Soil Water Repellency Index Prediction Using the Molarity of Ethanol Droplet Test

The profound impact of soil water repellency (WR) on vadose zone processes makes accurate characterization of this phenomenon paramount. Numerous WR measurement techniques exist, each having advantages and disadvantages with regard to laboriousness, resolution, and accuracy. The molarity of ethanol droplet (MED) test quantifies WR as the lowest ethanol concentration permitting droplet penetration within 5 s, or alternatively, the 90° liquid surface tension of the infiltrating droplet ($\gamma_{\text{ND}}$). This method is simple and rapid but poorly represents soil wetting behavior across measurement intervals. Although time consuming, water/ethanol sorptivity ratio calculation of the repellency index (R) generates a continuous, linear scale of WR that intrinsically isolates the effect of WR on infiltration. This study compared MED and R measurements of sand samples displaying varying degrees of WR. Each technique was performed at 20°C and 1.78 kPa H2O vapor pressure using duplicate subsamples of oven-dried (55°C) sands. A nonlinear association between R and $\gamma_{\text{ND}}$ or MED was observed. Regressing $\log_{10} R$ by $\gamma_{\text{ND}}$ revealed a statistically significant model, yet the 95% $\log_{10} R$ prediction interval included values less than the theoretical lower limit of R. Alternatively, regressing $\log_{10} R$ by MED generated the following model ($P < 0.0001, r^2 = 0.727$): $\log_{10} R = 0.705 + 0.5144(MED)$, capable of predicting R within the operation bounds of R theory. While the predicted R values are distributed across a wide interval, their availability offers cautious users an intuitive scale for enhanced interpretation of more commonly generated MED data.

Abbreviations: EtOH, ethanol; MED, molarity of ethanol droplet; R, repellency index; WDPT, water droplet penetration time; WR, water repellency.

Soil water repellency (WR) is a globally recognized phenomenon, significantly affecting seed germination, plant growth, surface runoff and erosion, preferential flow path development, and non-target movement of fertilizers and pesticides into surface and groundwater resources (Larsbo et al., 2008; DeBano, 2000; Doerr et al., 2000). Although severe WR is often observed regionally, soils exhibiting varying degrees of WR are widely distributed, reflecting differences in climate, microbial communities, vegetation, land use, and soil type (Bond and Harris 1964; Franco et al., 1995; Roberts and Carbon, 1972; Wallis et al., 1991; York and Canaway, 2000).

Appropriate assessment of soil WR is often confounded by inconsistencies in sample preparation and measurement protocol (Dekker et al., 1998; Wallis et al., 1991; Tillman et al., 1989). Recently recognized hydrologic impacts of minimally repellent soils make accurate characterization of soil wetting behavior critical (Letey et al., 2000; Tillman et al., 1989).

Soil WR, succinctly defined as an obtuse liquid–solid–vapor contact angle ($\theta$), is observed when the tension (or free energy) between a liquid droplet and the solid surface on which it rests ($\gamma_{\text{SL}}$) exceeds the solid–vapor tension ($\gamma_{SV}$) of the adjacent boundary (Gilboa et al., 2006). While the surface tension (or free energy) of any liquid at its vapor boundary ($\gamma_{LV}$) is indeed associated with both WR and $\gamma_{SL}$, the tendency of a liquid to either “disperse” ($\theta \leq 90^\circ$) or “attenuate” ($\theta > 90^\circ$) on a solid surface is fundamentally governed by the disparity between $\gamma_{SL}$ and $\gamma_{SV}$ Thus, for a given surface, Eq. [1] demonstrates how surface tension between a solid and its surroundings dictates the equilibrium contact angle at the liquid–solid–vapor interface (Young, 1805):

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV} - \gamma_{SL}$$

[1]
where $\gamma$ (mN m$^{-1}$) is the surface tension, or interfacial free energy (mJ m$^{-2}$), at each designated phase boundary and $\theta_Y$ is the experimental estimate of the equilibrium contact angle. Soil mineral surfaces generally demonstrate a $\gamma_{SV}$ that exceeds $\gamma_{SL}$ and are subsequently hydrophilic. Conversely, solid organic surfaces tend to exhibit free energy at water boundaries in excess of the adjacent $\gamma_{SV}$, making them hydrophobic (Zisman, 1964). Thus, the addition of organic materials to a soil matrix or adsorption of organic polymers onto soil mineral constituents alters the mean surface free energy and wetting behavior of soils.

Following this concept, the estimation of the liquid–solid–vapor contact angle ($\theta_Y$) provides a useful measure of WR (Letey et al., 1962). While the intrinsic characteristics of soils complicate its direct measurement, the equilibrium contact angle can be inferred through capillary rise assay, where the mean pore radius ($r$) of the soil is calculated from the capillary rise of a liquid (e.g., ethanol) having an apparent contact angle of $0^\circ$ (Letey et al., 2000):

$$h = \frac{2\gamma_{LV} \cos \theta}{\rho g} \tag{2}$$

where $h$ is the height of rise, $\gamma_{LV}$ is the liquid–vapor surface tension, $\theta$ is the equilibrium contact angle, $\rho$ is the liquid density, and $g$ is the gravitational constant. Although useful, this technique does not permit the measurement of $\theta_Y > 90^\circ$ and is time consuming (Letey et al., 1962; Watson and Letey, 1970).

The water droplet penetration time (WDPT) method reports the number of seconds elapsed before a standard-sized droplet of water completely infiltrates a soil, with greater WDPT values corresponding to higher degrees of WR (King, 1981). Essentially, the WDPT measures the amount of time required for $\gamma_{SL}$ to fall below $\gamma_{SV}$, thereby quantifying the persistence or stability of WR (Doerr et al., 2000; Letey et al., 2000; Watson and Letey, 1970). Granted that reports of WDPT values of $\sim 21,600$ s undoubtedly describe severe WR, the likelihood of preemptive runoff or evaporation from such a soil in the field limits meaningful interpretation of WDPT values (Dekker and Ritsema, 1994). Moreover, the limited surface area sampled by WDPT measures contributes to wide variability about the mean values (Hallett et al., 2001). Lastly, while the WDPT method demonstrates infinite resolution in severe WR assessment, it lacks the precision required to distinguish intermediate degrees of soil repellency (Dekker and Ritsema, 1994; Letey et al., 2000).

First developed by Watson and Letey (1970), the “critical” or “90°” surface tension ($\gamma_{ND}$) test quantifies WR as the greatest $\gamma_{LV}$ of a standard-sized aqueous ethanol droplet that will fully infiltrate soil within 5 s. This original index has since undergone minor modification. Dekker and Ritsema (1994) reported WR values as the volumetric ethanol percentage of the most dilute solution to rapidly infiltrate (<5 s), whereas de Jonge et al. (1999) quantified WR as the minimum $\gamma_{LV}$ of an aqueous ethanol droplet to remain on the soil surface $>5$ s.

While alterations to the $\gamma_{ND}$ test described above were minor in that they retained the procedural “critical infiltration time” of 5 s, King (1981) quantified WR as the molarity of an aqueous ethanol (EtOH; mol L$^{-1}$) droplet to fully infiltrate soil within 10 s. The ordinal nature of the MED test dependent variable prompted yet another modification by Roy and McGill (2002), who suggested that the MED test protocol instead report soil WR as the maximum $\gamma_{LV}$ to infiltrate in $<10$ s.

The solvent properties of aqueous solutions make the $\gamma_{SL}$ and $\gamma_{LV}$ of soil-applied droplets dynamic. Therefore, extension of the “critical infiltration time” from 5 to 10 s compromises precise evaluation of the initial wetting behavior, considered to be the essence of $\theta_Y$ estimation (Gilboa et al., 2006). This strengthens the assertion by Letey et al. (2000) that the $\gamma_{ND}$ test is most appropriate for estimating physically significant parameters governing liquid infiltration: soil $\gamma_{SV}$ and contact angle. Kawamoto et al. (2007) affirmingly redefined the $\gamma_{ND}$ (Watson and Letey, 1970) and MED tests (King, 1981; Roy and McGill, 2002) as analogous measures of EtOH solution infiltration within 5 s.

Although much attention has focused on soils identified as water repellent ($\theta > 90^\circ$), characterization of “subcritically repellent” soils ($\theta \leq 90^\circ$) is of equal or greater importance. Subcritically repellent soils are widespread and have been shown to influence vadose zone processes (Letey et al., 2000; Tillman et al., 1989; Wallis et al., 1991). The soil repellency index ($R$), a ratio of early-time $H_2O$ infiltration to that of a liquid demonstrating an infinitesimal liquid–solid–vapor contact angle (e.g., 5 mol L$^{-1}$ EtOH), is measured by the intrinsic sorptivity method (Hallett and Young, 1999; Hallett et al., 2001; Letey et al., 2000; Tillman et al., 1989). This technique provides a precise, continuous WR measure capable of distinguishing subcritical water repellency in soils characterized as wettable by other techniques (Wallis et al., 1991).

The MED test (Kawamoto et al., 2007) is a useful and practical evaluation of WR because it is more rapid than WDPT, sorptivity, or capillary rise measurements and is easily conducted in the laboratory or field (Dekker and Ritsema, 1994; Watson and Letey, 1970). As originally proposed by King (1981), however, the MED test presents an ordinal WR measure with limited power of statistical inference (Roy and McGill, 2002). Molarity of ethanol droplet test results have failed to accurately predict soil wetting behavior (Doerr and Thomas, 2000), even when transformed to $\gamma_{SV}$ (Gilboa et al., 2006).

In contrast, repellency indices are ratio measures that directly compare the effect of WR on water infiltration characteristics among soils. Moreover, because EtOH infiltration is assumed to be unaffected by WR, relative differences in EtOH sorptivity account...
for varying rates of liquid entry associated with other soil physical properties (e.g., volume, connectivity, and geometry of pores) (Tillman et al., 1989). This intrinsic isolation of WR by $R$ resolves the uncertain compatibility of independently derived MED data and furthers efforts toward combining standardized WR assessments for comparative purposes (Bisdom et al., 1993; Dekker and Ritsema, 1994; Doerr et al., 2000; Roberts and Carbon, 1971).

Furthermore, because $R$ is both continuous and proportional to early-time infiltration ($I$) of water into dry, porous media ($R \propto I^1$), it estimates WR-influenced runoff components of the water balance equation:

$$\Delta S = P + F - ET + \text{run-on} - \text{runoff} \quad [3]$$

where $\Delta S$ is water storage (resulting from precipitation or irrigation events), $P$ is precipitation, $F$ is upward water flux, and ET is evapotranspiration (Evett, 2000). Predicting runoff from soil water infiltration characteristics could prove valuable in assessing the efficacy of overhead irrigation systems. Water restrictions imposed on growers make irrigation efficacy essential, while runoff accounts for most avoidable water loss during irrigation and precipitation events (Troeh and Thompson, 2005). Where significant potential for the redistribution of overhead irrigation exists (i.e., dry, undulating surfaces) and early-time infiltration rate governs efficiency, $R$ estimates may prove useful. Disadvantages of the repellency index method are that it is time consuming, it requires specialized equipment, and it precludes field application for nearly all intents and purposes.

Both the advantages and disadvantages of WR characterization methods are summarized. The MED test is simple, rapid, and resolute but generates an ordinal variable poorly representative of soil wetting behavior across its measurement intervals. Repellency index measurements are complex, tedious, and costly, yet dependably describe the rate of water entry into water-repellent sands. Thus, the experimental objectives of this study were to: (i) identify the relationship between the MED and $R$ of water-repellent sands, and (ii) develop an empirical linear model to predict $R$ from MED measurements.

**Materials and Methods**

Sand samples (Table 1) were collected from the surface of a creeping bentgrass [Agrostis stolonifera var. palustris (Huds.) Farw.] putting green maintained in Griffin, GA ($n = 30$) or generated from an incubation study ($n = 432$) (Moody et al., 2009). Sand physicochemical characteristics are listed in Table 1, where a 1:1 (w/w) soil/deionized water paste was used for pH and electrical conductivity (Rhoades, 1996). The reported bulk densities are either the mean of undisturbed cores (core method; Blake and Hartge, 1986) collected from the Georgia putting green or the mean bulk density of original, loose or disturbed samples (American Society of Testing and Materials, 2000) of a Pennsylvania quarry sand used to formulate the experimental units of the incubation study (Moody et al., 2009). The samples were dried to a constant mass in a forced-air oven (55°C) as recommended for quantification of “soil potential WR” (Dekker and Ritsema, 1994), split into four subsamples, and stored in air-tight centrifuge tubes. Before each SWR measurement assay, the samples were packed into 10- by 35-mm-i.d. columns by dropping filled columns from a height of 1 cm above a lab bench five times.

Ethanol solutions were formulated by gravimetric addition of 95% anhydrous EtOH (EMD Chemicals of Merck KGaA, Darmstadt, Germany) to tared 1-L volumetric flasks. The MED test was conducted independently on two sand subsamples by pipetting a 40-μL droplet of 0.015, or 0.3 to 3.9 mol L$^{-1}$ EtOH (in 0.3 mol L$^{-1}$ increments) that subsequently infiltrated in <5 s. The measurements were collected under atmospheric conditions controlled at a H$_2$O vapor pressure near 1.78 kPa and 20°C temperature. Audible tones generated by a digital metronome facilitated accurate visual confirmation of infiltration.

Because $\gamma_{\text{ND}}$ is another commonly used scale of WR, respective $\gamma_{\text{ND}}$ (mN m$^{-1}$) of each infiltrating solution was calculated using the formula of Roy and McGill (2002). The effects of ethyl acetate (2%) and methanol (3%) additives in the stock EtOH were not considered in the final EtOH solution estimates of $\gamma_{\text{ND}}$ (Roy and McGill, 2002). Duplicate $\gamma_{\text{ND}}$ (mN m$^{-1}$) or MED (mol L$^{-1}$) values measured on the experimental units were averaged before statistical analysis.

Intrinsic sorptivity measurements were conducted at 20°C using a tension infiltrometer adapted from Hallett and Young (1999). The device consists of a 25-cm-long by 2.54-cm-i.d. clear polyvinyl

<table>
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<tr>
<th>Table 1. Physicochemical properties of the experimental sands.</th>
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<td>Sand source</td>
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<td>Griffin putting green (GA)</td>
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<td>Mapleton quarry (PA)</td>
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† 1:1 (w/w) soil/deionized water paste (Rhoades, 1996).
‡ Core method (Blake and Hartge, 1986).
chloride tube, capped at the soil contact interface with 48-μm nylon mesh. The top end was sealed with a barbed cap and connected to a closed liquid reservoir (200 mL) under a ~0.5-cm pressure head (Moody et al., 2009). Although earlier studies measured sorptivities at higher tensions (Hallett and Young, 1999; Hallett et al., 2001; Tillman et al., 1989), this apparatus was set to the lowest tension possible before liquid would spontaneously flow from the infiltrometer to maximize infiltration into the greatest number of pores. The relative pressure head was scaled ($h^*$) in accordance with the physical characteristics of the liquid in the supply reservoir:

$$h^* = \frac{pgh}{\gamma}$$ \hspace{1cm} [4]

where $p$ is the liquid density, $g$ is the acceleration due to gravity, $h$ is the desired pressure head, and $\gamma$ is the surface tension of the liquid in the liquid reservoir (Tillman et al., 1989). Sorptivity measurements of deionized water and 5 mol L$^{-1}$ EtOH (35.9 mN m$^{-1}$) were conducted using duplicate sand subsamples packed in columns having a slightly larger diameter (35-mm i.d.) than the infiltrometer apparatus (25.4-mm i.d.). The contact pressure at the sample–infiltrometer interface was adjusted to 3.87 Pa within 2 s of contact. A logging balance (AL-203 balance, Acculab Inc., Edgewood, NY) recorded the mass lost from the liquid reservoir at milligram resolution every 200 ms and transferred the data to a software wedge-equipped personal computer (WinWedge Pro, TA Tech Inc., Philadelphia, PA). Sorptivity ($S$) was calculated by least squares estimation of early-time, one-dimensional cumulative infiltration ($I$) (Clothier and Scotter, 2002; Philip, 1957; Tillman et al., 1989):

$$I = S(t)^{1/2}$$ \hspace{1cm} [5]

where $t$ is time. Repellency indices were calculated as

$$R = 1.39 \left( \frac{S_{5 \text{ mol L}^{-1} \text{ EtOH}}}{S_{\text{water}}} \right)$$ \hspace{1cm} [6]

The coefficient of the $S$ ratio, 1.39, is the ratio of $(\mu \gamma^{-1})^{1/2}$ of water and 5 mol L$^{-1}$ EtOH, where $\mu$ and $\gamma$ are the liquid’s dynamic viscosity and surface tension, respectively. This value represents the threshold of critical water repellency, whereas $R < 1.39$ would be considered a "subcritical" level of repellency (Tillman et al., 1989). Simple linear regression (JMP version 7.0, SAS Institute, Cary, NC) was used to model $R$ from paired $\gamma_{ND}$ (mN m$^{-1}$) or the EtOH concentration (mol L$^{-1}$) of the respective infiltrating solutions. Repellency indices were logarithmically transformed to satisfy linear model assumptions of normality, constant variance, independent errors (measurement order), and goodness-of-fit.

**Results**

Samples determined wettable by the MED test (0 mol L$^{-1}$ EtOH or 72.1 mN m$^{-1}$) were omitted from the data set. Justification for this was at least twofold. First, despite practical and theoretical variance in the wetting behavior of soils demonstrating $90^\circ \geq \theta_{\gamma} \geq 0^\circ$, the MED test designates all soils permitting early-time water infiltration in $<5$ s equally wettable. Because $R$ is sensitive to subcritical soil repellency and regression analysis implies causality at every regressor variable level, prediction of $R$ by the most general and imprecise MED results presents an avoidable non sequitur. Second, $R$ data associated with soils deemed wettable by the MED test ($n = 224$) showed wide distributions of variance compared with the remaining water-repellent soils.

Cursory analysis revealed nonlinear associations (Fig. 1) between $R$ and MED or $\gamma_{ND}$ (Table 2) data ($n = 238$). Regression of $\log_{10} R$ by $\gamma_{ND}$ produced the following linear model: $\log_{10} R = 5.06 - 0.067 \gamma_{ND}$. While this statistically significant ($P < 0.0001$, $r^2 = 0.74$) model met all required assumptions, the 95% $\log_{10} R$ prediction interval included non-positive values (Fig. 2). Thus, the inability to predict a theoretically valid repellency index by $\gamma_{ND}$ values > 65.1 mN m$^{-1}$ rendered this model inadequate. Alternatively, regression of $\log_{10} R$ by MED generated the following statistically significant ($P < 0.0001$, $r^2 = 0.727$) model:

$$\log_{10} R = 0.75 + 0.5144 \left( \frac{\text{MED [mol L}^{-1}]}{S_{\text{water}}} \right)$$ \hspace{1cm} [7]

Across the range of EtOH concentrations used to estimate $R$, the 95% prediction interval of this model fell within the operational

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**Fig. 1.** Plot of repellency index vs. (A) molarity of ethanol droplet test data and (B) 90° surface tension data estimated from MED test levels.
boundaries of repellency index theory (Fig. 3). Likewise, this model satisfies all the required linear regression assumptions. The model generated from the full data set was fit by a random subset fairly well (data not shown), with exactly 5% of data points falling outside of the 95% “single observation” prediction interval. Similar but independent \( R \) and MED data reported by Schlossberg et al. (2005) also fell within the 95% prediction interval of Eq. [7] (Fig. 3).

**Discussion**

The nonlinear association between \( R \) and MED was expected because \( R \) provides a continuous measure of WR by ratio calculation, whereas MED (mol L\(^{-1}\)) is reported on an ordinal scale. Linear models developed to predict the small-ring H\(_2\)O infiltration (SRI) rate (mm min\(^{-1}\)) using MED values also used logarithmic transformation of the dependent variable: \( \log_{10} SRI = 1.42 - 0.833(\text{MED}) \) (King, 1981). Likewise, similar approaches using MED test data to predict the liquid contact angle of water-repellent soils have generated nonlinear relationships (Carrillo et al., 1999; King, 1981).

Despite having measured the \( R \) of water-repellent sands using dissimilar intrinsic sorptivity measurement protocol, identically paired data reported by Schlossberg et al. (2005) were adequately fit by the above least squares linear model. Granted that these independent sets of water-repellent sands shared common attributes, the results shown warrant further investigation of improved WR standardization across hydrophobic soils using \( R \).

We would be remiss, however, not to caution potential users of the limited precision in \( R \) estimation from MED (mol L\(^{-1}\)) values. Moreover, the spatial variability of WR on the soil surface is likely to be a significant source of MED measurement error. While \( R \) is inherently scaled to account for soil physical properties other than WR (e.g., the volume, connectivity, and geometry of pores), MED measurements are not. Furthermore, repellency indices were calculated from liquid infiltration over a 5-cm\(^2\) soil surface area, while the soil surface area sampled in 40-\(\mu\)L MED measurements is limited by an approximate liquid-to-soil contact area of 0.14 cm\(^2\). Therefore, the spatial variability of WR and sample packing characteristics may significantly influence MED measurements.

<table>
<thead>
<tr>
<th>MED†</th>
<th>( \gamma_{\text{ND}})‡</th>
<th>( R)§</th>
<th>95% confidence interval for expected mean of ( R )</th>
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<tbody>
<tr>
<td>mN m(^{-1})</td>
<td>( \gamma_{\text{ND}})</td>
<td>( R)</td>
<td>Lower boundary</td>
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<tr>
<td>0.15</td>
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<td>3.9</td>
<td>39.2</td>
<td>514.23</td>
<td>402.4</td>
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† Molar concentration of ethanol infiltrating soil in <5 s.  
‡ Estimated liquid surface tension of infiltrating solution (Roy and McGill, 2002).  
§ Repellency index modeled by: \( \log_{10} R = 0.705 + 0.5144(\text{MED}) \) [mol L\(^{-1}\)].

Fig. 3. Plot of \( \log_{10} \) repellency index vs. molarity of an ethanol droplet penetrating the soil within 5 s.
While this model does not facilitate precise estimation of $R$ from MED measurements, these results do permit greater inference into the practical implications of WR. The current convention of quantifying WR by WDPT, $\gamma_{ND}$, or MED is less adequate in this context, as these methods merely provide logical operations (i.e., less than, greater than, or equal to) to compare soil wettability. Thus growers may benefit from repellency index estimates because this meaningful measure of WR could facilitate more efficient water use through refined cultural practices (e.g., localized watering or surfactant treatment).

Conclusions

Presuming strict adherence to the described methodology, the model resulting from this study allows estimation of useful soil water infiltration characteristics ($R$) from a simple and rapid procedure (MED). More precise $R$ prediction can be expected from user input of a sample mean of MED measures than from a single observation. The described model should be used only to predict $R$ of “critically” water-repellent soils.

References


