Water stable aggregates of Japanese Andisol as affected by hydrophobicity and drying temperature

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Abstract: Hydrophobicity is a property of soils that reduces their affinity for water, which may help impeding the pressure build-up within aggregates, and reducing aggregate disruption. The purpose of this study was to examine the relation of soil hydrophobicity and drying temperature to water stability of aggregates while preventing the floating of dry aggregates using unhydrophobized and hydrophobized surface Andisol. Soil was hydrophobized using stearic acid into different hydrophobicities. Hydrophobicity was determined using sessile drop contact angle and water drop penetration time (WDPT). Water stability of aggregates (%WSA) was determined using artificially prepared model aggregates. The %WSA increased as the contact angle and WDPT increased. Contact angle and WDPT, which provided maximum %WSA showing less than 1 s of floating, was around 100° and 5 s, respectively. Although the %WSA gradually increased with increasing contact angle and WDPT above this level, high levels of hydrophobicity initiated aggregate floating, which would cause undesirable effects of water repellency. Heating at 50°C for 5 h d⁻¹ significantly affected %WSA and hydrophobicity in hydrophobized samples, but did not in unhydrophobized samples. The results indicate that the contact angle and wetting rate (WDPT) are closely related with the water stability of aggregates. The results further confirm that high levels of hydrophobicities induce aggregate floating, and the drying temperature has differential effects on hydrophobicity and aggregate stability depending on the hydrophobic materials present in the soil.

Keywords: Aggregate stability; Contact angle; Floating time; Japanese Andisol; Hydrophobicity; Wetting rate.

INTRODUCTION

The slaking process after rapid wetting of aggregates is a key factor controlling the soil structural stability in dry soils. Slaking is linked with rapid pressure buildup within aggregates. In general, there are four key processes involved in aggregate deterioration; (i) slaking when dry aggregates are suddenly rehydrated; (ii) mechanical breakdown by the rain drop impact; (iii) mellowing after wetting-drying cycles; and (iv) differential swelling/dispersion when the soil is in contact with free water for a prolonged period of time (Le Bissonnais 1996; Zaher and Caron 2008). Hydrophobicity (water repellency) is a property of soils that reduces their affinity for water and their infiltration capacity (Feng et al., 2001; Wallis et al., 1991; Wallis and Horne 1992). By reducing the rate of infiltration into the aggregates, water repellency helps hampering the pressure buildup within aggregates, which will reduce aggregate disruption by slaking and mechanical impact of raindrops (Cosentino et al., 2010; Eynard et al., 2004; Tillman et al., 1989). However, if aggregates are too much hydrophobic, the accumulation of water on the soil surface will make them float (Leelamanie et al., 2013) and consequently increase the top soil erosion by the removal of floating aggregates with runoff water. Therefore, care should be taken not to exceed this critical hydrophobic condition. Initial wetting rates would be a simple index that can be connected to the aggregate stability, and for maintaining water stability of aggregate in an appropriate level.

It has long been established that heating of potentially water repellent soils influences their wettability. The degree of potential water repellency might change with different drying temperatures (Crockford et al., 1991; Dekker et al., 1998). DeBano and Krammes (1966) found that water repellency increased even at lower temperatures under prolonged heating

times. Considering that surface hydrophobicity might interrelate with aggregate stability, drying temperature or heating might affect the aggregate stability as well. Czachor and Lichner (2013) reported that exposure to temperatures between 100 and 200°C tends to decrease water sorptivity of aggregates.

The purpose of this study was to examine the relation of soil hydrophobicity and drying temperature to water stability of aggregates using artificially prepared model aggregates. Effort was made to identify the most suited initial wetting rates to achieve the most durable stability for aggregates while preventing the floating of dry aggregates.

MATERIALS AND METHODS

Unhydrophobized and hydrophobized Andisols were used in the experiment. Surface soil (0–5 cm depth) under vegetable cultivation was collected from the Field Science Center, School of Agriculture, Ibaraki University, Japan (36° 1' N 140° 12' E). Basic properties of the soil are given in Table 1.

Collected soil was thoroughly air-dried at 20°C and passed through 0.5 mm sieve before further analysis. Series of samples with different hydrophobicities was used to determine the relation of percentage of water stable aggregates (%WSA) to hydrophobicity. Stearic acid (Wako Pure Chemical Industries, Osaka, Japan), was used to hydrophobize Andisol into different initial hydrophobicities. Stearic acid was dissolved in diethyl ether and mixed with the soil in a fume hood to obtain soil samples with 0, 0.2, 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, and 15.0 g kg⁻¹ of stearic acid. The soil–stearic acid–diethyl ether mixture was stirred in the fume hood during volatilization of diethyl ether until the complete disappearance of wetness to prevent from non-homogeneous distribution of stearic acid in the soil (Lichner et al., 2006). Samples were left 2 h in the hood and then kept in

Table 1. Basic properties of Andisol used in the experiment.

Property	Value
Bulk density (Mg m^{-3})	0.66
Particle density (Mg m^{-3})	2.57
Porosity %	74.4
Coarse sand %	10.3
Fine sand %	38.1
Silt %	30.6
Clay %	21.0
Organic matter content %	7.8
pH	4.9
EC (mS m^{-1})	68

a thermostated room with $25 \pm 1^\circ\text{C}$ and $75 \pm 5\%$ of relative humidity for one day before preparing the samples for the hydrophobicity and aggregate stability measurements.

Acryl cylindrical blocks with approximately 10 cm^3 volume (2.4 and 2.2 cm in diameter and height, respectively) were used prepare model aggregates. Soil samples were uniformly wetted with deionized water ($0.45 \pm 0.05 \text{ kg kg}^{-1}$) and thoroughly mixed with spatula. The prepared soil cakes were filled into the blocks while taking care to fill approximately the same amounts to the blocks to maintain the homogeneity of aggregates. The average bulk density of aggregates was $0.82 \pm 0.03 \text{ Mg m}^{-3}$. Prepared aggregates were carefully taken out by gently pressing from one side with a cylindrical glass slab.

For sessile drop contact angle measurements (Bachmann et al., 2000), each soil sample was fixed on a double-sided $1.5 \text{ cm} \times 1.5 \text{ cm}$ adhesive tape adhered on a glass slide (Leelamanie et al., 2008a) with six replicates per stearic acid content.

All the prepared samples were kept 5 h d^{-1} in a laboratory oven with 50°C , and the remaining time of the day under 25°C in a sealed chamber with 75% RH (water potential = -40 MPa , $\text{pF} = 5.61$) for 7 d period. The RH in the chamber was maintained using saturated sodium chloride (NaCl) solution (Leelamanie et al., 2008b). Samples were placed 72 h in the thermostated room (25°C), inside the sealed chamber with 75% RH before using the samples for hydrophobicity and aggregate stability measurements. All experiments were conducted in the thermostated room ($25 \pm 1^\circ\text{C}$, $75 \pm 5\%$ RH).

To find the effect of drying temperature on %WSA, unhydrophobized and hydrophobized (5 g kg^{-1} stearic acid) samples were separately exposed to two experimental temperature conditions (25°C and 50°C) using the thermostated room and a laboratory oven. The sample with 5 g kg^{-1} was selected to compare with unhydrophobized samples considering the behavior of the hydrophobicity of the tested Andisol upon exposure to heat (Leelamanie and Karube, 2014). For 25°C drying treatment, samples were kept in the sealed chamber at $25 \pm 1^\circ\text{C}$ and 75% RH throughout the experimental period, whereas for 50°C drying treatment samples were kept 5 h d^{-1} in a laboratory oven with 50°C , and the remaining time of the day under 25°C . Before the hydrophobicity and aggregate stability measurements, samples exposed to 50°C were kept the sealed chamber with 75% RH (-40 MPa water potential) for 72 h. Hydrophobicity and aggregate stability measurements were taken at 3, 7, 14, 21, 28, and 40 d.

The %WSA was estimated using air dried model aggregates, in 3 replicates. Each aggregate was placed in a 0.5 mm sieve, carefully immersed the sieve in water, and kept overnight. The percentage of water stable aggregates larger than 0.5 mm

diameter (%WSA) was measured to represent the stability of aggregates. Once immersed in water, aggregates leap up to the water surface as a result of the entrapped air in intra-aggregate pores when the water entry into aggregates is slow enough. The total floating time of each aggregate, which demonstrated floating, was recorded.

For contact angle measurement, a deionized water drop of $10 \mu\text{L}$ was placed on each prepared soil surface and a digital micro-photograph of the drop was taken within 1 s using a digital microscopic camera. Using the microphotographs, initial advancing contact angle was directly measured considering the average of the contact angles of the drop at the both three-phase contact points.

Wetting rates of aggregates were determined using water drop penetration time (WDPT) test in three replicates (3 model aggregates) per stearic acid content. Three drops of deionized water with $50 \pm 1 \mu\text{L}$ volume was placed on each model aggregate surface using a micropipette (PipetGene, TKG, Tokyo, Japan) at about 10-mm height from the aggregate surface. Times taken for the complete penetration of the water drops were separately measured, where the average of the three WDPTs were taken as a single replica. Measurement was terminated after 1 h (3600 s). Samples with $\text{WDPT} \leq 1 \text{ s}$ were considered non-repellent, $1 < \text{WDPT} < 60 \text{ s}$ slightly repellent, $60 < \text{WDPT} < 600 \text{ s}$ strongly repellent, $600 < \text{WDPT} < 3600 \text{ s}$ severely repellent, and $\text{WDPT} \geq 3600 \text{ s}$ extremely repellent.

Data were statistically analyzed using STATISTICA software (Statsoft Inc., 2010), with ANOVA at 5% level of significance ($p < 0.05$). All the figures are given with error bars representing $\pm$ standard deviation.

RESULTS AND DISCUSSION

The %WSA and floating time of aggregates in relation to the hydrophobicity is presented in Figure 1. Both %WSA and floating time positively responded to the hydrophobicity as measured by contact angle (Figure 1a) and WDPT (Figure 1b). The %WSA remained below 50% for contact angles below 100° (Figure 1a), whereas it rapidly increased as the contact angle increased with increasing stearic acid content, exceeding 80% at 104° . Corresponding to the increasing hydrophobicity, floating of aggregates started when the contact angle exceeded 100° .

Similar trend was observed with WDPT measurements (Figure 1b). As the wetting rate decreased from instant wetting ($\text{WDPT} \approx 1 \text{ s}$) to 5 s of penetration time, the %WSA dramatically increased showing $\text{WSA} < 50\%$ at WDPT of 1 s and $> 80\%$ at WDPT of 5 s. Floating of aggregates appeared when the WDPT exceeded 2 s.

About 1 s of floating time was assumed to be harmless because the aggregates would float in water permitting the removal with overland flow only for 1 s. Considering the 1 s floating as the critical point, the hydrophobicity level and the wetting rate, which provide maximum %WSA, was found to be around 100° and 5 s, respectively, for the tested Japanese Andisol. Although the %WSA increased with increasing contact angle and WDPT above this level, the floating times also intensely increased showing an increasing slope, while %WSA showed a decreasing slope. Furthermore, WDPT should be longer than 40 s to achieve about 90% WSA, where the floating time was 5 s. Although the floating time might be considered to be acceptable in the viewpoint that 5 s is a short time, 40 s is a high value for WDPT. This would mean lowered infiltration rates resulting high amount of overland flow upon rainfall. At

Fig. 1. The percentage of water stable aggregates and floating time of aggregates in relation to (a) contact angle and (b) water drop penetration time. Error bars indicate $\pm$ standard deviation.

Fig. 2. Effect of drying temperature on percentage of water stable aggregates of (a) unhydrophobized and (b) hydrophobized (5 g kg^{-1} stearic acid) samples for 40 d experimental period. Error bars indicate $\pm$ standard deviation.

the suggested optimum condition, the %WSA was above 80%, showing no adverse effects of water repellency because the WDPT remained at a low level (5 s). In lands with almost flat topography, either 5 s-floating time or 40 s-WDPT might not cause considerable loss to the lands as expected in sloped landscapes. However, increase in WDPT and contact angle to high levels would introduce adverse effects of water repellency on soil hydrophysical parameters such as sorptivity and hydraulic conductivity (Lichner et al., 2012, 2013).

Effect of drying temperature on %WSA of unhydrophobized and hydrophobized (5 g kg^{-1} stearic acid) samples is presented in Figure 2. Heating at 50°C for 5 h d^{-1} did not significantly affect ($p > 0.05$) the %WSA of unhydrophobized samples (Figure 2 a), although unheated samples showed slightly higher %WSA compared with heated samples. Heating significantly decreased ($p < 0.05$) the %WSA (Figure 2 b), as well as the hydrophobicity (Leelamanie and Karube, 2014), of hydrophobized samples. Accordingly, decreased %WSA was attributed to the lowered hydrophobicity of the samples.

Fig. 3. Relation of contact angle to the percentage of water stable aggregates of unhydrophobized and hydrophobized (5 g kg^{-1} stearic acid) samples under both unheated (UH) and heated (H) conditions. Error bars indicate $\pm$ standard deviation.

Figure 3 shows the relation of contact angle to the %WSA of unhydrophobized and hydrophobized (5 g kg^{-1} stearic acid) samples under both unheated and heated conditions. The %WSA of hydrophobized samples showed an increasing trend, whereas that of unhydrophobized samples showed weak decreasing trend, with increasing hydrophobicity as measured by contact angle. These contrasting relations were observed as a result of conflicting response of unhydrophobized and hydrophobized samples to 50°C for 5 h d^{-1} . Contact angle increased in unhydrophobized samples, whereas it decreased in hydrophobized samples, when exposed to heat. This was considered as a result of possible reactions of stearic acid with cations in soil during the heating to produce hydrophilic salts of stearic acid. Irrespective of the hydrophobicity, %WSA was high in unheated samples. This might be a result of differential internal moisture conditions of heated and unheated aggregates.

CONCLUSIONS

Aggregate stability is a crucial factor of soil erosion and crust formation while the disintegration of aggregates is thought to be affected by wetting rate. The results indicate that the contact angle and wetting rate (WDPT) are closely related with the water stability of aggregates. The results further confirm

that high levels of hydrophobicities induce aggregate floating, and the drying temperature has differential effects on hydrophobicity and aggregate stability depending on the hydrophobic materials present in the soil.

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