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A Physically Based Model

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Preface

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Quantifying the Effect of Subcritical Water Repellency on Sorptivity: A Physically Based Model

Abstract Soil water wettability or water repellency is a phenomenon that can affect infiltration and, ultimately, runoff. Thus, there is a need to develop a model that can quantitatively capture the influence of water repellency on infiltration in a physically meaningful way and within the framework of existing infiltration theory. The analytical model developed in this study relates soil sorptivity (an infiltration parameter) with contact angle (a direct measure of water repellency) for variably saturated media. The model was validated with laboratory experiments using a silica sand of known properties treated to produce controlled degrees of water repellency. The measured contact angle and sorptivity values closely matched the model-predicted values. Further, the relationship between the frequently used water drop penetration time test (used to assess water repellency) and sorptivity was illustrated. Finally, the direct impact of water repellency on saturated hydraulic conductivity was investigated due to its role in infiltration equations and to shed light on inconsistent field observations. It was found that water repellency had minimal effect on the saturated hydraulic conductivity of structureless sand. A quantitative model for infiltration incorporating the effect of water repellency is particularly important for post-fire hydrologic modeling of burned areas exhibiting water repellent soils.

Plain Language Summary Wildfires can cause soils to become water repellent, which means that raindrops may not immediately enter the soil (infiltrate) and may instead flow over the land surface. In this way, water repellency is believed to contribute to the sometimes-devastating flooding and debris flows that follow rainfall events on burned mountainous areas. Currently, however, the effect of water repellency on infiltration and runoff cannot be accounted for directly. Through our research, we were able to quantitatively describe not only the degree of water repellency but also the effect of water repellency on infiltration. This quantification will allow for the improvement of runoff models to aid in post-fire flood prediction and emergency response.

1. Introduction

The occurrence of wildfires throughout the western United States can be catastrophic and is expected to increase (Doerr & Santín, 2013), as is flooding and erosion associated with rainstorms on fire-affected areas. Water repellency (WR)—when water does not immediately wet the soil—has been observed to occur frequently after fires (DeBano, 2000; Letey et al., 1962; Moody et al., 2013; Shakesby et al., 2000) increasing the potential for post-fire runoff and erosion. This is a particular concern during the first post-fire rainfall event when, such as in the western United States, post-fire precipitation is frequently characterized by high-intensity, short-duration rainfall on relatively steep slopes (Dennison et al., 2014; Sheppard et al., 2002). However, the infiltration equations used in runoff models do not directly account for changes in WR. As stated in a review of post-fire runoff and erosion research, “... no mathematical relations have been proposed that relate the degree of WR to runoff” (Moody et al., 2013). This gap severely limits our ability to simulate and predict land surface processes especially relevant under rapidly changing fire regimes in coupled human-natural systems.

In this study, we introduce a physically based model that defines the effect of the magnitude of WR on infiltration. The model capitalizes on the equivalence between two well-known approaches to simulate the flow of a liquid into a porous media: (a) Washburn’s (1921) model of liquid movement in a bundle of capillaries and (b) Philip’s (1957) diffusivity-based infiltration model using the capillarity-related property of sorptivity.

The model developed in this study was tested using silica sand treated to induce WR as a surrogate for natural field soil. Additional experimental data illustrate the applicability of the model to a WR test (water drop penetration time [WDPT]) and the effect of WR on saturated hydraulic conductivity and cumulative infiltration.

2. Theoretical Considerations

2.1. Soil Wettability, Hydrophobicity, and WR

Wettability of a solid surface with a liquid is defined by the contact angle, α , at a solid-liquid-gas interface (Adamson & Gast, 1997) with

$$\alpha = \cos^{-1} \left(\frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \right), \quad (1)$$

where γ_{sg} , γ_{sl} , and γ_{lg} represent the surface tensions between the solid-gas (sg), solid-liquid (sl), and liquid-gas (lg) phases, respectively. This form of the Young equation highlights the fact that the contact angle manifests the physiochemical interaction among the various phases of the system—here, the soil (s) matrix-water (l) system at the soil surface at atmospheric conditions (g). Based on the Young equation, the familiar capillary equation (2) allows for the calculation of the capillary rise, h , of a liquid in a cylindrical tube of radius r

$$h = \frac{2\gamma_{lg} \cos \alpha}{\rho g r}, \quad (2)$$

where ρ is the liquid density and g is the gravitational acceleration.

The contact angle at the liquid-solid interface can vary between 0° and 180° . A surface with $\alpha = 0^\circ$ is considered fully wettable, and a surface with $\alpha = 180^\circ$ is considered fully nonwettable, though these two limits are not generally encountered in soils. Therefore, we consider only a range of very small to very large contact angles ($0^\circ < \alpha < 180^\circ$) for which the solid-liquid interaction ranges from “wettable” (hydrophilic) to “non-wettable” (hydrophobic), respectively. A contact angle of 90° is typically considered a threshold in the nature of wettability and in capillary theory specifically.

Letey (1969, 2005), Letey et al. (2000), Doerr and Shakesby (2012), and Angulo-Jaramillo et al. (2016) defined WR as the condition under which water will not *spontaneously* enter the soil (without applying additional forces). Using the capillary equation (2), Letey reasoned this condition corresponded to soil-water contact angles equal to or greater than 90° . Tillman et al. (1989) noted that although some water repellent soils did wet spontaneously, the rate of wetting was reduced by some degree of WR, presumably at contact angles less than 90° . Tillman et al. (1989) referred to this condition of spontaneous but not necessarily *instantaneous* entry of water into the soil as “subcritical water repellency.” The reduction in infiltration due to subcritical WR is the focus of our research.

2.2. Water Infiltration Into Soil

In a series of papers titled “The Theory of Infiltration,” Philip (1957) presented an analytical model to calculate cumulative infiltration I into a homogenous and isotropic soil as a function of time t

$$I(t) = St^{1/2} + At, \quad (3)$$

introducing S , the sorptivity, and A , a function of hydraulic conductivity. Philip (1957) defined sorptivity as “a measure of the capacity of the medium to absorb or desorb liquid by capillarity,” which can be interpreted as the capillary-driven component of water infiltration into unsaturated soil. Philip noted that sorptivity was related to the contact angle, but neglected subsequent mention of the contact angle (Philip, 1958) and later rescinded his inclusion of the contact angle in his formulation of (intrinsic) sorptivity (Philip, 1957, 1969; Tillman et al., 1989). These early considerations by Philip and others motivated the exploration of sorptivity as a physically based measure for WR and therefore the link between WR and infiltration.

2.3. A Model to Describe the Sorptivity of Subcritical Water Repellent Soil

The role of capillary forces on sorption can be readily visualized using idealized porous media. Washburn (1921) described the penetration of a liquid into a horizontal cylindrical tube of circular cross section driven by capillarity as

$$x(t) = \left(\frac{r\gamma_{lg}\cos\alpha}{2\mu_l} t \right)^{1/2}, \quad (4)$$

where $x(t)$ is the distance traveled by the liquid-gas interface at time t , r is the radius of the tube, γ_{lg} is the surface tension between the liquid and the gas phase, and μ_l is the dynamic viscosity of the liquid. Assuming, as a first-order approach, absorption into a horizontal soil column can be modeled as liquid penetrating a bundle of horizontal, cylindrical tubes, Washburn's equation can be upscaled to calculate an average travel distance, $\bar{x}(t)$, of the liquid-gas interface into the bundle of capillaries as

$$\bar{x}(t) = \left(\frac{r^*\gamma_{lg}\cos\alpha}{2\mu_l} t \right)^{1/2}, \quad (5)$$

with r^* being the effective pore radius. For one-dimensional absorption of a liquid into a porous material, $\bar{x}(t)$ can be derived from conservation of mass for the liquid phase, which yields

$$\bar{x}(t) = \frac{I(t)}{\phi_e}, \quad (6)$$

where $I(t)$ is the cumulative amount of absorbed liquid and ϕ_e is the effective porosity of the material (i.e., the amount of pore space that can be filled by the absorbed liquid). Combining Equations 5 and 6 yields the following expression for cumulative absorption of a liquid into a porous material due to capillarity

$$I(t) = \phi_e \left(\frac{r^*\gamma_{lg}\cos\alpha}{2\mu_l} t \right)^{1/2}. \quad (7)$$

To describe water absorption into a horizontal soil column, Philip (1957) provided a simplified version of Equation 3:

$$I(t) = St^{1/2}. \quad (8)$$

Based on the similar structure of Equations 7 and 8, sorptivity S can be calculated, by analogy, as

$$S = \phi_e \left(\frac{r^*\gamma_{lg}\cos\alpha}{2\mu_l} \right)^{1/2}. \quad (9)$$

Equation 9 shows that sorptivity is related to the ratio of capillary to viscous forces. For water being absorbed into soil, the effective porosity ϕ_e can be defined as

$$\phi_e = \theta_f - \theta_i, \quad (10)$$

where θ_i is the initial volumetric moisture content of the soil and θ_f is the final volumetric moisture content of the soil. Combining Equations 9 and 10 yields the following expression for sorptivity:

$$S = (\theta_f - \theta_i) \left(\frac{r^*\gamma\cos\alpha}{2\mu} \right)^{1/2}. \quad (11)$$

The contact angle is particularly relevant for this study because it is the direct, physically based measure of WR. Note that Equations 9 and 11 are limited to contact angles $\leq 90^\circ$ —that is, subcritical WR.

To calculate sorptivity as a function of contact angle, the terms θ_i , θ_f , r^* , γ , and μ need to be determined. The parameters γ and μ can be found in published tables on the physical properties of water (e.g., Kuchling, 1989), and θ_i and θ_f can be measured reasonably well, or at least estimated. For example, if absorption leads to complete water saturation, the final volumetric moisture content will be equal to total porosity or saturated water content, or $\theta_f = \phi = \phi_s$. However, complete water saturation is problematic.

Klute (1986), therefore, defines “natural saturation” or “satiated” water content as $0.8\theta_s$ to $0.9\theta_s$ (i.e., only 80% to 90% of pores can be filled with water due to initial absorption or infiltration). Dullien (1992) indicated natural saturation may be $\leq 0.4\theta_s$.

The effective pore radius, r^* , can be interpreted as the radius of a cylindrical tube within which a liquid will rise to the same height, h , as the same liquid rises due to capillary forces in a column of porous material. By analogy, r^* can be calculated from measured capillary height, h , by rearranging the capillary equation (Equation 2) as

$$r^* = \frac{2\gamma_{lg}\cos\alpha}{\rho gh}, \quad (12)$$

with parameters as defined previously. For this study, we followed this analogy and treated r^* as an empirical parameter that can be determined experimentally provided that the contact angle α is known a priori. Conversely, for a porous material with known r^* , the contact angle, α , can be calculated from the capillary height, h , of an upward infiltration test by again rearranging Equation 2:

$$\alpha = \cos^{-1}\left(\frac{r^*\rho gh}{2\gamma_{lg}}\right). \quad (13)$$

3. Experimental Techniques and Data

3.1. Sand and Treatment Preparation

All experiments were carried out on a #40-70 grade sand (grain size 0.595-0.125 mm dia., 96% silica, particle density of $2,650 \text{ kg m}^{-3}$, Agsco Corporation). Silica sand instead of natural soil was used because the WR of silica sand was easier to control than the WR of natural soil. A particle size analysis of the #40-70 sand (Malvern Mastersizer 3000) yielded approximate D_{50} and D_{10} (particle diameter for which 50% and 10% by weight of material is finer, respectively) of 412 and 243 μm , respectively. The particle diameters of the smallest particle size class detected for the sand ranged from 150 to 125 μm (0.25%); the smallest equipment-detectable particle diameter was 0.01 μm .

Sand for all experiments was first washed with 0.5% (v/v) hydrochloric acid to eliminate any soluble material and then dried in a convection oven at 105°C for 24 hr. The acid-washed sand was then separated into two batches. The first batch (hereafter referred to as “treated sand”) was dyed with a water-based rhodamine dye (ARCOS Organics) to visually differentiate the treated sand from the untreated sand and then oven-dried at 105°C for 24 hr. The dyed sand was sprayed with commercially available Scotchgard™ to induce WR and then dried again at 105°C for 24 hr. Sand from the second batch was left untreated (hereafter referred to as “untreated sand”). Sand treatments of different levels of WR were achieved by mixing treated sand with untreated sand at specific mass ratios. For example, 20% water repellent sand treatment (20% WR) was composed of 20% treated and 80% untreated sand. A 0% WR sand treatment was composed of untreated sand only. Sufficient quantities of treated sand and untreated sand were prepared from the same batch of #40-70 sand to ensure all experiments used the same preparation of acid-washed sand. Fresh treated and untreated sand was used for each experiment; sand was not reused for experimentation.

3.2. Effective Pore Radius, Contact Angle, and Sorptivity

To determine the effective pore radius, contact angle, and sorptivity of the sand, a series of upward infiltration (also called “capillary rise” or “wicking”) experiments were carried out. Upward infiltration is a standard technique to determine the effective contact angle of porous media (Chau, 2009; Kwok & Neumann, 1999; Yuan & Lee, 2013). For all upward infiltration tests, sand columns were prepared by packing sand into clear acrylic cylinders (25 mm inner diameter, 500 mm height) with a fine nylon mesh (Soil Measurement Systems) tautly attached to the bottom. Consistent packing was achieved by adding sand to the cylinders at an angle and, once the cylinders were filled to the desired height, gently tamping the filled cylinders 10 times. The final height and mass of sand in the cylinders were recorded to calculate the bulk density and porosity of each sand column. The columns were then vertically suspended and lowered into a reservoir filled with liquid so that the bottom of the cylinder was submerged 3 cm below the reservoir liquid surface.

Figure 1. Upward cumulative infiltration data. Measured (circles) and fitted (dashed line) data are shown as a function of the square root of time for air-dry, untreated sand (0% WR). The best fit with Philip's upward infiltration equation (Equation 15) yields $I = 7.471 t^{1/2} - 0.5108 t$, and therefore a sorptivity of $7.471 \text{ mm s}^{-1/2}$.

A first set of upward infiltration tests was carried out to determine the effective pore radius, r^* , of the sand. Five columns with dry, untreated sand were prepared and lowered into reservoirs of ethanol. After 24 hr, no capillary rise was observed and the initially dry system was considered "satiated." The distance between the reservoir free liquid surface and the height of the ethanol-wetted sand column was recorded to determine the capillary height h of the ethanol infiltration front. Ethanol was used because it is considered to fully wet silica surfaces (i.e., ethanol is considered to have a contact angle of 0°) (Letey et al., 2000). Given a known contact angle, $\alpha = 0^\circ$, and measured capillary height, h , Equation 12 was then used to calculate an effective pore radius r^* .

A second set of upward infiltration tests was carried out to determine the sorptivity and contact angle of air-dry sand ($\theta_i = 0^\circ$) for 0%, 5%, 10%, 20%, 30%, and 40% WR treatments. Five replicate columns were prepared for each WR treatment, as described above, and sand-filled height and mass were recorded. The columns were vertically suspended in a reservoir of deionized water to a depth of 3 cm to start the upward infiltration experiment ($t = 0$). The column was then removed from the reservoir, quickly weighed, and then resuspended in the reservoir to the same depth. This procedure was repeated for a minimal total of approximately 240 s (no removal weigh time > 20 s to minimize water loss), or at least five times, to measure the mass gain of the columns as a function of time and capture early time upward infiltration behavior. Hall and Hoff (2012) recommended recording changes in column mass rather than visually tracking the infiltration front because they found that visually tracking the infiltration

front was less accurate than recording the column mass to measure cumulative infiltration as a function of time. After the last weighing cycle, the columns remained suspended vertically in the water reservoir for 24 hr. Similar to the experiments with ethanol, the distance between the free water surface in the reservoir and the infiltration front in the sand column was recorded as the capillary height h and used to calculate the contact angle of the sand for water (Equation 13) using the previously determined effective pore radius r^* . Sorptivity and contact angle were determined for each column from the same upward infiltration test.

Sorptivity was calculated following the procedures by Hall and Hoff (2012) and ASTM International Standards C1585-13 and C1403-15 (ASTM Standard C1403, 2015; ASTM Standard C1585, 2013). Cumulative infiltration as a function of time $I(t)$ was calculated from cumulative mass change as a function of time $m(t)$ as

$$I(t) = \frac{m(t)}{\rho A_c}, \quad (14)$$

where ρ is the density of water and A_c is the cross-sectional area of the cylinder. Cumulative infiltration was then plotted against the square root of time $I(t^{1/2})$. To determine sorptivity using data from upward infiltration into homogenous, fine-textured materials (e.g., clay and bricks), $I(t^{1/2})$ is linear and sorptivity is determined by fitting Equation 8 to the data. For upward infiltration tests where gravity effects cannot be neglected (e.g., for coarse-textured materials such as sand), $I(t^{1/2})$ may not be linear and sorptivity was determined by fitting Philip's solution modified for upward rather than downward infiltration (Philip, 1969; Talsma, 1969)

$$I(t)_{up} = St^{1/2} - At, \quad (15)$$

Hall and Hoff (2012) recommend using Equation 15 to fit nonlinear $I(t^{1/2})$ data, for which sorptivity is the coefficient of the first-order term. Figure 1 shows an example of the determination of sorptivity from upward infiltration data.

To determine the quantity $(\theta_f - \theta_i)$ in Equation 11, a third set of upward infiltration experiments were carried out. Initially dry, untreated sand was assigned $\theta_i = 0$. To determine θ_f , cylinders were filled with

untreated sand pre-mixed to known volumetric water contents. The cylinders were suspended in water for 24 hr. The experiments were repeated for increasing water contents until no capillary rise was observed after 24 hr. This water content was considered the satiated final water content, θ_f . Using three replicates for each initial water content tested, it was determined that $\theta_f = 0.19$ or $(\theta_f - \theta_i) = 0.19$.

To validate the contact angle measurements from the upward infiltration experiments, the contact angles of sand treatments ranging from 0% WR to 100% WR were determined at two independent laboratories (Mechanical Engineering Department, University of Nevada, Las Vegas, and Chemical and Material Engineering Department, University of Nevada, Reno) using optical tensiometers (Attension Theta, Biolin Scientific). The initial contact angle of a water drop on a horizontal stage holding an approximately 2 mm thick sample of sand was measured. Additionally, the mixing model by Cassie and Baxter (1944) was used to estimate contact angles for sand with different WR treatments

$$\cos \alpha_c = f_1 \cos \alpha_1 + f_2 \cos \alpha_2, \quad (16)$$

with f_1 and f_2 representing the mass fractions of sand with contact angles α_1 (for 0% WR) and α_2 (for 100% WR), respectively.

For all calculations, the liquid property values at 25°C (ambient laboratory temperature) were used. The density and surface tension for values for ethanol were 787 kg m⁻³ and 21.78 mN m⁻¹, respectively (Kuchling, 1989), and the density, surface tension, and viscosity values for water were 997.04 kg m⁻³, 71.98 mN m⁻¹, and 0.8901 mPa·s, respectively (Hall & Hoff, 2012).

3.3. WDPT

One of the most common methods to measure WR is the WDPT test (Doerr, 1998). Therefore, the degree of WR for all sand treatments was measured using WDPT. Using an eyedropper, timing began as five drops of deionized water were dropped from a height of 1 cm onto the surface of the sand samples. The elapsed time at which the drop was absorbed was noted as the WDPT. Drops were timed individually for samples where drop times were less than approximately 5 min. The reported WDPTs are medians of the five individual drops. Although the average times are sometimes reported in the literature, the average and median WDPTs were virtually indistinguishable for our WDPT tests and any differences were found to be due to the mixing homogeneity of the sand treatments.

3.4. Saturated Hydraulic Conductivity

The saturated hydraulic conductivity, K_s , of 0%, 20%, and 40% WR sand was measured using the falling-head method (Jury et al., 1991). Sand samples were packed into acrylic cylinders with a nylon mesh and screen securely attached to the base. The cylinders were 6 cm in diameter, filled to a height of approximately 5 cm, then suspended in a reservoir such that the sand surface was 1 cm below the reservoir surface but separated from the reservoir water by the acrylic cylinder. The cylinders were soaked in deionized water for 24 hr. Falling-head measurements were carried out by further filling the cylinder with water and measuring the time the water level fell 2 cm. Five replicate columns were prepared for each of the three WR treatments.

4. Results and Discussion

4.1. Effective Pore Radius and Contact Angle

Initial independent column packing trials ($n = 5$) using untreated sand yielded an average bulk density of 1,744 kg m⁻³ (SD = 8.9 kg m⁻³). An average effective radius r^* of 49.4 μm (SD = 2.2 μm) was calculated from 24-hr capillary heights measured in upward infiltration experiments using ethanol and untreated sand in combination with Equation 12. The upward infiltration method proved to be a robust method for determining the effective pore radius of the experimental sand. However, this method is limited to laboratory settings. Finer-textured field soils may require columns that are meters long, which are measured after long periods of time (i.e., months) to reach final capillary height (Kumar & Malik, 1990). We explored the relationships between the effective pore radius and soil particle diameter information that could be inferred from readily available particle size distributions. Assuming equivalence between pore size and particle size, the experimentally derived effective pore radius of 49.4 μm—or corresponding effective pore diameter of 98.8 μm—was smaller than the smallest detected particle diameter of approximately 125 μm, which was obtained

Figure 2. Contact angles and %WR. Average contact angles (with SD) were measured using upward infiltration tests (open circles and bars), sessile drop methods with an optical tensiometer (triangles), and predicted contact angles using the Cassie and Baxter (1944) mixing equation (solid line). The dashed line indicates 90°.

from the particle size analysis of the #40-70 sand. Lu and Likos (2004) presented empirical relationships between capillary height and D_{10} based on earlier studies by Lane and Washburn (1946) and stated that D_{10} may better represent the smallest pores functionally associated with capillarity in soils than the median particle diameter D_{50} . For the rather narrow pore size distribution of the experimental sand, the measured effective radius corresponded to approximately 12% of the D_{50} and 20% of the D_{10} .

Figure 2 shows the average effective contact angles ($n = 5$) calculated from the upward infiltration experiments for 0%, 5%, 10%, 20%, and 40% WR sand. This figure also shows the contact angles from the optical tensiometer measurements for 0%, 20%, 40%, and 100% WR sand. There is a clear relationship between the effective contact angle and the level of WR of the sand, indicating that the contact angle is not only theoretical (Equation 1) but also a practical measure of WR. The results in Figure 2 also show that different mixtures of untreated and treated sand can be used to engineer sand with specific contact angles ranging from 42° for 0% WR to 120° for 100% WR sand. Contact angles from upward infiltration and optical tensiometer measurements closely agreed. For the upward infiltration experiments, only sand treatments up to 40% WR could be tested, yielding a maximum contact angle of 88°. A contact angle of 90° is considered the operational, upper limit for the upward infiltration test, which is consistent with the definition of subcritical WR. In an upward infiltration experiment with 100% WR sand (data not shown), no upward infiltration into the sand column was evident after 7 days.

The optical tensiometers were able to measure contact angles >90° and yielded a contact angle of 120° for the 100% WR sand.

It is worth noting that the untreated silica sand (0% WR) exhibited a contact angle of 42°. This phenomenon has also been reported by Letey et al. (1962), who found contact angles between 43° and 52° for untreated quartz sand. Similar results were reported by King (1981), Kumar and Malik (1990), and Bachmann et al. (2003), who found that samples of field soils exhibited nonzero contact angles (measured by various methods) generally ranging from 42° to 141°. Tillman et al. (1989) suggested that these nonzero contact angles are the rule rather than the exception. A contact angle of 0°, which is commonly assumed for soil, is unlikely to occur.

The mixing model by Cassie and Baxter (1944) (Equation 16) provides a relationship similar to that measured between %WR treatments and the contact angle (Figure 2). However, the contact angles calculated using Equation 16 systematically underestimated the measured contact angles for the %WR treatments (except for the 0% WR and 100% WR treatments, which were used as input for the mixing model calculations). The difference between measured and predicted contact angles is likely due to other phenomena that affect contact angles, such as surface or liquid heterogeneities or particle surface topography, which result in an apparent contact angle (Adamson & Gast, 1997) that is not accounted for in the mixing model. For example, Ghezzehei (2004) showed that the contact angle of water on a silica glass surface can range from less than 10° up to 34° depending on the degree of surface sterilization. For practical purposes, the Cassie and Baxter (1944) equation can provide a valuable but conservative estimate for the contact angle of a sand mixture when the contact angles and mass fractions of the respective components are known.

4.2. WDPT and Contact Angle

The WDPT test is arguably the most frequently used procedure to assess the degree of WR in the laboratory and in the field. Therefore, WDPT tests were performed on air-dry samples of treated and untreated sand for which both the treatment (%WR) and associated contact angles were known. The results (Figure 3) demonstrated a clear but nonlinear relationship between median WDPT and average contact angle, with increasing contact angles associated with increasing WDPT. The times ranged from the visually instantaneous disappearance of the drop (shown as a WDPT of 0.01 s) for a sand with a contact angle of 42° (0% WR) to nearly 5,700 s for a sand with a contact angle of 88° (40% WR).

Figure 3. Contact angles and WDPT. Average effective contact angles from upward infiltration experiments are shown as a function of median WDPTs for treated sands of 0%, 10%, 20%, 25%, 30%, and 40% WR. A threshold of 5 s WDPT is highlighted, defining the wet table and water-repellent domains. The data point for 25% WR (open circle; WDPT measured, contact angle interpolated from data in Figure 2) was added to better illustrate the relationship between contact angle and WDPT at the transition from wettable to water repellent. The upper limits for WDPT class intervals and persistence ratings are given according to Doerr and Shakesby (2012). Only sand treatments with effective contact angles less than 90° were included in the study.

There are several classification schemes associating WDPTs to the degree of WR. One classification scheme by Doerr and Shakesby (2012), incorporating the features and data from other studies, has been superimposed on the data shown in Figure 3. Using this classification, soils with WDPTs less than 5 s are considered “wettable.” For the sand, this included treatments having contact angles of 42° to 71° (0% WR to 20% WR sand, respectively). All but the 0% WR sand in our experiments exhibited some degree of WR (visual WDPT > 0 sec). Although the results are specific to the sand tested, they indicate inconsistency between a general classification of the interpretation of WDPT and actual process-based measurements of WR (i.e., contact angle). Ultimately, along with Angulo-Jaramillo et al. (2016), the approximate nature of the WDPT is acknowledged, and therefore, grouping WDPT times for all soils into a few WR classes may be misleading for hydrologic applications.

4.3. Sorptivity and Contact Angle

Figure 4 shows the arithmetic means for sorptivity and contact angles measured for 0%, 5%, 10%, 20%, and 40% WR sand treatments, with error bars representing 95% confidence intervals (CIs). The data show sorptivity decreased as contact angles increased. The greater degree of variability in sorptivity data than in the contact angle data was likely due to the upward infiltration method used to determine the sorptivity, which involved removing the column from the water reservoir, weighing the column, then resuspending the column in the reservoir. The predicted relationship between contact angle and sorptivity is shown as a solid line in Figure 4, which exhibits an inverse and nonlinear relationship. The comparison of associated measured and predicted sorptivity values yielded a remarkably close agreement ($R^2 = 0.97$, $p = 0.002$).

The measured and predicted data shown in Figure 4 illustrates several features of sorptivity. First, sorptivity is clearly a function of contact angle, and therefore, sorptivity directly manifests WR. Second, sorptivity is greatest at a contact angle of 0° and decreases as the contact angle increases. Eventually, sorptivity ceases at a contact angle of 90°, which is consistent with capillary theory. Third, sorptivity is not strictly equivalent to capillarity. Equation 11 indicates sorptivity is the result of a balance between capillary forces and viscous forces. Fourth, due to the dependence of viscous dissipation on the square of the pore size, sorptivity is directly related to an effective pore size, expressed in terms of the effective pore radius, r^* , whereas

Figure 4. Measured contact angles and measured and calculated sorptivities for an initially air-dry soil ($\theta_i = 0$). Symbols represent arithmetic means ($n = 5$) for sorptivity and contact angles for 0%, 5%, 10%, 20%, and 40% WR sand. Error bars indicate 95% confidence intervals ($df = 4$), $R^2 = 0.97$, $p = 0.002$. Equation 11 was used to calculate sorptivity as a function of the measured contact angle (solid line) using an effective pore radius of $r^* = 49.4 \mu\text{m}$, initial volumetric moisture content of $\theta_i = 0$, and final volumetric moisture content of $\theta_f = 0.19$.

capillarity is inversely related to pore size. Fifth, sorptivity changes as a function of initial moisture content θ_i although all results presented so far have been based on dry initial moisture conditions ($\theta_i = 0$), which ensures comparable effective porosities. But changes in the initial moisture will alter the effective porosity and resulting sorptivity (Equation 11). From their measurements and statistical analyses, Moody et al. (2019) indicated that the sources of variability in post-fire soil hydraulic properties (among them, sorptivity) were due to particle size, initial soil moisture content, and packing. Our model (Equations 9 and 11) includes and quantifies the effects of particle size (i.e., r^*), initial soil moisture content (i.e., θ_i), packing (i.e., ϕ_e), and, importantly, WR (i.e., α) on the hydraulic property of sorptivity.

4.4. Sorptivity and WDPT

As WDPT is frequently used to assess the degree of WR, we explored the relationship between WDPT and sorptivity for the experimental sand. Figure 5 shows relative sorptivity, S/S_0 as a function of WDPT for 0%, 10%, 20%, 30%, and 40% WR sands.

Relative sorptivity decreases logarithmically with increasing WDPT, and the two parameters are closely correlated ($R^2 = 0.92$). This close correlation may be limited to the experimental sand but indicates that similar relationships may exist for soils of other textures. The relationship shown in Figure 5 allows for the estimation of the extent to which WR, expressed in terms of WDPT, reduces sorptivity. For example, a WDPT of 5 s indicates a reduction of sorptivity by 36% relative to the reference sorptivity for 0% WR sand. For WDPT of 100 s, sorptivity is reduced by 52%, and for WDPT of 1,000 s, sorptivity is reduced by 63%. Fundamentally, the

Figure 5. Sorptivity and WDPT. Relative sorptivity, S/S_0 , as a function of water drop penetration time for 0%, 10%, 20%, 30%, and 40% WR sands. The term S_0 is defined as the average sorptivity of the untreated sand calculated for $\theta_i = 0$ and at a contact angle = 42° .

relationship in Figure 5 demonstrates a quantitative link between the commonly used WDPT and infiltration.

4.5. Saturated Hydraulic Conductivity of Water Repellent Sand

Figure 6 shows the arithmetic mean and standard deviation of saturated hydraulic conductivity K_s measurements for 0% WR, 20% WR, and 40% WR sand (contact angles of 42° , 71° , and 88° , respectively).

The average K_s of 40% WR sand (contact angle = 88°) was 13% lower than the average K_s of 0% WR sand (contact angle = 42°). For comparison, the same difference in WR decreased sorptivity by 83%, as shown in Figure 4. The data displayed a discernable but small decrease in average K_s with increasing WR. However, the K_s data were collected under optimal laboratory conditions, and the small differences would be difficult to detect under field conditions.

Figure 6. Averaged saturated hydraulic conductivity, K_s , for 0%, 20%, and 40% WR sand. Error bars represent standard deviation ($n = 5$).

Saturated hydraulic conductivity K_s is a soil hydraulic property frequently measured to assess fire effects on soils and watershed conditions. Post-fire studies have reported differences in pre- and post-fire K_s ; others have been at a loss to explain the lack thereof (Ebel et al., 2018; Moody et al., 2013, 2019). From a physical perspective, K_s (or more generally, intrinsic permeability k) is a structural property of a porous media and “a constant for rigid, saturated soil in a given geometric configuration” (Jury et al., 1991). Unless the pore structure of the soil changes during a fire, K_s should not be affected (assuming other soil physical properties have not changed). However, Albalasmeh et al. (2013) and Jian et al. (2018) have shown that even relatively low-intensity fires can weaken secondary (aggregate) soil structure with subsequent environmental factors (e.g., wetting/drying or freezing/thawing) leading to soil structural changes. For the experimental sand with single grain structure (i.e., structureless sand), the observed small changes in K_s are unlikely to reflect the structural changes of the sand. A more likely reason for decreasing K_s values with increasing WR is due to incomplete saturation of the water repellent sand in the falling head experiments.

Figure 7. Infiltration of water repellent sand. Cumulative infiltration as a function of time is simulated using the Philip's equation $I(t) = St^{1/2} + 0.5K_s t$ and measured sorptivity for 0% WR and 40% WR sands. No change in K_s was included per results in Figure 6.

4.6. Infiltration Into Water Repellent Sands

The effect of altered WR on cumulative infiltration was illustrated using measured values for sorptivity and K_s and the Philip's equation (Equation 3) with $A = 0.5K_s$ (Tindall et al., 1999). The results appear in Figure 7 showing cumulative infiltration as a function of time over an 1,800 s (30 min) simulation period.

The data shown in Figure 7 illustrate the effect of altered sorptivity reflecting an increase in WR. Increasing the degree of WR (increased contact angle from 42° to 88° and related decreased sorptivity) reduced infiltration by 34%. The K_s remained unaltered for the simulation, but changes in K_s as reflected in Figure 6 resulted in decreased 30-min cumulative infiltration from 8% to 13% (data not shown for clarity). Using data from the controlled laboratory experiments, the reduction in cumulative infiltration due to WR is predominantly a response to the decrease in sorptivity rather than to decreased K_s . Because cumulative infiltration is non-linear, the overall effect of altered sorptivity (i.e., WR) is strongest at early times. In addition, $A = 0.5K_s$ represents the upper limit for the second term of Philip's equation (Equation 3). For infiltration into initially dry soil, incomplete saturation is likely ($\theta_f < \theta_s$), and therefore, the proportionality factor A is likely < 0.5 as well. In general, when $\theta_f < \theta_s$, the effect of S compared to K_s on infiltration will be even more pronounced.

5. Summary and Conclusions

The objective of this research was to develop a physically based model that quantitatively associates WR with infiltration. The model is geared toward post-fire hydrology applications governed by short precipitation events (30 min or less) and dry initial soil moisture conditions that are, for example, characteristic of rainfall events after the wildfire season in the western United States.

As a first step, we developed a model from first principles to quantitatively associate WR with the infiltration parameter of sorptivity. Model parameters include an effective contact angle (the direct measure of WR), pore size (expressed in terms of an effective pore radius), initial and final moisture content, and surface

tension and viscosity. The sorptivity model was validated in the laboratory using a well-characterized fine silica sand as a proxy for soil. Various degrees of water repellent sand were created by mixing known quantities of water repellent (treated) sands with untreated sand. We independently measured the sorptivity and contact angle of the sand treatments and then calculated the sorptivity for contact angles from 0° to 90° using the model. There was remarkable agreement between measured and model-predicted sorptivity.

Systematically testing the model on a sand of known properties not only allowed for model verification but also provided insight into the nature of sorptivity and WR. Sorptivity is functionally related to WR through the contact angle. Sorptivity is greatest at a contact angle of 0° and decreases in a cosine-like manner as the contact angle (WR) increases, which results in zero sorptivity at a contact angle of 90°. This is consistent with capillary theory. However, sorptivity is not equivalent to capillarity but is rather the result of a balance between capillary and viscous forces. Also, sorptivity is directly related to pore size (expressed in terms of the effective pore radius, r^*), whereas capillarity is inversely related to pore size.

A close correlation was found between sorptivity and WDPT, which should be explored further for field applications. All sand treatments had contact angles less than 90° and were therefore considered subcritically water repellent, even though some of the water repellent sands were classified as “severely water repellent” (80° contact angle) and “extremely water repellent” (88° contact angle) using WDPT test categories. Additionally, we measured the saturated hydraulic conductivity, K_s , of sands with contact angles of 42°, 71°, and 88° (0%, 20%, and 40% WR treatments). Increasing WR induced only a small decrease in average K_s , a decrease likely not discernable in field measurements. Thus, an association of a decrease in K_s solely due to increased WR may be unfounded.

Using Philip's infiltration equation, we simulated the effect of WR on cumulative infiltration by explicitly altering sorptivity. Comparing simulated 30-min cumulative infiltration for a 0% WR sand and a 40% WR sand (contact angles of 42° and 88°, respectively) resulted in a 34% decrease in infiltration. Because cumulative infiltration is a nonlinear function of time, the overall effect of sorptivity is greater at shorter infiltration times than at longer infiltration times.

The premier outcome of this study is the sorptivity model, which directly relates WR with infiltration. Since physically based, the model is applicable to any soil that can be treated as a porous material. Minimally, the sorptivity model can be used to guide the data collection and analyses needed to improve our understanding of the effect of WR on infiltration. Sorptivity is rarely measured, and sorptivity data are essentially nonexistent for the modeling of post-wildfire infiltration and runoff, when wildfires are known to induce WR. Ultimately, the sorptivity model developed in this study suggests testable hypotheses necessary to direct further research and development on the hydraulics of water repellent soils needed not only to improve the prediction of post-wildfire runoff and floods specifically but also to better understand water flow in variably wettable, unsaturated porous media in general.

Conflict of interest

The authors do not have any financial conflict of interest that may impact this work nor do they have affiliations that may be perceived as having a conflict of interest with respect to the results of this paper.

Data Availability Statement

All data used to generate the results may be accessed online (<https://doi.org/10.21079/11681/38202>).

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14. ABSTRACT Soil water wettability or water repellency is a phenomenon that can affect infiltration and, ultimately, runoff. Thus, there is a need to develop a model that can quantitatively capture the influence of water repellency on infiltration in a physically meaningful way and within the framework of existing infiltration theory. The analytical model developed in this study relates soil sorptivity (an infiltration parameter) with contact angle (a direct measure of water repellency) for variably saturated media. The model was validated with laboratory experiments using a silica sand of known properties treated to produce controlled degrees of water repellency. The measured contact angle and sorptivity values closely matched the model-predicted values. Further, the relationship between the frequently used water drop penetration time test (used to assess water repellency) and sorptivity was illustrated. Finally, the direct impact of water repellency on saturated hydraulic conductivity was investigated due to its role in infiltration equations and to shed light on inconsistent field observations. It was found that water repellency had minimal effect on the saturated hydraulic conductivity of structureless sand. A quantitative model for infiltration incorporating the effect of water repellency is particularly important for post-fire hydrologic modeling of burned areas exhibiting water repellent soils.					
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