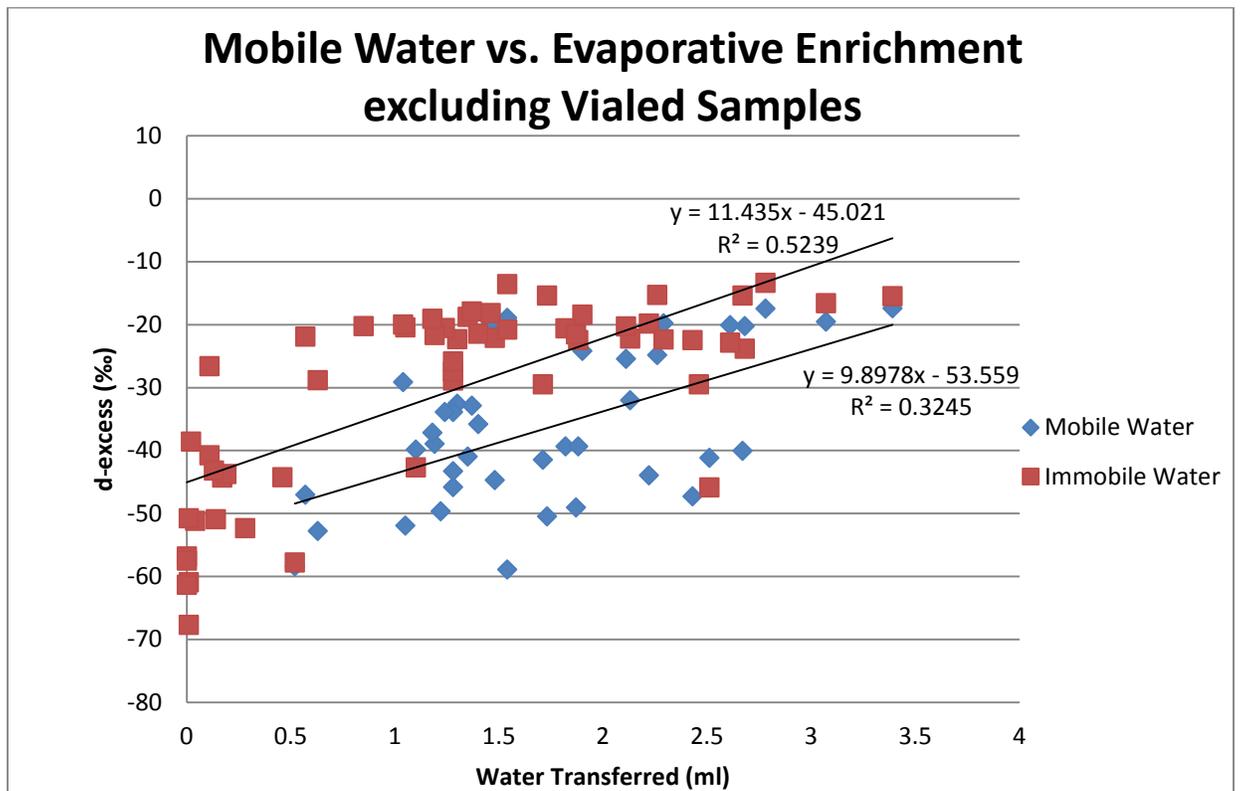


Figure 9: The d-excess of both mobile (rod) and immobile (soil) vs. total water captured by the ceramic rods during centrifugation but excluding frozen samples and samples stored in vials.

When the vial samples and frozen samples are excluded the relationship between the amount of mobile water and d-excess becomes much stronger. The correlation is still fairly low but this change is substantial enough to suggest that the vial samples experienced less evaporation regardless of their amount of water. The lower correlation can also be explained by random

changes in how long each sample was stored after centrifugation and how well each Whirl-Pak® was sealed. If evaporation during centrifugation represented a significant portion of the evaporation in the samples than the vial samples would have been as susceptible, which the change in R² values refutes.

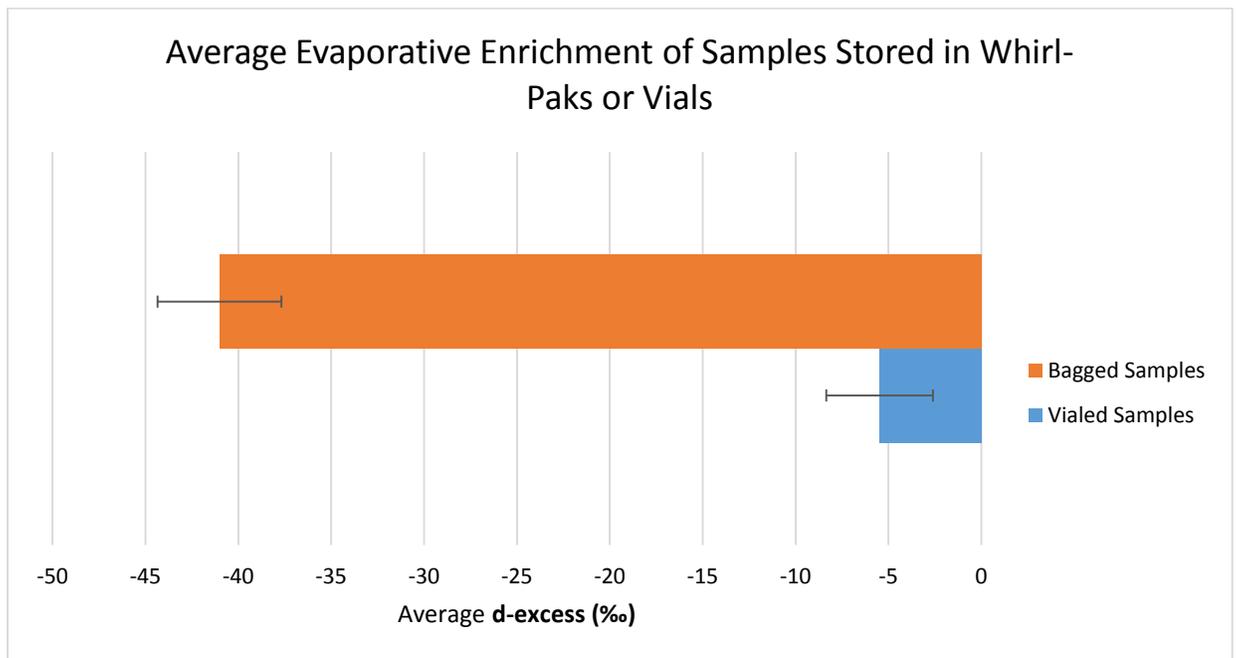


Figure 10: Average d-excess of the 09-25-2013 sampling event for both vial samples and those that were stored in Whirl-Paks. Error bars represent the standard error of the mean.

Because the vial samples were not randomly distributed among all the samples but rather were all part of the 09-25-2013 sampling, this difference in evaporative enrichment could simply be indicative of less enriched soil at that point in time, although this is unlikely considering that September is an extremely dry period. However, to correct for this, the vial samples are directly compared to the other samples taken during that event but that were stored in baggies (Figure 10). From the large difference shown in Figure 10 it is clear that the samples stored in vials experienced less evaporation than those stored in Whirl-Paks. The

consequence of this conclusion is that the vast majority of isotopic data collected in this study are not useful because of evaporative fractionation.

Even though most of the samples are fractionated, the data do show some salvageable insights. The isotopic graph of the mobile water, does not show much variation with depth, which is to be expected if one assumes that it is more or less freely mixing (Figure 11). However, the immobile water samples taken at 100cm depth deviate less from the global meteoric water line than samples taken at other depths (Figure 12). They cluster at the much more depleted end of the graph, which resembles some of the results from Brooks et. al (2010). This is consistent with Brooks' conclusion that after the initial recharge at the beginning of the water year, the tightly bound water at 100cm depth is to some extent isolated from the other pools of water, as well as the from the effects of evaporation. Tightly bound water higher up in the soil profile is not as shielded from evaporation and is repeatedly dried and then recharged from precipitation and mobile water.

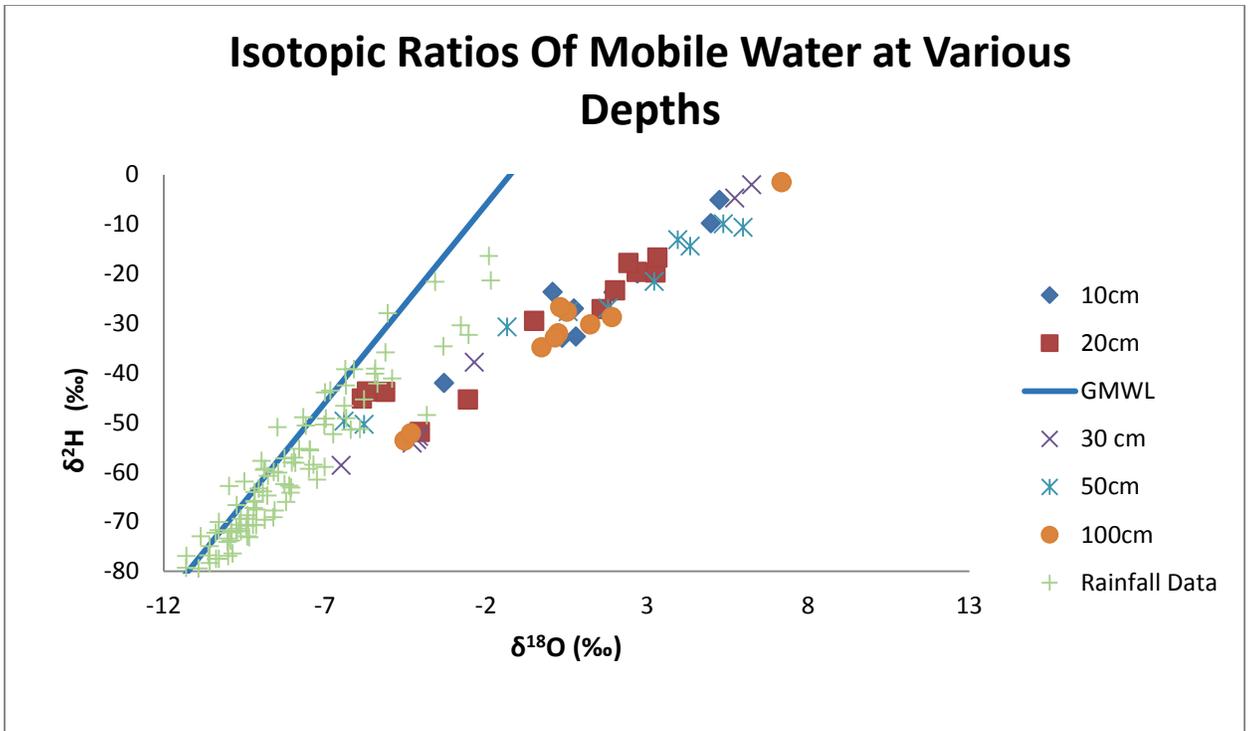


Figure 11: Isotopic ratios of mobile (rod) water separated by depth.

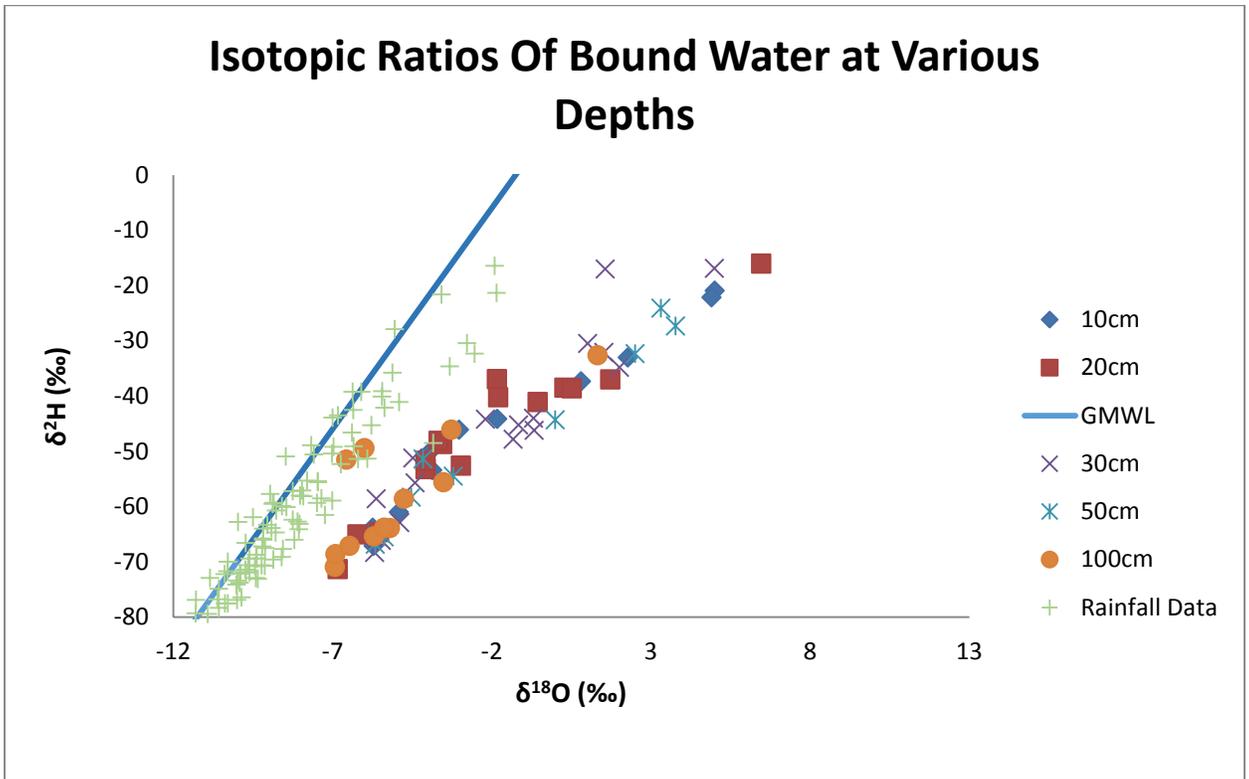


Figure 12: Isotopic ratios of immobile (soil) water separated by depth.

The average d-excess of mobile, immobile, and precipitation samples from September 2013 to June 2014, with the precipitation value representing the averaged samples of each month between November 2009 and December 2013 support the conclusions drawn from the depth analysis (Figure 13) It is clear once again that the samples have experienced significant evaporation from storage, as none of the average samples come close to the range of d-excess values of precipitation. However, the general trend starts with highly evaporated soils (to the point where there is not enough recoverable mobile water to analyze) from the summer dry season that begin to be replenished by isotopically depleted Autumnal rains until they are saturated. After this, the immobile water fluctuates very little until and appears to be independent of the precipitations varying. The mobile water shows a high variability over the season, and very generally follows the pattern of variation of the precipitation samples. These trends further support the conclusions of Brooks et al. (2010) where less tightly bound water mixes with precipitation and flows to streams while tightly bound soil water is largely segregated.

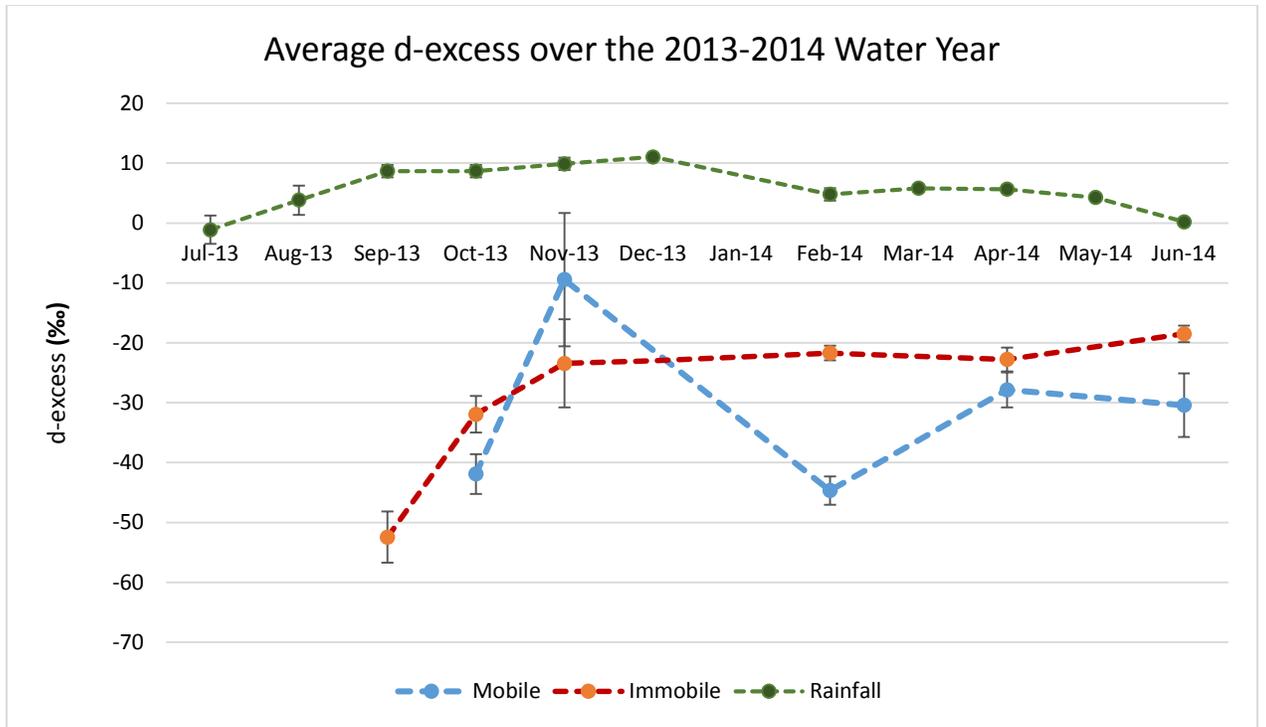


Figure 13: Average d-excess of mobile (rod) water, immobile (soil) water, and averaged historical precipitation samples at each sampling event. Note: Rainfall data is an average of precipitation data from November 2009 to December 2013. Error bars represent standard errors of the mean.

Conclusions

The results from the centrifugal extraction trials show promise as a method for capturing soil water at specific ranges of matric potentials and allowing it to be re-extracted for analysis. As an alternative to using porous pressure plates, it takes only a fraction of a time and experiences very little evaporation during the process, which is important for isotopic study. However, the process needs to be further explored to establish it as a reliable method. Trials need be run to characterize exactly how the air-entry values of the ceramic rod and the types of soil affect the time needed to reach hydrostatic equilibrium and the precision and accuracy of the matric potentials created in the soil column. A potential problem is that because the ceramic rod is dry initially, if the soil sample does not have sufficient soil water to fully wet the ceramic rod then the water column will be shorter than r_0 , which will produce a lower matric potential than predicted. Future efforts in refining the method should also include designing air-tight devices to minimize evaporation during spinning.

Comparison of the evaporative enrichment between samples stored within Whirl-Paks® and those few stored within vials clearly indicates that the major culprit in evaporation was storage within the Whirl-Paks®. Because the volumes of mobile water samples were almost always lower than the volumes of immobile water and the same amount of evaporation fractionates smaller volumes more than larger ones, this error in methodology rendered direct comparison inconclusive.

Although an improper storage method made the comparison outlined in the hypothesis ineffective, the identifiable trends are consistent with Brooks' et al. (2010) conclusions about

the separate “water worlds.” The deeper immobile water samples are significantly more isotopically depleted and the d-excess of the soil samples start very low then rise throughout the fall until holding constant. This is consistent with the conclusion that soil micropores are recharged at the beginning of the water year and then do not interact with more mobile water throughout the year until dry summers allow vegetation to create sufficient suction to access it. I recommend repeating the study with the proper storage in 2 to 4 ml glass vials with conical caps and using ceramic rods with higher air-entry values to increase consistency in extraction pressure.

The institutional resources and knowledge of how to study water isotopes have greatly increased from refining the centrifugal extraction method and setting up the cryogenic vacuum distillation units. Further development of the centrifugal extraction method has important implications on the isotopic approach to studying soil hydrology by allowing the separation of different pools of water by matric potential. Investigations made possible by this could greatly increase understanding of hydrology, contaminant transport, soil mechanics, and other fields.

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