



Time-dependent contact angle and repellency persistence in water-repellent Japanese forest soils in relation to droplet geometry and line tension

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Abstract: Water repellency (WR) restricts the spontaneous wetting of soil and lowers the affinity between soil and water. Studies focused on temporal alteration of droplet contact angles on hydrophobic soil substrates and their relation to persistence of WR are highly limited. This study examined time-dependent contact angle and WR persistence considering geometry and line tension droplets using six hydrophobic forest soils. Soils were collected from Japanese cedar (*Cryptomeria japonica*, CED1, CED2), Japanese cypress (*Chamaecyparis obtusa*, CYP1, CYP2), and cedar/cypress mixed (MIX1, MIX2) forests. The time-dependence of apparent and geometric soil-water contact angles (θ_A and θ_G , respectively) and repellency persistence, using the water drop penetration time (WDPT), were determined. In all tested soils, both θ_A and θ_G showed a gradual continuous decline with increasing time to reach zero within a period of ~5–6 min, with strong negative exponential correlations ($R^2 \geq 0.90$). The θ_A showed a strong positive linear correlation with θ_G ($R^2 > 0.99$; $p < 0.05$), indicating the preservation of a fair spherical segment shape of droplets during spreading irrespective of the possible roughness on granular soil surfaces. The line tensions at the periphery of the contact circle of the water droplet on the tested hydrophobic soil surfaces were in a range of 200–300 $\mu\text{J m}^{-1}$, which was within the previously reported order-of-magnitude range (10^{-5} – $10^2 \mu\text{J m}^{-1}$). The time-dependent nature of the contact angle in the present study can most likely be attributed to water molecule adsorption processes or amphiphilic molecular reorientation processes. The soil-water contact time until contact angle receded below 90° ($\text{CT}-\theta_{90^\circ}$) was not equivalent to WDPT, emphasizing that the time-dependent decline of contact angle would not correspond with water infiltration into the soil matrix. Still, the strong positive linear correlation between $\text{CT}-\theta_{90^\circ}$ and WDPT ($R^2 = 0.926$; $p < 0.05$) indicated a close relation between these two parameters.

Keywords: Droplet geometry; Line tension; Repellency persistence; Soil water repellency; Time-dependence of contact angle.

1 INTRODUCTION

Water repellency (WR), or hydrophobicity, of soil explains a phenomenon that soils resist spontaneous wetting when water droplets are placed on the soil surface due to reduced affinity between soil and water (Doerr et al., 2000). Its occurrence relates to the presence of organic substances in soil, either as coatings on mineral particle surfaces or as intermixed materials in the soil matrix, whereas its severity relates to the content as well as the composition of organic matter (Leelamanie, 2016; Rodríguez-Alleres et al., 2007). Organic substances released to the soil through the types of vegetation that are rich in hydrophobic resins and waxes, which primarily consist of compounds such as alkanes, alkanolic acids, and esters, are identified as being associated with the WR of soils (Ma'shum et al., 1998; Franco et al., 2000). The hydrophobic substances incorporate into the soil as microbial metabolic and decomposition byproducts, hydrophobic root exudates (Mao et al., 2014), and fungal products (Doerr et al., 2000; Feeney et al., 2006). These various organic substances can induce hydrophobic conditions on the surface and in the soil matrix, restricting water from entering the soil and lowering the soil water storage capacity (Klamerus-Iwan et al., 2024).

Diminished infiltration capacity in soil causes numerous undesirable impacts on soil and environment, such as increased surface runoff, topsoil erosion, initiation of preferential flow or

finger flow paths, nutrient leaching, and reduced germination of sown crops (Doerr et al., 2000; Feeney et al., 2006; Jordán et al., 2013). However, WR has beneficial impacts on soil structure as it helps improve structural stability through the diminished buildup of water pressure within intra-aggregate pores (Goebel et al., 2011). Furthermore, some studies focus on utilizing the hydrophobic conditions for the benefit of mankind, primarily through artificially hydrophobized granular materials that can be used in ground infrastructure, where delayed or restricted water infiltration is required for their successful establishment (Ng and Lourenço, 2016). Therefore, a comprehensive understanding of the phenomena of soil WR is crucial, from the perspectives of both eluding its demerits and utilizing its merits.

Solid-liquid contact angle helps determine the degree of WR and quantify the degree to which water spreads on solid surfaces, and the entry of water into the capillaries of granular materials such as soil. It is a result of interfacial phenomena that reflects the interactions of solid-liquid, solid-gas, and gas-liquid molecules, and the contact-line forces that are ascribed to the interfacial tensions/free energies. Contact angle studies provide an extensive amount of information on the wetting behavior of soil and soil-water interactions. In general, measurement of contact angle is considered one of the most effective and reliable methods to quantify the water-repellent levels of soils, and therefore, has long been extensively used in numerous studies on soil WR. The sessile drop method (SDM) has been widely used

to determine solid-liquid contact angles (Neumann and Good, 1972). Since a direct measurement of the contact angle of granular materials such as soils is usually not possible, various indirect approaches have been used (Letey et al., 2000; Roy and McGill, 2002). Bachmann et al. (2000) introduced the modified SDM as a direct approach to measure the contact angle on soils using a soil monolayer fixed to an adhesive tape. The technique prevents water infiltration into soil, making optical image analysis possible with a fair level of accuracy.

Experimental conditions such as the droplet volume, the solid water contact time, and droplet spreading, affect the measured contact angle. Numerous studies have specifically focused on the drop-size dependence of contact angles on solid surfaces (Amirfazli et al., 1998; Good and Koo, 1979). Although there has been a widespread interest in the behavior of droplet spreading on solid substrates such as polymer surfaces and the corresponding changes in solid-liquid contact angles (Du et al., 2021; Kafle et al., 2024; Shanahan et al., 1994), the attention focused on the time dependence of contact angle is comparatively limited.

The time-dependence of the contact angle of water droplets relates to the spreading of droplets. The process begins with the initial impact that occurs with the placement of a liquid droplet on the solid surface. It is then followed by macro-scale and molecular-scale processes such as spreading, adsorption, and evaporation of the liquid (Kafle et al., 2024). The time-dependent nature of contact angles has been characterized for situations involving polymer surfaces, hydrophobized solid surfaces (Varenes and Schreiber, 2001; Wang et al., 2005), and in some modeling studies (Wang and Wallach, 2020, 2021). Only limited attention has been given to the time-dependent contact angles associated with droplet spreading on hydrophobic soil substrates.

Based on the available evidence regarding the time-dependent contact angle of liquid droplets on solid surfaces, it was noted that contact angles generally decrease exponentially over a period that can range from a few minutes to nearly an hour, before reaching a specific equilibrium value that depends on the properties of the solid material (Leelamanie and Karube, 2009; Subedi et al., 2012; Varenes and Schreiber, 2001). In general, contact angles above 90° in soil indicate hydrophobicity, which prevents wetting and water entry into the soil (Goebel et al., 2011), while those below 90° indicate

subcritical WR, or complete wettability (Bachmann et al., 2007). The major factors that control the wetting process of solids and the spreading of droplets on solid surfaces are the properties of the liquid, the solid surface roughness, and the properties of the solid material (Huang et al., 2010; Zhang et al., 2023). The WR persistence of soil is measured by the time it takes for a water drop to penetrate the soil completely. It remains unclear how the major factors that control the wetting process and the decreasing contact angle over time caused by droplet spreading on a soil surface and its subsequent drop below 90° might induce water entry into the soil matrix and the persistence of WR.

The purpose of this paper was to investigate the temporal changes in soil-water contact angles of sessile droplets on water-repellent forest soils, considering how the declining contact angle might influence the persistence of WR. Since the spreading of a liquid droplet on a solid surface alters the solid/liquid interfacial contact area, the solid/liquid contact radius, and the length of the three-phase contact line at the outer edge of the droplet, geometric alterations of water droplets and contact line forces were also studied. Temporal changes in droplet parameters were examined by dynamically tracking the contact angle of sessile droplets over time through optical image analysis, using six water-repellent Japanese forest soils.

2 MATERIALS AND METHODS

2.1 Sample collection and initial preparation

Water-repellent soil samples were collected from Japanese cedar (*Cryptomeria japonica*, CED) (CED 1: $35^\circ14'25.29''$ N $134^\circ2'59.68''$ E; CED 2: $35^\circ14'24.76''$ N $134^\circ3'0.10''$ E), Japanese cypress (*Chamaecyparis obtusa*, CYP) (CYP 1: $35^\circ14'25.05''$ N $134^\circ2'56.78''$ E; CYP 2: $35^\circ14'27.18''$ N $134^\circ3'4.74''$ E), and cedar and cypress mixed (MIX) forests (MIX 1: $35^\circ14'25.03''$ N $134^\circ2'58.42''$ E; MIX 2: $35^\circ14'26.76''$ N $134^\circ3'2.34''$ E) in Tsuyama city, Okayama prefecture, Japan (Fig. 1). According to the Köppen-Geiger climate classification, the climate of the area is warm temperate fully humid (Cfa) (Kottek et al., 2006). The litter layer composed of dry leaves, twigs, and the partially decomposed litter material on the forest floor was carefully and completely removed before collecting soil samples.

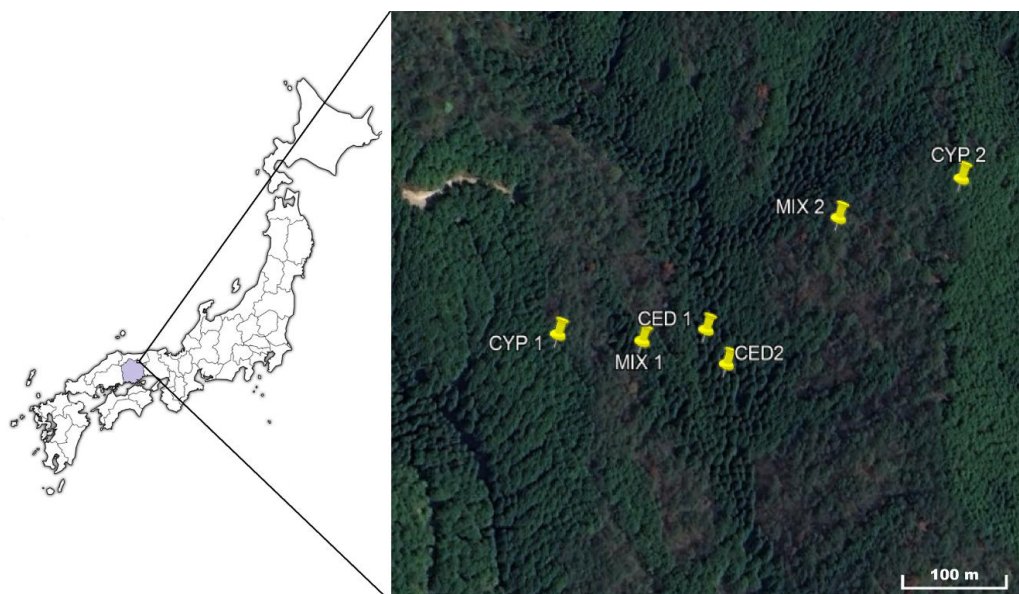
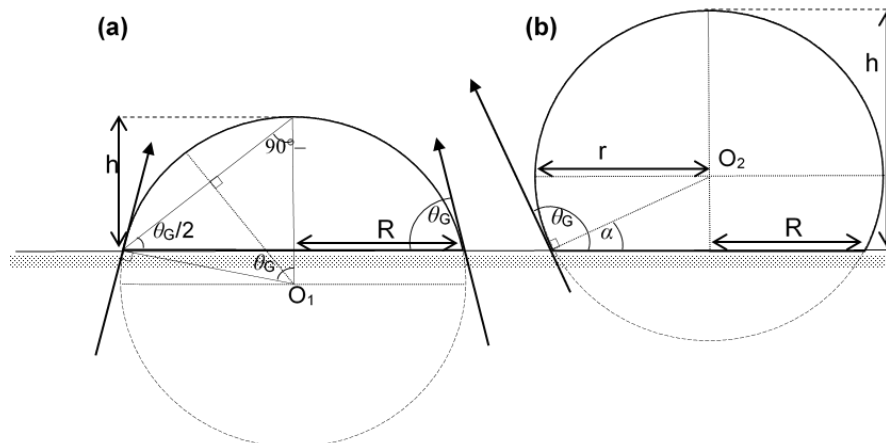


Fig. 1. Sampling location in Tsuyama city, Okayama Prefecture, Japan.

Table 1. Basic properties of the tested soils. CED: cedar; CYP: cypress; MIX: cedar and cypress mixed; EC: electrical conductivity.

Property	CED1	CED2	CYP1	CYP2	MIX1	MIX2
Sand (%)	77	79	71	78	78	71
Silt (%)	10	10	12	7	9	16
Clay (%)	13	11	17	15	13	13
Texture	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy loam
pH	4.3	4.8	4.2	4.7	4.2	4.4
EC (dSm ⁻¹)	0.083	0.070	0.080	0.065	0.066	0.052
C (%)	7.8±0.2	5.6±0.6	9.8±0.2	6.5±0.02	8.8±0.1	8.9±0.04
N (%)	0.47±0.01	0.37±0.04	0.49±0.01	0.37±0.00	0.51±0.01	0.53±0.03

**Fig. 2.** Schematic diagram of droplets indicating the geometric parameters to geometrically calculate the contact angle (θ_G) when (a) contact angle $< 90^\circ$ and (b) contact angle $> 90^\circ$. h : droplet height; R : radius of the wetting circle of the droplet; r : radius of the respective circle; O_1 , O_2 : centers of the circles.

Undisturbed core samples and bulk samples of soil were collected separately from 0–5 cm depth. The collected samples were placed in sealed plastic bags and transported to the laboratory. Before using for measurements, the soil samples were thoroughly air-dried for 7 days under laboratory conditions, while breaking natural aggregates, and then sieved using a 2-mm sieve. The basic soil characteristics were determined using standard laboratory procedures (Table 1). For the texture determination, particle size was analyzed using Pipette method (Kettler et al, 2001). The C and N contents were measured using a total N and total C analyzer (SUMIGRAPH NC-TRINITY, Sumika Chemical Analysis Service Ltd., Japan), following Afrida et al. (2025).

2.2 Measurement of soil-water contact angle

The soil-water contact angle was measured using the sessile drop method proposed by Bachmann et al. (2000), which uses monolayers of soil fixed on a double-sided adhesive tape attached to a glass slide. The sieved soil was sprinkled on the adhesive tape fixed on a glass slide and pressed carefully to obtain a monolayer of soil on the adhesive tape. Care was taken to prepare the soil monolayer with a homogeneous surface to the maximum possible extent. The prepared soil samples were placed at $25 \pm 2^\circ\text{C}$ room temperature in a sealed chamber with $94 \pm 2\%$ relative humidity (RH) for a period of 3 days to obtain the highest potential level of WR. For the measurement of contact angles, a droplet (10 μL) of deionized water was placed on the surface of prepared soil monolayers, and the microphotograph of the horizontal view of the water droplet was recorded within 1 s as the initial measurement (Leelamanie and Karube, 2009). The droplet shape was continuously monitored

and recorded at 1 s intervals for ~ 2 min, and then at 2–3 s intervals, as it spread with increasing soil-water contact time until the drop completed the spreading on the prepared soil monolayer.

The RH of the measuring environment was kept close to 90% to minimize the loss of water through evaporation, and to prevent any changes in the soil monolayer due to the desorption of water molecules that can change the level of WR responding to changes in RH, during the measurement. The experimental procedure was repeated for each soil sample in triplicate. The apparent soil-water contact angle (θ_A) was taken as the average of the two angles measured on the left and right ends of the droplets at the three-phase (soil-water-air) contact line of the recorded droplet images.

2.3 Measurement of repellency persistence

To determine the relation between the decreasing contact angle of the spreading droplet on the monolayer of water-repellent soil and the entry of water into water-repellent soil, the persistence of WR of soils was measured using the water drop penetration time (WDPT) test. About 7 g soil subsamples were placed in stainless steel containers (inner diameter: 35 mm; height: 15 mm) and kept in an airtight chamber with $94 \pm 2\%$ relative humidity at $25 \pm 2^\circ\text{C}$ for a period of 3 days before the measurements. To measure the WDPT, a drop ($50 \pm 1 \mu\text{L}$) of deionized water was placed on the soil surface using a micropipette (Pipetman, Gilson Inc., France) from a height of 10 mm, and the time taken for the water drop to completely enter into the soil surface was recorded using a stopwatch. When the penetration times exceeded a period of 60 s, the containers were covered with a transparent film to minimize the evaporation

during the experiment. The RH of the measurement environment was kept close to 90% during the measurement. WDPT values below 0.5 s, including the instantaneous penetrations, were assigned a WDPT value of 0.5 s. The measurements were continued for 2 h.

2.4 Droplet shape and geometry

2.4.1 Geometric contact angle

The contact angle can also be calculated using the geometric parameters of a liquid droplet placed on a solid surface, following the spherical approximation of the droplet (Annaka, 2006; Leelamanie and Karube, 2012). For this purpose, the droplet is assumed to be in a perfect spherical shape, where the two-dimensional appearance captured in the microphotograph would represent a part of a perfect circle. Equations can then be developed to calculate the geometric contact angle (θ_G) using droplet geometric parameters (Fig. 2). Geometrically analyzing the droplet parameters can be performed separately for the situations where the θ_G is below and above 90° .

For situations where $\theta_G < 90^\circ$ (Fig. 2a);

$$\tan \frac{\theta_G}{2} = \frac{h}{R}$$

$$\theta_G = 2 \tan^{-1} \left(\frac{h}{R} \right) \quad (1)$$

For situations where $\theta_G > 90^\circ$ (Fig. 2b);

$$\sin \alpha = \left(\frac{h-r}{r} \right)$$

$$\theta_G = 90^\circ + \sin^{-1} \left(\frac{h-r}{r} \right) \quad (2)$$

The θ_G was calculated using the geometrical parameters of the droplets using either Eq. 1 (when $\theta_G < 90^\circ$) or Eq. 2 (when $\theta_G > 90^\circ$).

3 RESULTS

3.1 Water repellency of soils

Table 2 presents the initial contact angle and the WDPT of the tested soils. The contact angles reported here are the initial apparent contact angles (θ_A) of the samples, which were measured from the microphotographs recorded within 1 s of placing the water droplets on the soil monolayers. According to the initial θ_A , CYP1 soil showed the highest WR. The same soil showed the highest WDPT, indicating the highest WR as measured by both parameters. Similarly, the CYP2 soil, which exhibited the lowest θ_A , also showed the lowest WDPT. Results showed that all the tested soil samples had contact angles above 90° , indicating a high level of hydrophobicity.

Table 2. Contact angle and water drop penetration time (WDPT) of the tested soils ($25 \pm 1^\circ\text{C}$; $94 \pm 2\%$ relative humidity). Values represent mean $\pm$ standard deviation. CED: cedar; CYP: cypress; MIX: cedar and cypress mixed.

Sample	Contact angle ($^\circ$)	Log WDPT (s)
CED1	123 $\pm$ 6	2.81 $\pm$ 0.03
CED2	117 $\pm$ 2	2.43 $\pm$ 0.03
CYP1	131 $\pm$ 3	3.86 $\pm$ 0.00
CYP2	103 $\pm$ 7	2.28 $\pm$ 0.01
MIX1	124 $\pm$ 3	3.28 $\pm$ 0.05
MIX2	120 $\pm$ 4	2.43 $\pm$ 0.05

3.1 Droplet spreading and temporal alteration of contact angle

The contact angle decreased gradually over time in all the tested forest soils. Fig. 3 shows the optical illustration of the temporally declining contact angle captured in microphotographs. Figure 4 explains the temporal change in θ_A , which was determined using microphotographs. With increasing time, θ_A declined gradually and continuously corresponding to the spreading of water droplets. The decline of θ_A continued for a period of about 5–6 min and finally reached a value of 0 concurrent with the disappearance of the droplet due to complete spreading. In all tested samples, the decline in θ_A with time revealed a strong negative exponential correlation ($R^2 = 0.90$ and 0.99 , respectively, for CED1 and CED2 soils; $R^2 = 0.99$ and 0.95 , respectively, for CYP1 and CYP2 soils; $R^2 = 0.99$ and 0.95 , respectively, for MIX1 and MIX2 soils). The regression analysis linearized through log transformation (Linear regression equations for CED1: $y = -51.603x + 136.44$; CED2: $y = -62.526x + 146.49$; CYP1: $y = -61.81x + 171.91$; CYP2: $y = -41.408x + 124.31$; MIX1: $y = -70.029x + 171.99$; MIX2: $y = -46.465x + 141.95$) showed that the correlations in all the tested soils were statistically significant ($p < 0.05$), confirming the correlation.



Fig. 3. Optical illustration of temporal declining contact angle.

3.3 Apparent and geometric contact angles, and droplet geometry

The θ_G of the tested soils was calculated using the changing droplet geometrical parameters with increasing time as the

droplets spread on the soil surfaces, as shown in Eq. 1 and Eq. 2. The θ_G of all soils gradually decreased with time, showing strong negative exponential correlations indicating that θ_A and θ_G of all samples show an almost similar pattern of temporal change corresponding to the droplets spreading. To examine the correlation between the actual and geometrically calculated contact angles, θ_A was plotted against θ_G . The regression line was conformed to satisfy a proportional relationship. As shown in Figure 5, θ_G displayed statistically significant ($p < 0.05$) strong ($R^2 = 0.99$) positive linear correlations with θ_A for all samples tested. The proportionality of all correlations across all six soils remained closer to 1.0, with only a <4% deviation from an identity relation. The features of droplet spreading are generally defined by the droplet contact angle, the solid-liquid contact radius, and the droplet height. In the present study, the apparent contact angle, θ_A , and the θ_G calculated using droplet geometric parameters, such as solid-liquid contact radius and droplet height, showed strong and statistically significant positive proportional correlations ($y = mx$), where the proportionality of the regression line was almost 1.0.

3.4 Time-dependent contact angle and repellency persistence

The time taken for penetration of a water droplet into a soil matrix, which was measured by WDPT, can represent entry of water into capillaries when the soil-water contact angle on the surface changes to be $< 90^\circ$ as a result of interactions between soil and water during the period of contact. Although the WDPT values of all samples exceeded ~ 200 s (Table 1), the contact angle measured on the soil monolayer receded to reach $\leq 90^\circ$ within a very short period (Fig. 4), corresponding to the gradual spreading of the droplets. The soil-water contact time (CT) taken for the decreasing contact angle to recede to be $\leq 90^\circ$ (CT- θ_{90°) for the soils were in a range of 4–40 s (CED1: 12–14 s; CED2: 14–16 s; CYP1: 35–40 s; CYP2: 6–8 s; MIX1: 26–32 s; MIX2: 4–6 s). Therefore, it was clear that the CT- θ_{90° and WDPT are not comparable for the tested hydrophobic soils.

To understand the relationship between these two parameters, the CT- θ_{90° was plotted against the WDPT. Figure 6 presents the correlation between the persistence of WR, as measured by the WDPT (log), and the CT- θ_{90° (log) for all the tested soils. The parameters showed a statistically significant ($p < 0.05$), strong ($R^2 = 0.926$) positive linear correlation following a proportional relationship.

4 DISCUSSION

4.1 Water repellency of soils

A significant amount of research exists on the occurrence, nature, behavior, and impacts of soil water repellency. Among the tested three types of vegetations, CYP1 showed the highest SWR as represented by the initial contact angle, followed by MIX1 and CED1 (Table 2, Fig. 4). Considering the soil C levels (Table 1), it was clear that the sample with the highest soil C level (CYP1) showed the highest water repellency. However, the repellency level of all samples, specifically the MIX soils, could not be related to the soil C contents. Still, for CED and CYP soils, the difference in contact angle can be related to the C content of the soil, where the high level of water repellency interrelated with high level of C (Table 1, 2). Although different opinions have also been reported, water-repellent soils generally contain higher contents of organic matter compared with non-repellent soils (Fu et al., 2021). The onset of water repellency is generally considered to be associated with the presence of long-chain organic compounds (Doerr et al., 2000). However, most

available information is highly location-specific, and the differences in sampling and measurement techniques make integrating the results from different studies difficult (Smettem et al., 2021).

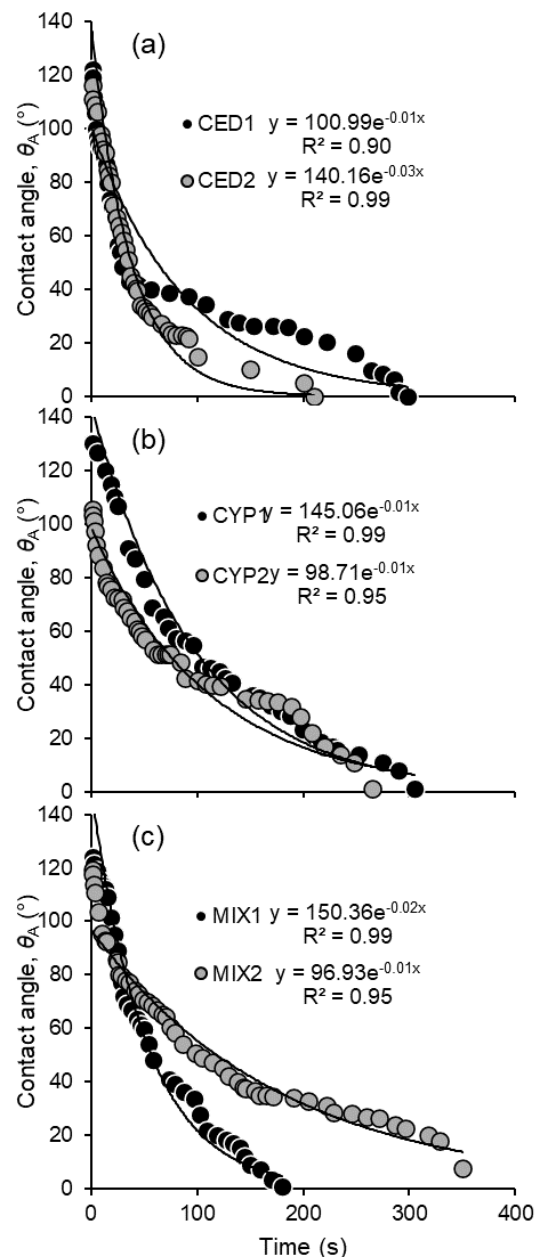


Fig. 4. The temporal change in apparent contact angle (θ_A) determined using microphotographs in (a) cedar (CED), (b) cypress (CYP), and (c) cedar and cypress mixed (MIX) forest soils.

4.2 Droplet spreading and temporal alteration of contact angle

The contact angle depends on the features of the solid, such as surface roughness and chemical heterogeneity, and the properties of the liquid (Erbil, 2014). When a sessile droplet is placed on a solid surface, the solid/liquid interfacial area and the peripheral length of the droplet at the three-phase contact line are expected to advance rapidly to a certain extent and then to cease moving resulting in a stable contact angle. Still, the available reported evidence on the time-dependent behavior of contact angle confirms that contact angle of a liquid droplet placed on a solid surface decreases gradually with increasing time for a few

minutes, or longer periods close to an hour (~10–50 min) before settling, showing an exponential correlation, rather than rapidly stabilizing (Leelamanie and Karube, 2009; Subedi et al., 2012; Varennes and Schreiber, 2001; Wang et al., 2005).

Results of the present study also confirmed the exponential decrease in contact angle for the tested water-repellent soils (Fig. 4). However, in contrast to previous studies that reported a stabilizing of contact angle after some period, we observed a continuous decline in contact angle to reach zero, concurrent with the complete spreading of water droplets on water-repellent soil monolayers within a period of 5–6 min.

The reason for the time-dependence of contact angle on a solid surface is still subject to debate (Wang et al., 2005). Local deformation of the soft solid surface and related viscoelastic dissipation (Shanahan and Carré, 1994), strong interaction between water and solid molecules (Weikart et al., 1999), reorientation of the amphiphilic molecules near the solid-water contact line (Starov, 2004; Wang and Wallach, 2020), and the adsorption of water molecules onto the solid surfaces and related changes in the interfacial energies (Leelamanie and Karube, 2009; Songok et al., 2014) are some of the suggested concepts.

Songok et al. (2014) explained that water adsorption on the solid surface is controlled by molecular processes occurring at the advancing liquid front. The adsorption and condensation of water molecules onto solid surfaces ahead of the advancing liquid front can alter interfacial tensions, resulting in lowering of the contact angle and prompting further spreading (Rosenholm, 2007; Songok et al., 2014). The tested hydrophobic soil monolayers are not perfect solid surfaces, and the hydrophobicity precludes any soil-water attractive forces. Therefore, local surface deformations and related viscoelastic dissipation processes, or strong attractive forces between water and solid molecules (Shanahan and Carré, 1994; Weikart et al., 1999) cannot be considered as responsible for the droplet spreading. The spreading and receding contact angles of water droplets on the water repellent soil surfaces in the present study may be interpreted using water molecular adsorption processes or amphiphilic molecular reorientation processes, as explained in other reports (Leelamanie and Karube, 2009; Rosenholm, 2007; Songok et al., 2014; Starov, 2004; Wang and Wallach, 2020). The complete disappearance of the spreading droplet, resulting in a contact angle reaching zero without stopping at a steady level, can be attributed to the heterogeneous nature of the naturally hydrophobic soil monolayers.

Some reports stipulate the importance of evaporation on the time-dependent nature of the contact angle. Semenov et al. (2014) reported that the spreading and evaporation of liquid droplets take place simultaneously, where the evaporation initially has no impact but becomes effective at a later stage, resulting in either a receding contact angle with a constant wetting radius or a constant contact angle with a receding wetting radius. In the present study, however, we did not observe either a receding contact angle while maintaining a constant wetting radius or a receding wetting radius while maintaining a constant contact angle, indicating that the evaporation process had no significant impact.

4.3 Apparent and geometric contact angles, and droplet geometry

The features of spreading droplets are generally defined by the droplet contact angle, solid-liquid contact radius, and the droplet height. In the present study, the apparent contact angle, θ_A , and the θ_G calculated using droplet geometric parameters, such as solid-liquid contact radius and droplet height, showed

strong and statistically significant positive proportional correlation, where the proportionality of the regression line was almost 1.0.

When the spreading of a droplet happens following a non-spherical spreading pattern, the measured geometric parameters r , R , and h (Fig. 2) would show lower or higher values than those measured in the situation with fair spherical spreading. In such cases, the θ_G calculated using geometric parameters, as shown in Eq. 1 and Eq. 2, would be higher or lower compared with situations where the droplet spreading pattern remains perfect circular, and the droplet shape remains a spherical segment. The statistically significant positive proportional correlation between θ_A and θ_G (Fig. 5) confirms that the droplets maintained spherical segment features during the spreading process on the soil surfaces.

4.4 Repellency persistence and relation to time-dependent contact angle

The WDPT of soils is only sensitive in a narrow range of contact angles around 90°. The designated transition domain zone is within the range of WDPT values from several seconds to 1 hour. Contact angles associated with this range of WDPT are typically 70° to 90° (Bachmann et al., 2007). According to theoretical capillary principles and experimental findings, water can enter soil capillaries only when the soil-water contact angle is below 90° (Leelamanie et al., 2021; Letey et al., 2000).

When the contact angle of a sessile drop placed on a soil monolayer (Bachmann et al., 2000) is time-dependent and declines within a few minutes to drop below 90°, it might seem that the water droplet may enter the soil matrix if the droplet penetration has not been intentionally prevented for experimental purposes. The persistence of water repellency, as estimated by the WDPT, indicates the time a water droplet on a soil surface takes to completely penetrate the capillaries due to changes at the soil-water contact surface. Since this would occur only when the soil-water contact angle is below 90° (Letey et al., 2000), a question arises as to whether the time taken for the temporally changing droplet contact angle to drop below 90°, $CT-\theta_{90^\circ}$, is the same as the WDPT.

In the present study, the temporally changing contact angle decreased to below 90° within a short period, where the droplets completely spread on the soil, resulting in zero contact angle within a 5–6 min period (Fig. 6), showing that the WDPT is remarkably longer (Table 2) than the $CT-\theta_{90^\circ}$. The results clearly confirm that the $CT-\theta_{90^\circ}$ does not represent the WDPT, and therefore, no equivalent parameters. To establish the relationship between the two parameters, we conducted a regression analysis (Fig. 6). Interestingly, these two parameters (logarithmic) showed a statistically significant ($p < 0.05$) strong positive linear correlation ($R^2 = 0.926$) following a proportional ($y = mx$) relationship. This signifies that the $CT-\theta_{90^\circ}$ changes at a constant rate with respect to the WDPT.

The proportionality of the correlation revealed that $CT-\theta_{90^\circ}$ is only ~37% of the WDPT. The proportional nature of the correlation indicated that although the WDPT and the $CT-\theta_{90^\circ}$ are not the same, they are in fact strongly correlated. The WDPT, which is the time for droplet penetration, is a function of the surface and below-surface capillary pore structure and relates essentially to a three-dimensional water movement process. In contrast, $CT-\theta_{90^\circ}$ is a surface-only phenomenon that occurs with a two-dimensional spreading of water on a soil monolayer, where the vertical penetration is prevented. The different natures of these two processes might be the reasons for the WDPT and $CT-\theta_{90^\circ}$ to give different values.

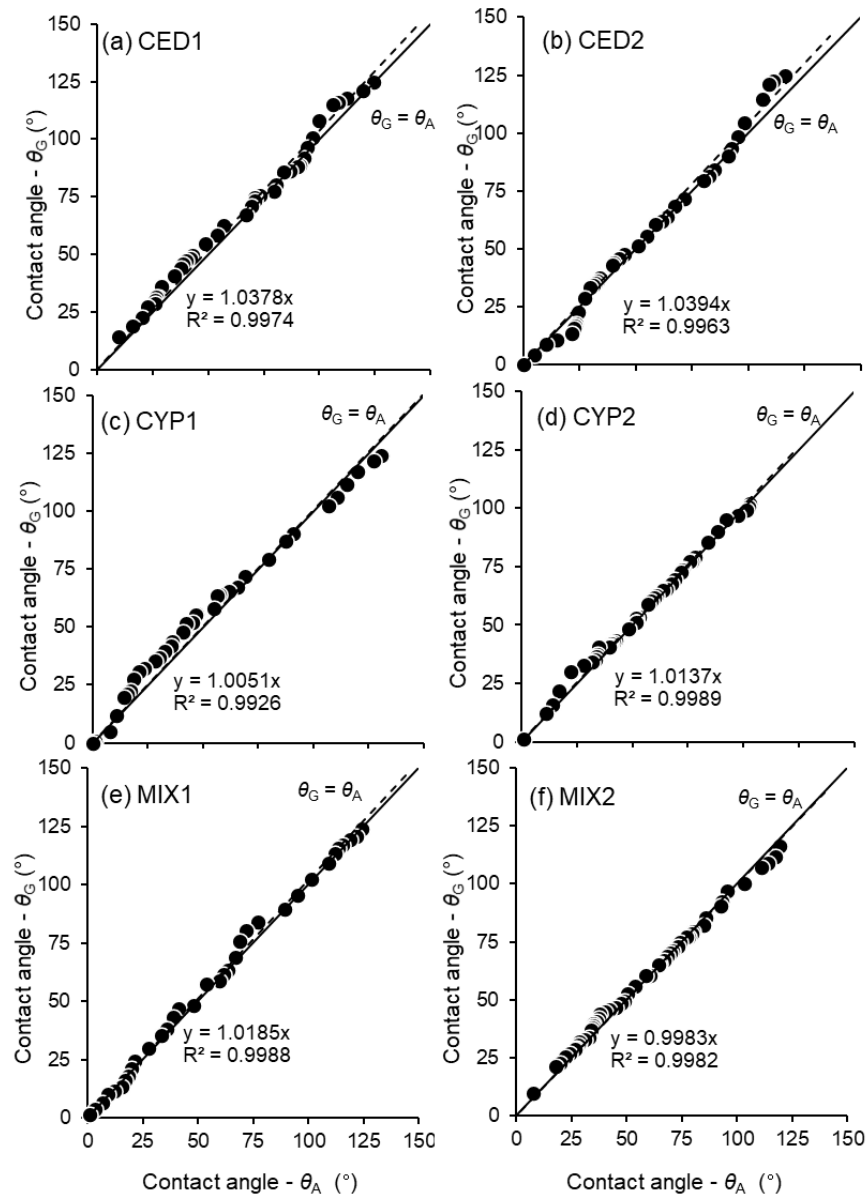


Fig. 5. The correlation between the apparent contact angle (θ_A) and the geometrically calculated contact angle using droplet geometric parameters (θ_G) of the tested soils. Solid lines represent the perfect positive correlation model, where $\theta_G = \theta_A$. Dashed lines represent the regression line of actual data. CED: cedar; CYP: cypress; MIX: cedar and cypress mixed.

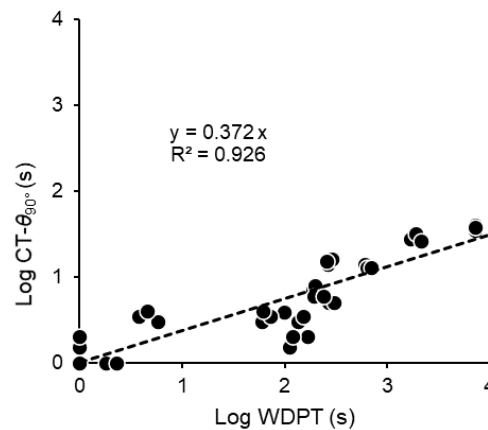


Fig. 6. The correlation between the persistence of water repellency, as measured by the water drop penetration time (WDPT), and the soil-water contact time taken for the temporally changing apparent contact angle to recede below 90° (CT- θ_{90°).

4.5 Interfacial relations of the three-phase contact line

The solid-liquid contact area, or the wetted area, of a sessile drop is circumscribed by the three-phase contact line at the solid/liquid interface. Work on wettability shows that the solid/liquid contact angle strongly depends on the surface quality of the solid, which cannot be generally regarded as perfectly smooth or homogeneous, and free from impurities (Kwok and Neumann, 2000). Wetting behavior and contact angles are also known to be influenced significantly by the Attributes of the three-phase contact line of first spreading droplet (Extrand et al., 2007).

There have been fundamental questions on whether the wetting or droplet spreading process is controlled by the interactions at the solid/liquid contact area or only at the three-phase contact line formed around the droplet. By reviewing available evidence, Erbil (2014) explained that the interactions of the particular liquid and solid at the three-phase contact line alone are important for the contact angle made by the liquid on rough and chemically heterogeneous solid surfaces, while the interfacial area within the contact perimeter of a droplet is irrelevant. The attributes of the three-phase contact line of a droplet significantly influence the wetting and contact angles of not only smooth structured surfaces but also wrinkled or rough surfaces, rather than the surface roughness or the liquid-solid interfacial contact area (Chung et al., 2007; Extrand et al., 2007).

The free energies (or surface/interfacial tensions) of solid-vapor, liquid-vapor, and solid-liquid interfaces are related in the well-known Young's equation (Young, 1805). It explains that for the equilibrium of water droplet on a solid surface (Fig. 7), the force balance in the horizontal direction is given by:

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (3)$$

where γ_S , γ_L , and γ_{SL} are respectively the solid-vapor, liquid-vapor, and solid-liquid interfacial tensions. However, Young's equation does not account for the molecular interactions at the three-phase contact line.

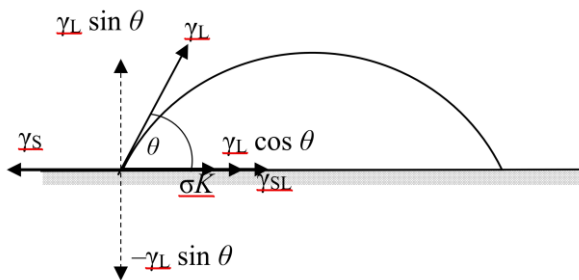


Fig. 7. Force balance at the three-phase contact line of the droplet, indicating free energies (or surface/interfacial tensions) of solid-vapor (γ_S), liquid-vapor (γ_L), and solid-liquid (γ_{SL}) interfaces, and line tension (σ) component. θ : contact angle; K : constant.

There have been fundamental questions on whether the wetting or droplet spreading is controlled by the interactions at the solid/liquid contact area or at the three-phase contact line formed around the droplet. By reviewing available evidence, Erbil (2014) explained that the interactions of the liquid and solid at the three-phase contact line alone are important for the contact angle made by the liquid on rough and chemically heterogeneous solid surfaces, while the interfacial area within the contact perimeter is irrelevant. The attributes of the three-phase contact line of a droplet significantly influence the wetting and contact

angles of not only smooth structured surfaces but also wrinkled or rough surfaces, rather than the surface roughness or the liquid-solid interfacial contact area (Chung et al., 2007; Extrand et al., 2007).

The line tension of a liquid droplet lens is defined as the available excess free energy of a unit length of the three-phase (solid-liquid-gas) contact line, a one-dimensional analog of the surface tension (Gibbs, 1948) that occurs at the periphery of the three-phase contact circle (Amirfazli and Neumann, 2004). Considering the molecular interactions between the three phases at the vicinity of the contact line of the water droplet (Fig. 7), the concept of linear tension, or the line tension (σ), can be introduced to develop a modified Young's equation (Li, 1996);

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} - \sigma K \quad (4)$$

where K is the local curvature of the three-phase line on the solid surface. Assuming an ideal situation where the droplet is truly axisymmetric, the solid surface is rigid, horizontal, planar, and homogeneous, and the three-phase contact line is a smooth circle, the curvature of the three-phase contact line, K can be related to the radius of the three-phase contact surface, R (Li, 1996).

$$K = 1/R \quad (5)$$

Combining Eq. 4 and Eq. 5;

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} - \frac{\sigma}{R} \quad (6)$$

In case that the R is very large, which can be considered infinity, σ/R will be zero, Eq. 6 would be equal to the classical form of Young's equation (Eq. 3). For the equilibrium of the three-phase contact line of a drop with a very large R and a contact angle of θ_∞ :

$$\gamma_L \cos \theta_\infty = \gamma_S - \gamma_{SL} \quad (7)$$

Combining Eq. 6 and Eq. 7, a linear relation can be developed (Amirfazli et al., 1998).

$$\cos \theta = \cos \theta_\infty - \frac{\sigma}{\gamma_L} \frac{1}{R} \quad (8)$$

Eq. (8) dictates that the contact angle is dependent on the line tension and the solid-liquid contact radius, R , and the line tension effect becomes more significant when the droplet size is smaller. The line tension is given more attention with the changes in droplet volume (Amirfazli et al., 1998; Leelamanie and Karube, 2012). However, in situations where θ and the R are changing with the droplet spreading, the contribution of the line tension to the force balances at the three-phase contact line of the water droplet will also be changing because the relative proportion of molecules in the vicinity of the solid-water contact line changes with the changes in R . In such cases, a linear correlation can be generated between $1/R$ and $\cos \theta$, and the line tension can be determined using the slope of the linear regression line. Accordingly, the line tension related to the water droplets on soil monolayers of the six tested soils was determined using the temporally changing θ_A and R . Figure 8 explains the correlation between $\cos \theta_A$ and $1/R$ for the six tested soils, where the R represents the temporally changing radius of the soil-water contact area as a consequence of the droplet spreading. The $\cos \theta_A$ of all soils showed strong and statistically significant negative linear correlations with $1/R$ ($R^2 = 0.98 - 0.99$). As given in Eq.

8, the slope of the regression line is σ/γ_L , where σ and γ_L are the line tension and the liquid surface tension, respectively.

Considering the surface tension of water (at 25°C) as approximately 71.96 mN m⁻¹ (equivalent to 0.072 $\mu\text{J mm}^{-2}$), the line tension at the periphery of the contact circle of the water droplets on the soil monolayers was calculated. For a stable thermodynamic equilibrium of an ideal solid-liquid system, the line tension should be positive (Li, 1996). Still, the literature provides evidence for positive, negative, or both positive and negative signs of the line tension (Amirfazli et al., 1998; Drelich et al., 1996; Gu, 2001; Wang et al., 2024). According to Eq. 6, as R increases, the contact angle will decrease when the line

tension is positive, and will increase when the line tension is negative. Since the liquid surface tension, γ_L , is always positive, a negative slope as shown in Fig. 8 indicates a positive line tension. The order of magnitude of line tensions is reported to vary from 10^{-5} to $10^2 \mu\text{J m}^{-1}$ (Amirfazli et al., 1998; Gaydos and Neumann, 1987; Gu, 2001; Wang et al., 2024). The line tensions related to the temporally spreading water droplets on CED1, CED2, CYP1, CYP2, MIX1, and MIX2 soils were 235, 211, 206, 298, 228, and 263 $\mu\text{J m}^{-1}$, respectively, showing that although the values are somewhat higher, their order of magnitude ($10^2 \mu\text{J m}^{-1}$) was within the range of previously reported values.

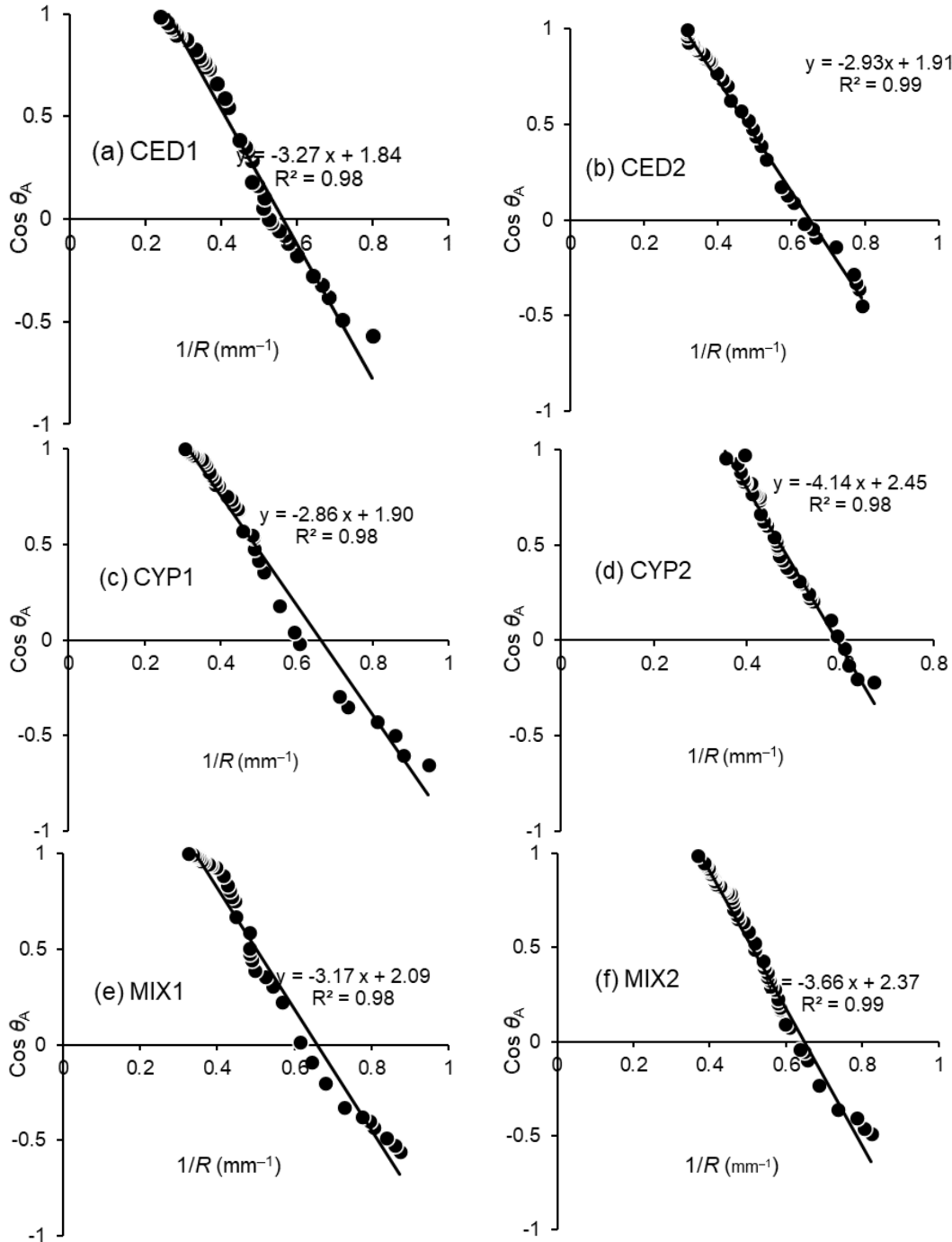


Fig. 8. The correlation between $\cos \theta_A$ and $1/R$. CED: cedar; CYP: cypress; MIX: cedar and cypress mixed; θ_A : apparent contact angle; R : radius of the soil-water contact area.

5. CONCLUSIONS

While the initial soil-water contact angle has been used to characterize the water repellency of soils, the time-dependent nature of the contact angle and its decrease with time have often been ignored. Studies focused on spreading water droplets on hydrophobic soil substrates and the concurrent decline in contact angle are highly limited. In this study, we examined the temporal alteration of soil-water contact angle with droplet spreading, considering the droplet geometric parameters and interfacial interactions at the periphery of the spreading droplet, using six hydrophobic Japanese forest soils.

The presence of strong positive linear correlation between θ_G and θ_A explains the preservation of a fair spherical segment-shaped droplet during the spreading process supporting the validity of the geometric assumptions of the analysis of dynamic contact angles. The comparison between the soil-water contact time for the contact angle to drop below 90° and WDPT revealed that they are not equivalent parameters. This reflects the distinction between two-dimensional surface wetting related to liquid spreading processes and three-dimensional infiltration processes. However, their strong positive linear correlation indicated the close relationship between the surface wetting dynamics and subsurface water entry. This highlights the potential for integration of dynamic contact angles with more conventional water repellency indices to reach more comprehensive analysis of water repellency dynamics. The line tension at the periphery of the contact circle remained within the previously reported range of order of magnitude, indicating that the droplet spreading on natural soils particles follows the theoretical concepts of spreading droplets irrespective of the surface roughness and heterogeneous nature of particles.

The reason for the contact angle to be time-dependent is still subject to conjecture. The exact reason for the receding contact angles with increasing soil-water contact time in concurrent with the spreading of water droplets on the water-repellent soil surfaces in the present study could not be specifically identified or verified with the conducted experiments. However, some of the processes that have previously been suggested such as local deformation of solid surfaces, viscoelastic dissipation, and strong solid-water interactions could be logically eliminated. Therefore, the declining contact angle in the present study might be attributed either to water molecule adsorption processes or to amphiphilic molecular reorientation processes as reported in previous studies. Future studies specifically focused on those processes are needed for verifying of the exact phenomena. In general, this study highlights the significance of time-dependent wetting dynamics in assessments of water repellency and the connection of interfacial processes of droplet-scale to macroscopic processes such as water infiltration.

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13

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