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Determining soil hydraulic properties with different wetting liquids

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Abstract

Soil hydraulic properties such as hydraulic conductivity, water retention and plant water relationships dominate the water movement processes. For example, the infiltration, evaporation and water flow within the soil. As a widespread phenomenon in soil, soil water repellency alters the soil hydraulic functions by resisting the water flow into the soils. Moreover, the hydraulic properties not only depend on the pore system of soil but also are affected by the physicochemical properties of the pore surfaces. Compared to water, ethanol is not affected by the water repellency due to its lower surface tension. The purpose of using ethanol is to eliminate the effect of soil water repellency on hydraulic properties measurements. However, applying pure ethanol into natural soil can degrade the soil organic materials and lead to changes in physical properties. Therefore, the aqueous ethanol solutions can be an alternative option. Nevertheless, the feasibility of using aqueous ethanol for determining soil liquid retention curve remains unknown. This study aims to test the feasibility of the aqueous ethanol solutions (0, 10 %, 20 %, 30 %, 40 %, 50 % and 100 % v/v) for establishing liquid retention curve under a small range of applied pressure in coarse sand samples with different wettability and organic amended natural soil (Templeton silt loam (TSL) with mushroom compost, biochar, dairy effluent, and municipal compost, the application rate was 15 % by weight). The result showed that the desorption of testing aqueous ethanol solutions compared to water was quicker by approximately 1 to 3x based on the liquid content at the same applied pressure and the time for reaching each equilibrium. The outcomes from the sand experiment suggested that when the concentration of aqueous ethanol solution was below 50 %, the losses via evaporation were less than 1% and the relative differences between testing liquid and water was lower than

10 %. However, the evaporation losses were 11.06 % and 24.6 %, and the relative differences were all around 15 % and 30 % in 50 % and 100 % ethanol solution, respectively. In contrast, the organic amendments in Templeton silt loam not only increased the water retention capability but also reduced the evaporation losses. The evaporation losses in TSL soil and TSL with organic amendments soil were with 1 % in solutions with less than 50 % ethanol content. Evaporation losses of 50 % and 100 % ethanol were 2.8 % and 2.9 %, respectively. The relative differences between water and testing liquid were similar to the sand experiment when the testing liquid concentrations were below 50 %. However, the relative differences in 50 % and 100 % ethanol solution were smaller than in the sand sample with around 10 % and 15%, respectively. Additionally, the analysis of relative difference suggested that almost all aqueous ethanol solutions had lower volumetric liquid content at the same supplied pressure compared to water, which was a reflection of the aqueous ethanol solutions desorbed faster than water under equivalent pressure. Therefore, 10 % to 40 % of ethanol solutions could be considered an alternative for determining soil hydraulic properties due to their faster desorption rate and not being affected by soil water repellency. Due to the evaporation and dissolution of organic material, aqueous ethanol solutions above 50% concentration were not suitable for coarse sand or medium-textured soil.

Keywords: Aqueous ethanol solution, soil water repellency, liquid retention curve, organic amendments, ceramic plate, intrinsic hydraulic properties, wetting liquid, wettability, coarse sand

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Chapter 1

1 Introduction

Soil hydraulic properties are the dominating factors controlling infiltration and runoff processes (Chen et al., 2012). Properties, such as infiltration rate and hydraulic conductivity, are described by the hydraulic conductivity function (Arriaga et al., 2009). These parameters are used to partition rainfall into runoff and infiltration, and help to schedule agricultural management practices (irrigation and fertiliser application) (Mohawesh et al., 2017). Moreover, soil hydraulic properties are used in simulation models to predict water flow and contaminant transport in agroecosystems (Ghavidelfar et al., 2015).

Soil hydraulic properties are the macroscopic relations between chemical potential, the phase concentration, and transmission behaviour of water and gasses in soil (Durner and Fluhler, 2005). These relations depend on multiple factors, including pore space geometry, surface properties of the soil matrix, soil temperature, chemical composition of the soil solution, and the properties of the fluid (Durner and Fluhler, 2005). Hydraulic properties are obtained from analysing sorptivity, hydraulic conductivity, and soil water retentivity functions (Russo and Bresler, 1981).

The soil water retention curve (SWRC) is the relationship between soil water matric potential and volumetric soil water content when it reaches equilibrium under applied pressure (Novak and Hiavacikova, 2018). Generally, the traditional wetting liquid for determining the soil water retention curve is water. However, when using water to determine the soil water retention curve in natural soils, some issues can be encountered, such as swelling, shrinking and hysteresis. Soils containing clay mineral and organic compounds could be shrinking and

swelling when the soil water content changes; the changes in soil water content lead to soil volume change (Novak and Hlavacikova, 2019). The shrinking and swelling process will affect the soil physical and hydrophysical properties such as density, porosity, hydraulic conductivity, and soil water retention (Novak and Hlavacikova, 2019). In terms of hysteresis, the definition of hysteresis is that equilibrium soil water content at any particular suction is less under wetting conditions than drying conditions (McLaren and Cameron, 1996). This phenomenon occurs when determining the soil liquid retention curve by water (McLaren and Cameron, 1996).

On the other hand, soil texture and organic material could also affect the soil water retention capability. For example, sandy soil has larger pores and higher saturated conductivity than finer-textured soil such as clay soil (Hultine et al., 2006). At lower water potential, sandy soil retains less water than finer-textured soil (Hultine et al., 2006). Besides, soil pore size also influences evaporation. For example, sandy soil contains a higher proportion of large soil pores, allowing water to drain fast ((McLaren and Cameron, 1996). Large pores, especially macropores (>0.08 mm), promote free drainage of water, aeration, evaporation and gas change within soil profile (Easton and Book., 2016). Furthermore, organic material could improve soil water retention capability. Especially adding organic amendments to the soil enhances soil quality, such as enhancing infiltration, water retention, aggregation, and aeration (Sojka et al., 2007). However, many authors concluded that organic compounds could contribute to the development of soil water repellency (Wijewardana et al., 2016, Doerr et al., 2000, Regalado et al., 2008, Leelamanie and Karube., 2007).

Soil water repellency is also a primary factor that could affect the measurement of the soil water retention curve. Hydrophobic soil cannot be fully wetted, and the water retention curve

is highly influenced by the degree/persistence of soil water repellency (Diamantopoulos et al., 2013). To overcome this problem, ethanol is considered as another wetting liquid for determining SWRC in repellent soil due to its physicochemical properties. Ethanol is a completely wetting liquid due to its lower surface tension (Watson and Letey., 1970; Lamparter et al., 2000).

1.1 Ethanol

Lamparter et al. (2010) tested that the applicability of using ethanol for determining hydraulic properties in mixed artificial hydrophobic and hydrophilic sand. This experiment successfully proved that ethanol could be used to measure the intrinsic hydraulic properties (not influenced by soil surface properties) without the influence of water repellency on porous media under controlled conditions (temperature and initial water content) (Lamparter et al., 2010).

In the case of the capillary pressure-saturation function, under the same supply pressure, an increase in soil water repellency resulted in a decrease in the water content, but the ethanol content remained the same (Lamparter et al., 2010). Their result indicated that ethanol was not affected by the soil water repellency (Lamparter et al., 2010). Figure 1. shows the capillary pressure-saturation function measured with water and ethanol in repellent soils with different contact angles.

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Figure 1. Capillary pressure-saturation function measured with water and ethanol in repellent soil with different contact angles (Lamparter et al., (2010)).

The saturated hydraulic conductivity and unsaturated hydraulic conductivity were also measured by Lamparter et al. (2010). The intrinsic saturated hydraulic conductivity (took ethanol's viscosity and density into account) of ethanol was equal to the saturated hydraulic

conductivity with water (Lamparter et al., 2010). There were no significant differences between saturated hydraulic conductivity and repellent sand samples, which identified that ethanol is unaffected by the soil water repellency (Lamparter et al., 2010). Remarkably, when compared to the actual hydraulic conductivity (measured by the constant head method), the intrinsic hydraulic conductivity determined by ethanol did not change with an increase of soil water repellency (Lamparter et al., 2010). Figure 2. shows the saturated hydraulic conductivity (water and ethanol) in the sand with different contact angles. The contact angle for wettable soil is less than 90° but over 90° in repellent soil (Beatty et al., 2014)

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Figure 2. Saturated hydraulic conductivity (water and ethanol) in the sand with different level of contact angle. Retrieved from Lamparter et al. (2010). The % showed in each column was the percentage reduction of hydraulic conductivity caused by hydrophobicity when the testing liquid was water.

The infiltration rate of ethanol was always the same regardless of the contact angle (Lamparter et al., 2010). When the physicochemical liquid properties (viscosity and density) were taken into account, there was no significant difference between water and ethanol (Lamparter et al., 2010). Figure 3 shows the flux of ethanol and water at different supply potential, and the water flux decreased with an increase in the degree of water repellency. However, ethanol flux was not affected by the degree of water repellency (Lamparter et al., 2010). Figure 4 shows the hydraulic conductivity in the wettable material of water and ethanol under different supply pressures. When liquid physicochemical properties such as viscosity were not taken into account, the hydraulic conductivity of ethanol showed significant differences to water (Figure 4A). However, when the liquid physicochemical properties were

considered, there were no significant differences ($p < 0.05$) between water and ethanol in hydrophobic porous media (Lamparter et al., 2010).

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Figure 3. The flux of ethanol and water at different supply potential. Retrieved from Lamparter et al. (2010).

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Figure 4. Hydraulic conductivity in wettable material of water and ethanol under the supply pressure, A is the hydraulic conductivity of ethanol and water in hydrophilic sand, B is the intrinsic hydraulic conductivity in comparison to the hydraulic conductivity measured with water. Retrieved from Lamparter et al. (2010).

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Figure 5. A linear relationship between the contact angle and the air entry value. Retrieved from Lamparter et al. (2010)

Figure 5. shows the relationship between the air entry value of sand and glass beads of different wettability (contact angle). This relationship indicated that contact angle could be used in the prediction of the decrease in hydraulic conductivity on well-defined substrates in the laboratory because of the wettability and its impact acted on the same spatial scale (Lamparter et al., 2010). However, there is still a challenge in using the contact angle to predict the changes in hydraulic properties in the natural soil system due to the uneven distribution of hydrophobic materials.

Besides, Sciortino et al. (2010) has conducted a model experiment to investigate the impact of ethanol flow in the vadose zone. The relationship between solution viscosity and hydraulic conductivity was studied. Figure 6 shows the relationship between hydraulic conductivity and the concentration of the ethanol solution.

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Figure 6. Relationship between hydraulic conductivity and the viscosity of aqueous ethanol solution. Retrieved from Sciortino et al. (2010).

The ν_0/ν was the hydraulic conductivity scaling factor, where ν_0 is the viscosity of water ν is the viscosity of aqueous ethanol solutions (Sciortino et al., 2010). When the ethanol concentration reached 45 % ethanol (weight basis), the hydraulic conductivity dropped to its minimum value. When the concentration of ethanol was above 45 %, the Ks increased gradually until the concentration reached 100 % (Sciortino et al., 2010). Sciortino et al. (2010) pointed out that with the increase in ethanol concentration, the viscosity of ethanol solution increased and reached the maximum viscosity around 45 %; when the ethanol content was above 45 %, the viscosity of ethanol solution decreased until the ethanol concentration reached 100 %. Furthermore, the model also calculated and fitted the relationship between surface tension, viscosity, and the liquid retention curve. As Figure 7 shows below, the retention scaling factor σ/σ_0 decreased for increasing the concentration of ethanol solution, which indicated the reduction in surface tension (Sciortino et al., 2010), where σ_0 is the surface tension of water and σ is the surface tension of ethanol (Sciortino et al., 2010).

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Figure 7. Relationship between surface tension and viscosity (depends on the concentration of aqueous ethanol solution) and the retention curve. Retrieved from Sciortino et al. (2010).

Based on Lamparter et al. (2010) and Diamantopoulos et al. (2013) who have also studied the soil hydraulic properties in repellent soil with similar methodology. The soil samples used in these experiments were natural sand (M1) treated with dichloro-dimethyl-silane to produce the hydrophobic sand. 7.5 % (M2) and 15 % (M3) hydrophobic sand were added into natural sand to create a different degree of soil water repellency (Diamantopoulos et al., 2013). Besides,

another hydrophilic sand sample (M4, fine sand with 0.1-0.3 mm particle size) was made to compare with hydrophobic sand samples (Diamantopoulos et al., 2013). According to their results, the water could not absorb into dry soil material under negative pressure in M2 and M3. In contrast, the ethanol was absorbed into M2 and M3 without an issue (Diamantopoulos et al., 2013). Moreover, they have not observed any difference in the imbibition of ethanol into samples with increasing hydrophobic levels (Diamantopoulos et al., 2013).

1.2 Aqueous ethanol solutions

Beatty and Smith (2014) conducted an infiltration experiment using water and three aqueous ethanol solutions (5 %, 25 % and 50 %) and pure ethanol in wettable, non-wettable and mixed porous media. The results of their experiment generated a meaningful representation of the difference in fractional wettability, which is defined as the uneven distribution of hydrophobic material (Beatty and Smith, 2014). When they considered cumulative infiltration with time and porous media, the differences attributed to fractional wettability and contact angle dynamics were observed (Beatty and Smith., 2014). Overall, in the repellent material, ethanol presented the highest infiltration rate, and water took the longest infiltration time (Beatty and Smith., 2014).

According to their observation, pure ethanol in wettable media (char, sourced from burnt vegetation and accumulated 0.5-12 cm thick soil layer in topsoil) had the lowest infiltration rate, which was only 1/5 of the water. They assumed that the infiltration and dispersion of pure ethanol would form a zone with lower mobility than either antecedent water or ethanol solution and further caused this observation. The 50 % aqueous ethanol solution was only half as fast as water infiltrating. The explanation of this finding was the increase in ethanol concentration

(increase in viscosity of the liquid) resulted in a decrease in fluid mobility (Beatty and Smith., 2014). Due to the increase in the viscosity, the cumulative infiltration slowed down in the wettable soil (Beatty and Smith., 2014). Figure 8 and figure 9 showed the result of cumulative infiltration versus times for wettable media at the early time and late time.

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Figure 8. Cumulative infiltration versus times for wettable media char at the early time. WAT, AES and ETH denoted the replicates of water, aqueous ethanol solution (5 % in v/v), and ethanol. Retrieved from Beatty and Smith (2014).

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Figure 9. Cumulative infiltration versus times for wettable media char at the late time. WAT, AES and ETH denoted the replications of water, aqueous ethanol solution (5 % in v/v), and ethanol. Retrieved from Beatty and Smith (2014).

The water presented the lowest infiltration rate with 10^{-3} to 10^{-4} cm s⁻¹ in the non-wettable media (brown soil, scorched by wildfire), while for ethanol, it was approximately 2x higher. The 50 % aqueous ethanol solution showed a similar rate with ethanol at the early time but two times faster than water at steady-state conditions (Beatty and Smith., 2014). This result in the repellent soil could be associated with ethanol concentration and contact angle. The surface tension of 50 % ethanol solution was lower than the surface tension of the repellent surface and behaved as pure ethanol to eliminate soil water repellency on infiltration. (Beatty and Smith., 2014). Figures 10 and 11 show the cumulative infiltration versus times for non-wettable (Brown) materials at early time and at steady state.

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Figure 10. Cumulative infiltration versus times for non-wettable (brown) material at the early time. WAT, AES and ETH denoted the replications of water, aqueous ethanol solution (50 % in v/v), and ethanol. Retrieved from Beatty and Smith (2014).

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Figure 11. Cumulative infiltration versus times for non-wettable (brown) material at the late time. WAT, AES and ETH denoted the replications of water, aqueous ethanol solution (50 % in v/v), and ethanol. Retrieved from Beatty and Smith (2014).

Beatty and Smith (2014) also tested the infiltration rate of testing liquids in mixed porous media. In the early-infiltration phase, the infiltration behaviours of pure ethanol, aqueous ethanol solution and water showed separation (Beatty and Smith., 2014). In the early time, the infiltration rate of 50 % aqueous ethanol solution was approximately twice compared to water but slightly faster than water at a steady state (Beatty and Smith., 2014). Figure 12 shows the cumulative infiltration versus time for mixed material at the early time.

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Figure 12. Cumulative infiltration versus times for mixed material (scoring soil and fibrous organic matter) at the early time. WAT, AES and ETH denoted the replications of water, aqueous ethanol solution (50 % in v/v), and ethanol. Retrieved from Beatty and Smith. (2014).

1.3 Organic amendments on soil hydraulic properties

Apart from testing liquid, the effects of the organic amendments on soil hydraulic properties should also be studied. Ouyang et al. (2013) found that the application of biochar increased the saturated water content and decreased the residual water contents (water content when the hydraulic gradient become 0) in sandy loam soil and silty clay soil (Ouyang et al., 2013).

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Figure 13. Effect of biochar application on soil water retention curve of four treatments. The SC is the silty clay soil, SCB is the silty clay soil with biochar, SL is the sandy loam soil, and SLB is sandy loam soil with biochar. Retrieved from Ouyang et al. (2013)

Figure 13 shows the effect of biochar application on the soil water retention curve of sandy loam and silty clay soil. The biochar application increased water content in the lower suction

range but decreased residual water content at the higher suction range (Ouyang et al., 2013). The biochar increased the average saturated water content of sandy loam soil and silty clay soil by 7.4 % and 2.2 %, respectively (Ouyang et al., 2013). However, the average residual water content of sandy loam soil and silty clay soil decreased by 19 % and 15%, respectively (Ouyang et al., 2013). The explanation was that biochar promoted soil aggregate formation and decreased soil initial bulk density increasing the total porosity (Ouyang et al., 2013). Biochar application improved soil structure by increasing the number of macroaggregates and decreasing the number of microaggregates (Ouyang et al., 2013). The reduction in microaggregates leads to available water content increases in the sandy loam soil (10.6 %) and silty clay soil (5.2 %).

Additionally, Taban and Naeini. (2007) found that organic compost incorporation in loamy and loam sandy soil increased the water content in soil (Taban and Naeini, 2007). Figure 14 shows the soil moisture content of both soils and both soils incorporated with organic amendments. Compared to control groups, the average water content in a loam soil with organic compost and loamy sandy soil with compost increased by approximately 12 % and 11 %, respectively. Additionally, Shiralipour et al. (1992) pointed out that compost application could improve the number of storage pores (0.5-50 μm) and thus improving water holding capacity

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Figure 14. The soil moisture content of loam, loamy sandy soil, and the soil moisture content of both soil incorporated with organic compost. L is the loam soil, and LS is the loamy sand soil. Retrieved from Taban and Naeini (2007).

Besides, Taban and Naeini (2007) also pointed out that the application of organic compost could block soil pores and reduce evaporation. A similar conclusion was also found by Wang et al. (2018). The latter suggested that biochar application reduced evaporation losses, and the

ratio of evaporation losses decreased when the application rate increased, as shown in Figure 15. Moreover, they also suggested that a higher biochar application rate could enhance the inhibition of soil evaporation (Wang et al., 2018). Biochar particle size also affected the ratio of evaporation losses. For example, when the application rate was at 10 and 50 g kg⁻¹, the smallest biochar particles of less than 0.25 mm reduced the ratio of evaporation losses by 55.4 %. Compared to the smallest particles, this reduction in the largest biochar particles (1-2 mm) was only 37.8 % (Wang et al., 2018).

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Figure 15. The relationship between the biochar application rate and the ratio of evaporation losses. The S series is the soil type: S1 is the Eum-Orthic Anthrosols, S2 Isohumisols, S3 is Loessal soil, S4 is sandy loessal soil, S5 is the Aeolian sandy soil. Retrieved from Wang et al. (2018)

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Figure 16. The relationship between the biochar application rate and the ratio of evaporation losses. The symbols are the biochar size (2-1 mm, 1-0.25 mm, and <0.25 mm). Retrieved from Wang et al. (2018).

Due to high moisture absorption capacity, biochar could increase soil water holding capacity significantly (Wang et al., 2018). Moreover, biochar application changed soil structure by increasing the number of micropores that had low water conductivity. As a result, the hydraulic conductivity decreased and reduced water being transported to the soil surface (Wang et al., 2018).

1.4 Research gaps

The traditional wetting liquid for establishing soil water retention curves is water. Compared to water, ethanol is not affected by soil water repellency (Lamparter et al., 2010). Moreover, Watson and Letey (1970) have suggested that ethanol can be considered as a

thoroughly wetting liquid regardless of the soil repellency level due to its low surface tension. Tillman et al. (1989) have successfully proven the feasibility for measuring the intrinsic sorptivity of soil by using ethanol. The definition of intrinsic sorptivity is that the soil sorptivity only depends on the pore geometry of the porous system, not the surface property. Besides, Tillman et al. (1989) introduced the repellency index to characterise the wettability of porous media by relating the sorptivity of ethanol to the sorptivity of water. Compared to water, ethanol has several advantages for determining hydraulic properties. Due to the lower surface tension of ethanol (22.4 mN m^{-1}), less applied pressure was required to empty the ethanol content in the porous system, thus under the same applied pressure, the ethanol will release faster than water (Lamparter et al., 2010).

Another important factor for considering ethanol as the alternative wetting liquid is related to the contact angle. Letey et al. (1962) suggested that the ethanol-soil contact angle equalled 0, which simplified the capillary rise equation from the uncertainty of the $\cos \theta$ (contact angle) of water. As described above, the applicability of ethanol for determining soil hydraulic properties was tested by Lamparter et al. (2010). Lamparter et al. (2010) pointed out that the ethanol could dissolve organic matter and thus change the porous system. Therefore, the effect of ethanol on soil organic material should also be studied. Besides, organic amendments could increase water retention capability and reduce evaporation losses of water. However, the effects of organic amendments on ethanol retention capability and the possibility of minimising ethanol evaporation losses remain unknown in laboratory conditions.

In terms of aqueous ethanol solutions, Beatty and Smith (2014) proved that the aqueous ethanol solution produced a quicker response in hydrophobic soils. The fluid mobility did not

impact the infiltration rate in repellent soils but show the effects on wettable soil. However, using different concentrations of aqueous ethanol solutions could produce more understanding of the key difference between non-wettable and wettable fractions within fractionally wettable soil material (Beatty and Smith, 2014).

However, several issues should be considered when using ethanol as the wetting liquid. Ethanol solutions are sensitive to temperature and volatile (Beatty and Smith., 2014; Roy and McGill, 2002). Evaporation of ethanol-water mixture highly depends on the concentration of the solution: higher ethanol concentration results in higher evaporation losses (O'Hare et al., 2008). Therefore, when using ethanol solution with higher concentrations, the evaporation losses should be taken into account. Besides, Lamparter et al. (2010) suggested that the ethanol could dissolve organic matters and change the soil pore structure.

To date, no studies have proven that the aqueous ethanol solutions could be used to determine the hydraulic properties such as soil liquid retention curve, and its applicability remained unknown. So the question of whether aqueous ethanol solutions can be used to determine the soil liquid retention curve and how it is close to the water in the porous system with different textures, wettability, and organic amendments, has not been answered.

1.5 Hypotheses and objectives

According to the literature findings, ethanol and aqueous ethanol solution can be used to determine the hydraulic properties in repellent soil. However, the feasibility of determining the soil liquid retention curve with ethanol and different concentration of aqueous ethanol solutions on soils with different textures, wettability and organic amendments has not been tested. The hypotheses of this study are: (1) aqueous ethanol solutions would require less time than water

for measuring soil hydraulic properties in soils with different texture, wettability, and organic amendments; (2) aqueous ethanol solutions could produce an accurate result with $\pm 10\%$ relative difference between testing liquids and water; (3) finer-textured soil could retain more water than coarse-textured soil, and it also applied to aqueous ethanol solutions (4) organic amendments have influences on the ethanol retention capability and reduce the losses of ethanol solution through evaporation.

The first objective of this study is to test the feasibility of using aqueous ethanol solutions for determining the liquid retention curve on a homogeneous porous system with different textures and wettability. To achieve this goal, the concept of intrinsic hydraulic properties is used to measure the soil hydraulic properties, which are only dependent on the soil pore system and not the soil surface property interacting with water (Lamparter et al., 2010).

The second objective of this study is to test the applicability of using aqueous ethanol solutions for determining liquid retention curves on natural soil with different organic amendments (Templeton silt loam with 4 types of organic amendments). The third objective is to identify the issues and limitations related to the concentrations of aqueous ethanol solutions.

Chapter 2

The feasibility of using aqueous ethanol solutions to determine soil hydraulic properties on a homogeneous porous system with different wettability

2.1 Introduction

The hydraulic properties of soil govern the water movement within the soil profile (Caplan et al., 2017) and are essential in irrigation and drainage studies for agricultural practices (Rousseva et al., 2017). The hydraulic properties such as soil water retention capability are closely related to the soil texture and structure (Ouyang et al., 2013) and influenced by the soil water repellency (Lamparter et al., 2010).

Soil texture (or particle size distribution of the soil) controls soil hydraulic characteristics such as saturated hydraulic conductivity, plant available water content, and soil water storage (Hultine et al., 2006). For example, coarse texture soils contain larger pores and higher saturated conductivity than finer textured soils (Hultine et al., 2006). However, coarse-textured soil loses more liquid at lower water potential and has lower conductivity than finer-textured soil (Hultine et al., 2006). The water retention of soil is strongly affected by soil texture and structure and other factors such as organic matter (Tuller et al., 2004). For example, clay soils always have a higher water content than sandy soil in unsaturated conditions (McLaren and Cameron, 1996). This difference is that clay contains finer texture with smaller pores than sandy soil and thus more water held at the same potential (McLaren and Cameron, 1996). Besides, soil pore size

also influences evaporation. For example, sandy soil contains a higher proportion of large soil pores, allowing for faster water release ((McLaren and Cameron, 1996).

On the other hand, soil water repellency (SWR) is a primary factor that affects soil hydraulic properties, such as infiltration and water retention in the soil (Filipovic et al., 2019). The phenomenon of soil water repellency has been found widely in most soil (Lamparter et al., 2010). Moreover, compared to wettable soil, the water content at equivalent pressure is different in repellent soil (Lamparter et al., 2010). In addition, the degree of soil water repellency changes with the water content and the contact time with water (Lamparter et al., 2010). Therefore, the measurement of soil hydraulic properties encounters difficulties and could lead to erroneous results when using water as the wetting liquid in repellent soil (Lamparter et al., 2010). Furthermore, the hysteresis problem would also occur during the soil liquid retention curve measurement when using water as a wetting liquid (McLaren and Cameron, 1996). The definition of hysteresis is that equilibrium soil water content at any particular suction is less under wetting conditions than drying conditions (McLaren and Cameron, 1996).

Watson and Letey (1970) suggested that ethanol can be considered as a completely wetting liquid regardless of the degree of water repellency in soil. It has been used to measure the intrinsic sorptivity of soil (Tillman et al., 1989). Lamparter et al. (2010) successfully tested the applicability of ethanol for measuring intrinsic hydraulic properties of artificially hydrophobised sands. The difference between hydraulic properties and intrinsic hydraulic properties is that the latter depends on the porous system instead of its surface properties (Lamparter et al., 2010). Using ethanol provides the possibility of measuring hydraulic properties such as liquid retention curve and eliminate the effect of soil water repellency.

However, when using ethanol as the wetting liquid, several issues should be taken into consideration. Firstly, ethanol solutions are sensitive to temperature (Beatty and Smith, 2014) and volatilise (Roy and McGill, 2002). O'Hare et al. (2008) pointed out that the evaporation rate of ethanol and ethanol-water mixture is highly dependent on the concentration of the solution, and the evaporation rate would decrease when ethanol concentration decreased. Therefore, when using ethanol solution with higher concentrations, the evaporation losses should be taken into account. Secondly, when applying ethanol to the natural soil, the ethanol could dissolve organic matter and change the soil pore structure (Lamparter et al., 2010).

The feasibility of using aqueous ethanol solution to determine the liquid retention curve has not been well addressed. To address this question, the quartz sand can be considered as the homogenous porous system standard similar to the one used by Lamparter et al. (2010).

The major objective of this study is to test the feasibility of using aqueous ethanol to determine the liquid retention curve in the coarse sand fine sand sample. The second objective is to test the applicability of aqueous ethanol for measuring the liquid retention curve in quartz sand with different wettability.

The hypotheses of this study are: (1) the aqueous ethanol solution would drain quicker than water and could be used to determine the soil liquid retention curve in the homogeneous sand. (2) the aqueous ethanol solutions could not be affected by soil water repellency effect on the soil surface.

2.2 Material and methods

2.2.1 Sample description

The first experiment was designed to test aqueous ethanol solution performance in coarse sand samples. The sand samples passed through a 1.4 mm sieve, then packed into three different groups according to the particle size with fine sand and coarse sand sample. Each group contained five replicates. The cores of all samples were built using rings sized 4.7 cm diameter and 1.5 cm height, rubber bands and nylon mesh. Table 1 shows the packed information of each group.

Table 1. The packing information of the sand sample.

Sample	Labelling	Volume (cm ³)	Weight (g)	Bulk Density (g cm ⁻³)
Fine sand	F1	25.85	38.2	1.47
	F2	25.85	38.1	1.47
	F3	25.85	38.3	1.47
	F4	25.85	38.1	1.47
	F5	25.85	38.11	1.47
Coarse sand	CS1	26.024	37.5	1.47
	CS2	26.024	36.24	1.47
	CS3	26.024	36.7	1.47
	CS4	26.024	37.6	1.47
	CS5	26.024	37.1	1.47
Slightly repellent (WDPT 65S)	SL1	26.024	38.30	1.47
	SL2	26.024	38.30	1.47
	SL3	26.024	38.30	1.47
Strongly repellent (WDPT 168S)	SM1	26.024	38.22	1.47
	SM2	26.024	38.22	1.47
	SM3	26.024	38.22	1.47

To alter the wettability of the coarse sand potassium methyl silicate ($\text{CH}_3\text{K}_3\text{O}_3\text{Si}$) was added to create a strong and persistent degree of hydrophobicity. The hydrophobic sand was mixed with pure coarse sand (not passed 1.4 mm sieve) to create two groups of the sand sample

with different severity levels. The degree of hydrophobic samples was measured by Water Drop Penetration Time method (WDPT). The labelling of those two types of the sample was sand with slight hydrophobicity (SL) and sand with strong hydrophobicity (SM). Table 1 also shows information about the artificial hydrophobic sand samples.

2.2.2 The physical properties of aqueous ethanol solutions and capillary rise equation

When using ethanol as a replacement for water, it is necessary to consider the density and surface tension of ethanol solution; table 2 shows the information of ethanol solution in different concentrations.

Table 2. The density, viscosity, and surface tension of ethanol in different concentrations. Retrieved from Beatty and Smith (2014)

Image removed for copyright compliance

With the increase of ethanol concentration in the solution, the surface tension will decrease. Thus, equivalent pressure, the ethanol content in the soil will be lower in higher concentration treatment, which means less suction or pressure will be required to empty smaller pores in higher ethanol concentration treatment group under the same pressure level.

Therefore, to calculate the certain pore radius under the equivalent pressure, the capillary rise equation is given as (1)

$$\psi = \frac{2 \sigma \cos\alpha}{r \rho g} \quad (1)$$

Where ψ is the pressure, σ is the surface tension (mN m^{-1}), α is the contact angle ($^\circ$) assuming to be 0 for ethanol, r (m) is the pore radius draining to empty at a certain pressure, g is the gravity (m s^{-2}), ρ is the liquid density (g cm^{-3}). Using the information provided in table 2,

the r (pore radius that can be emptied at different supplied pressure) value can be obtained, as shown in table 3. Based on the capillary rise equation, the certain pore radius that can be emptied at different pressure is calculated. Due to its physical properties, the aqueous ethanol solutions can be drained through smaller pores at the same pressure (equivalent pressure). Therefore, it is necessary to form the graph into pore size- liquid content frame. Besides, it also provides a better understanding of the pore size distribution of soil samples.

2.2.3 Set up apparatus

In testing the liquid retention curve, two methods are mainly used to determine the water retention curve, namely is the pressure plate and tension table. The basic principle of the pressure plate is using different pressure to empty the liquid in a certain pore radius. The basic theory of the tension table is to determine water retention characteristics from saturation to a minimum matric potential of about -5.0 m. Saturated soil samples are placed on a porous barrier subjected to suctions. The porous barrier has one or more layers which are made by fine materials such as fine sand or gypsum. When the equilibrium is reached, the volumetric water content θ_v and the related matric head, h_m (m), are determined. These two variables represent the soil water retention curve (Romano et al., 2002).

However, the hysteresis should be taken into consideration, and this phenomenon occurs when the soil is undergoing continuous wetting and drying. The hysteresis will influence the accuracy because the moisture content at the desorption condition is higher than the sorption condition at the same suction (McLaren and Cameron, 1996). Moreover, Cresswell et al. (2008) also reported two significant causes for pressure plate error, including the sample shrinkage on desaturation of the sample and soil dispersion blocking pores in the porous plate. Those two

problems resulted in the loss of hydraulic contact (Cresswell et al., 2008). Furthermore, the gypsum bed sometimes cracked when applying ethanol solution to the tension table (B. Mohamed, personal communication, January 2020). Thus, the final decision is to combine the porous ceramic plate with the tension table method. Another reason for this combination is to test the applicability of aqueous ethanol solutions for measuring liquid retention curves under a lower suction or pressure condition.

The 1 bar ceramic pressure plate was placed on the container and connected to the suction bottle with a plastic tube. The bottom container was covered by another container and sealed to mitigate the evaporation losses during the experiment period. Moreover, one cup of the testing solution was placed inside the container to maintain the humidity within the chamber. For example, when using 10 % aqueous ethanol solution to saturate samples, a cup of 10 % aqueous will be placed in the chamber. A test sand sample was packed and saturated with other samples. After the saturation phase, this sample was taken out and placed beside the pressure plate to test the evaporation losses. The weight of the evaporation sample was measured every 24 hours.

During the experimental period, the evaporation losses in the lower concentrations solutions were less than 1 % of the total liquid weight every 24 hours. The losses were around 11.06 % in 50 % concentration and 24.6 % in 100 % concentration. Figure 17 below shows the apparatus set-up.

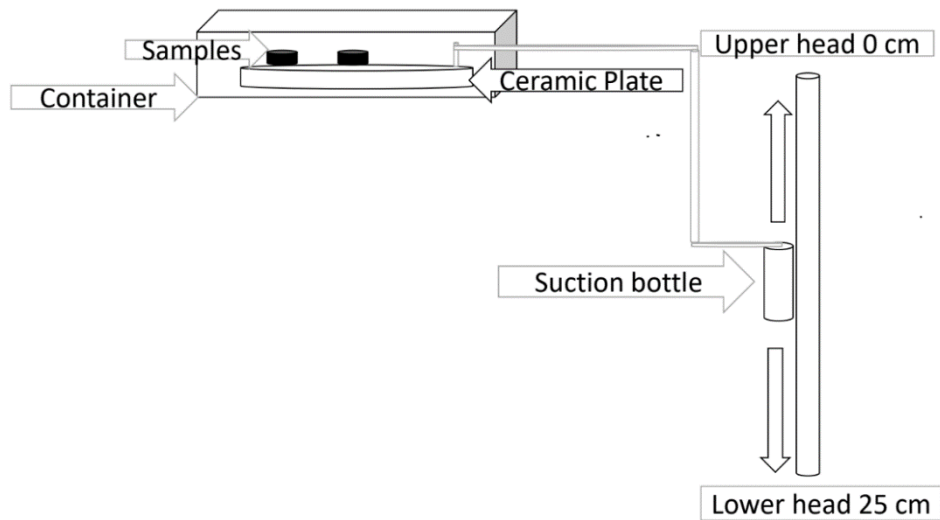


Figure 17. The diagram of the apparatus set up

2.2.4 Ethanol and water retention curve

The suction range for this experiment ranged from 0.001 bar to 0.025 bar, which equals 10 cm to 25 cm. The concentrations of aqueous ethanol solution used were 10 %, 20 %, 30 %, 40 % and 50 % volume basis. The DI water and pure ethanol (100 % in volume) were used as comparison liquids.

Samples were saturated with liquid for 48 hours in the container. The suction bottle moved to the first level to allow the suction applied. After reaching each equilibrium, recorded the sample weight and moved the suction bottle to the next level.

The adjustment of suction applied was using the capillary rise equation (1). Table 3 shows the conversion of the suction into pressure, and the pore size (diameter, millimetre) can be emptied under certain pressure (refer to equation 1).

Table 3. The pore size (mm) can be emptied under different suction levels and different fluid properties.

Suction in cm	Pressure (bar)	Ethanol 0 %	Ethanol 10 %	Ethanol 20 %	Ethanol 30 %	Ethanol 40 %	Ethanol 50 %	Ethanol 100 %
10	0.0096	0.15	0.1	0.079	0.067	0.063	0.0599	0.059

15	0.0144	0.1	0.07	0.052	0.044	0.042	0.04	0.039
20	0.0192	0.07	0.05	0.039	0.033	0.0316	0.03	0.029
25	0.024	0.06	0.04	0.031	0.0267	0.0252	0.024	0.023

2.2.5 Statistical analysis and desorption rate of liquid release

Statistical analyses were conducted using analysis of variance to determine significant differences ($p < 0.05$) in selected parameters measured. Besides, the relative differences of volumetric liquid content between water and aqueous ethanol solution were also compared to analyse the percentage change of volumetric liquid content at the same supplied pressure. Additionally, the quantities of liquid retained at different supplied suction, the relative differences between water and aqueous ethanol solution and the time for reaching each equilibrium can be seen as the reflection of liquid desorption rate.

2.3 Result

The overall trend of the wettable fine and coarse sand groups was similar, and there was no significant difference between lower concentrations which were below 50 % of ethanol solutions ($P > 0.05$).

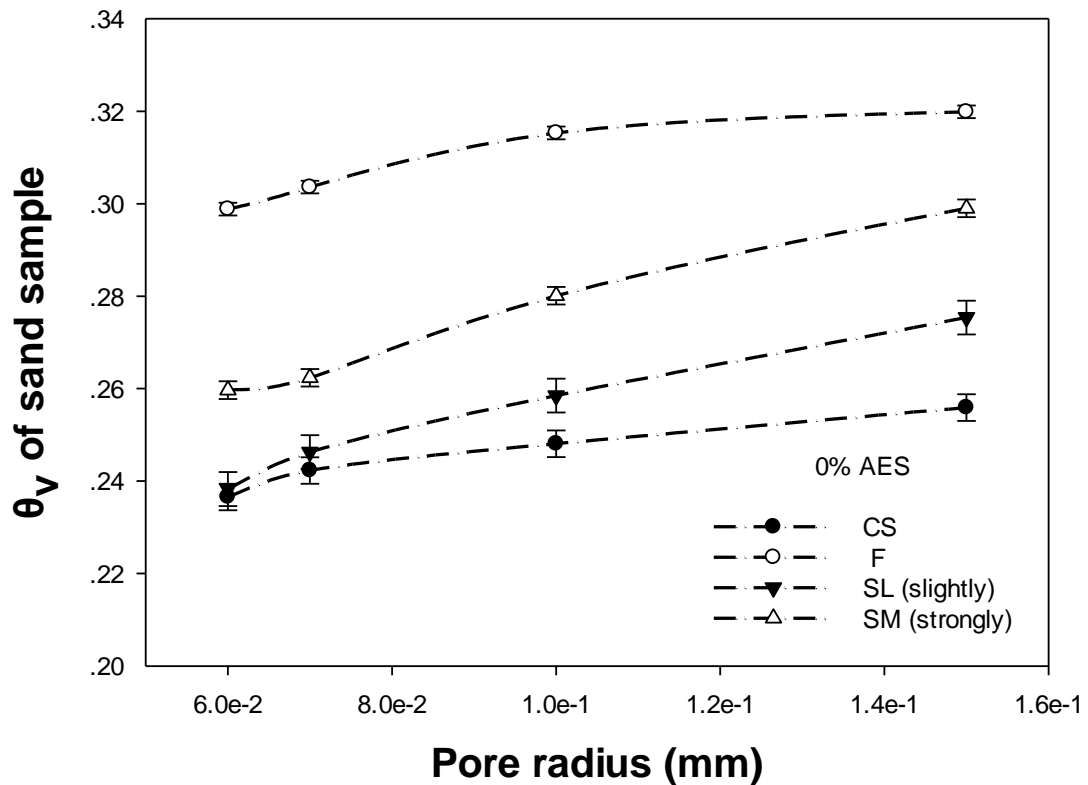


Figure 18. The water retention curve of sand samples with different textures and wettability. Where CS is coarse sand, F is fine sand, SL is a strongly repellent sample. The error bars are obtained from standard error (n=3).

Figure 18 showed the water retention curve of all sand samples with different textures and wettability. Volumetric water content (θ_v) in fine (F) sand samples was the highest. Followed by strongly repellent sample, slightly repellent sample and coarse sand sample retained less water content at sample supplied pressure (Fig 18). The higher volumetric water content in repellent samples SL and SM indicated that soil water repellency influenced soil water movement either in evaporation or water release.

Figures 19 and 20 showed the aqueous ethanol retention curve in all sand samples compared to water; a similar pattern was applied to the 10 % aqueous ethanol solution retention curve. However, the aqueous ethanol retention curves of repellent samples (SL and SM) were separated from similar textured sample CS indicating the 10% ethanol did not eliminate the soil

water repellency effect. When the concentration of testing liquid increased to 20%, the liquid retention curve of the slightly repellent sample merged with the coarse sand sample (CS), indicating the 20% ethanol solution eliminates soil water repellency in the slightly repellent sample. Moreover, similar results were also found in 30% aqueous ethanol solution.

There were no significant differences in testing liquid concentration ranging from 0 to 50 % ($p > 0.05$) but with a substantial difference in 100 % ethanol solution ($p < 0.05$). For testing liquids with concentrations less than 50 %, the retention curves had minor differences and a p-value of 0.187 (SM) and 0.132 (SL). There were no significant differences between the lower concentration of aqueous ethanol solutions.

In the case of ethanol content at similar supplied pressure, fine sand samples (Figure 19 and 20) had smaller pore sizes, more liquid retained in the fine sand sample compared to all coarse-textured samples. However, aqueous ethanol solutions with 50 % and 100 % concentration showed significant differences compared to other concentrations ($p < 0.05$). Moreover, there was also a significant difference between 100 % and 50 % concentration ($p = 0.012$).

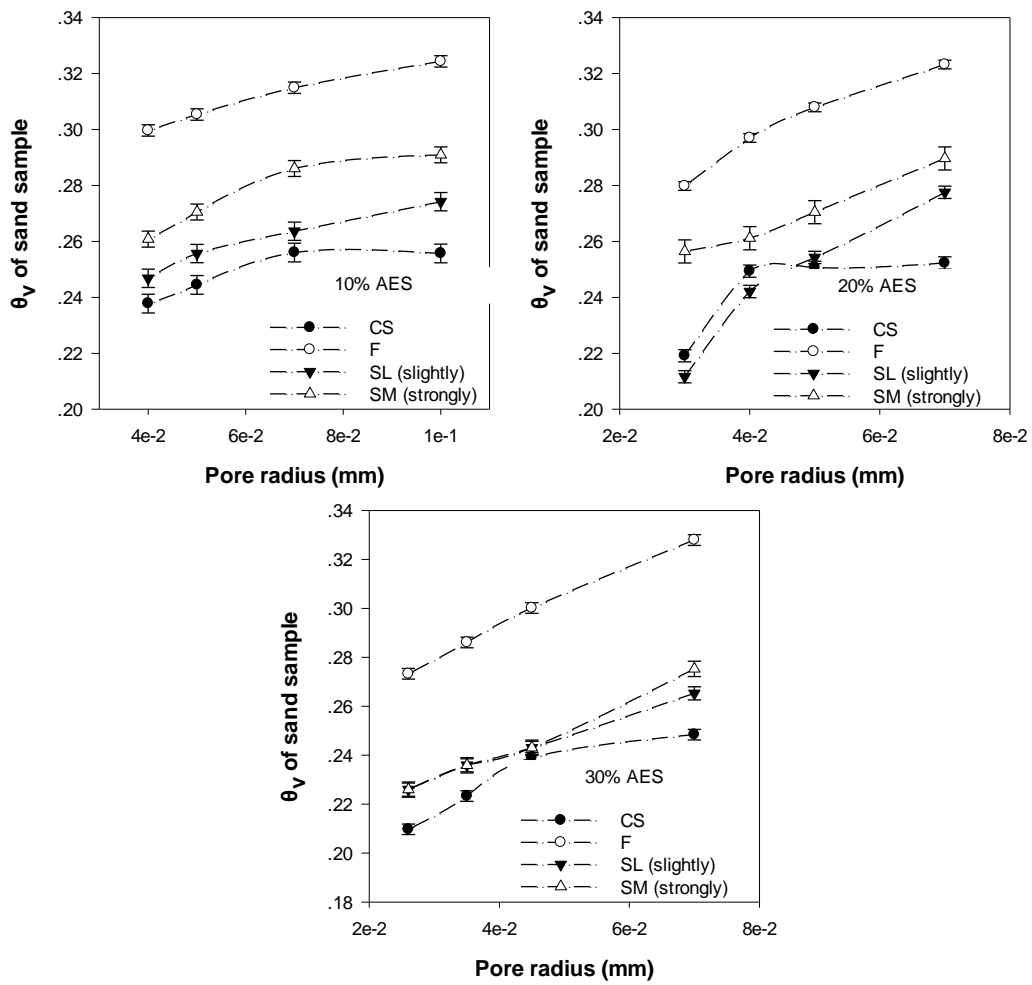


Figure 19. Aqueous ethanol (10% to 30% concentration, v/v) retention curves of the sand sample with different textures and wettability. The error bars are obtained from standard error (n=3).

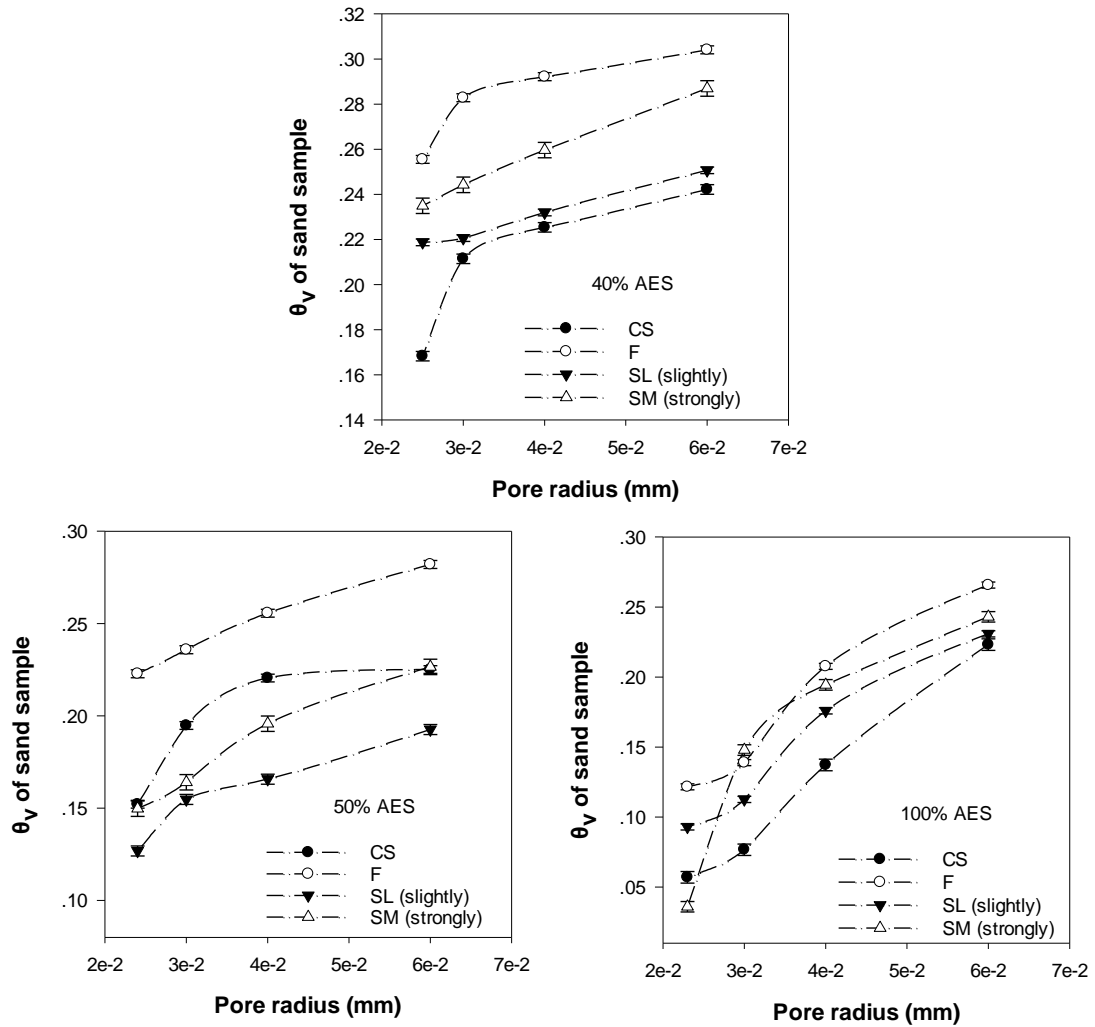


Figure 20. Aqueous ethanol (40%, 50% and 100% concentration, v/v) retention curves of the sand sample with different texture and wettability. The error bars are obtained from standard error ($n=3$).

Table 4. The relative difference of volumetric liquid content between water and each concentration of testing liquid in sand samples

Relative difference	Water	10% AES	20% AES	30% AES	40% AES	50% AES	100% AES
CS	1	0.9%	1.3%	5%	10.1%	15.6%	29%
F	1	0.38%	3.7%	4.9%	9%	18.5%	38%
SL	1	1.8%	2.8%	4.7%	8.4%	32%	31%
SM	1	0.38%	1.4%	7.1%	5.7%	30%	35%

The relative differences were obtained from comparing the volumetric ethanol content and volumetric water content at the same pressure in the same sample. The original thought of this comparison was to evaluate the percent change when switching wetting liquid from water to aqueous ethanol solution. It can be used to express how the aqueous ethanol solution was close to the water at equivalent pressure. Moreover, these numbers can be seen as a reflection of the liquid release rate at equivalent pressure.

As table 4 shown above, the relative differences of volumetric liquid content between water and aqueous ethanol solution were less than 10 % when the concentration of testing liquid was below 50 % (v/v). However, the relative difference of volumetric liquid content was quite high in 50 % and 100 % aqueous ethanol solution.

On the other hand, one unexpected outcome was presented in the repellent sample SL and SM. Compared to other sand samples, the relative difference between 10 % aqueous ethanol solution and water was lower than 1% but with 1.8 % in the SL sample. Particularly, the relative difference in the wettable sand sample (CS) was higher than in the strongly repellent sample (SM0 with 0.9% and 0.38%, respectively. A similar outcome was also appeared in the strongly repellent sample (SM) when the concentration of testing liquid reached 30 % (v/v) with 7.1 %. However, this relative difference in the same-textured sample (CS and SL) was 4.9 % and 4.7 %, respectively.

Table 5. Time for testing liquid reaching each equilibrium in the coarse sand sample

Testing liquid	Water	10% AES	20% AES	30% AES	40% AES	50% AES	100% AES
Time for reaching each equilibrium	>24 hours	>24 hours	>24 hours	18 to 22 hours	18 to 22 hours	< 16 hours	< 16 hours

Table 5 showed the time for each testing liquid to reach each equilibrium. When increasing ethanol content in aqueous ethanol solutions, the time for reaching each equilibrium (water release ceased) declined gradually. The water took around 24 hours to reach each equilibrium. After the ethanol concentration reached 30 %, the time for equilibrium was approximate 18 to 22 hours. 50 % and 100 % ethanol solution took less than 16 hours to get each equilibrium.

2.4 Discussion

2.4.1 The influence of physical properties of AES on Liquid retention curve

As expected, the results of the liquid retention curves and observations suggested that aqueous ethanol solutions drained quicker than water, either in wettable or hydrophobic sand samples. In comparison between volumetric liquid content, the water content in each sand sample was higher than either pure ethanol or aqueous ethanol solution under the same applied pressure. This value increased with the increase in ethanol content of testing liquid. For example, volumetric water content was approximately 1.03 times higher than 10 % ethanol solution and around 1.5 times higher than 50 % ethanol solution. When ethanol content reached 100 %, this proportion increased to 3. Increasing ethanol content in the aqueous solution decreased the surface tension, which resulted in the less negative pressure head at the same supplied pressure and less suction to retain liquid (Antonella and Leij, 2011). Furthermore, a decrease in density of ethanol solution (increase in concentration) caused more negative pressure head resulting in less volumetric ethanol content at the same supplied pressure (Antonella and Leij, 2011).

One main variable affected the result for the wettable sand samples. One primary variable affected the result: concentrations of testing liquid (surface tension) for the wettable sand

samples. Increasing ethanol concentrations in testing liquid resulted in a decrease in liquid surface tension and thickening of the liquid. However, in this study, the viscosity of aqueous ethanol solutions was not taken into consideration. The reason was the viscosity of liquid influenced the liquid flow mobility but only related to the ethanol penetration through the profile and hydraulic conductivity (Antonella and Leij, 2011). According to their result, the hydraulic conductivity showed a significant difference between water and aqueous ethanol solutions only appeared when the liquid penetration depth reached around 20 cm and the penetration time above 4 hours (Antonella and Leij, 2011). However, when the soil depth was about 5 cm, the hydraulic conductivities of aqueous ethanol solutions (different viscosity), the difference between each liquid was minor (Antonella and Leij, 2011).

2.4.2 50 % and 100 % ethanol solution

In the hydrophobic sand samples, there was a significant difference compared to the wettable sand sample. The retention curve of water did not merge with any aqueous ethanol solution. However, one unexpected outcome was that in both hydrophobic sand sample groups, the θ_r value of 50 % ethanol solution at 10 cm and 15 cm suction (pore size with 0.06 mm and 0.04 mm respectively) was lower than 100 % ethanol solution. This outcome might be indicating that the 50 % ethanol could yield a quicker response in repellent soil under lower suction. According to Beatty and Smith (2014), the aqueous ethanol solutions with 50 % concentration (v/v) could produce a faster response because of their partial wetting property.

Another important observation was the liquid absorption and losses via draining in the hydrophobic sand samples SL (slightly repellent quartz coarse sand sample) and SM (strongly repellent quartz coarse sand sample). The lower concentration of ethanol solution not wetted

up all hydrophobic sand samples. The evidence was the sample weight when using lower concentration ethanol solution such as water and 10 % ethanol solution; the losses through drainage were lower than the wettable coarse sample. This observation could explain that the hydrophobic soil trapped the liquid inside soil pores by preventing the liquid losses from evaporation and making the liquid harder to move through. Li et al. (2019) also reported that the soil water repellency resulted in the higher volumetric water content and low aeration in the soil. In addition, Hillel et al. (1975) also pointed out that the hydrophobic soil can be used as a mulch in dryland and irrigated farming systems to conserve water and reduce the evaporation losses while keeping the soil moisture underneath.

2.4.3 Evaporation issues in 50 % and 100 % ethanol solution

A dramatic decrease in the volumetric liquid content was shown in 50 % and 100 % ethanol solution. This decrease in liquid content was evaporation loss. The ratios of evaporation loss which were calculated from the weight loss based on the saturated aqueous ethanol content every 24 hours in 50 % and 100 % ethanol solution, were 11.06 % and 24.6 %, respectively. Besides, for coarse sand, the water drained rapidly through macropores (<0.08 mm), which promoted the free drainage of water and evaporation due to fewer suction forces holding the water (Easton and Book., 2016).

2.4.4 The aqueous ethanol solution in the repellent samples

Aqueous ethanol solutions were typically used to detect the critical surface tension (severity) of repellent soil due to its lower surface tension (Doerr et al., 2000). The surface tension of repellent media was usually higher than water, which caused water cannot infiltrate (Doerr et al., 2000). As described in the result section (table 4), the relative difference of

volumetric liquid content between water and ethanol indicated that the 10 % aqueous ethanol solution was released faster in the slightly repellent sample than other same textured sand samples. This outcome also applied to the strongly repellent sample (SM) when the concentration of testing liquid reached 30 %. Doerr. (1998) stated that the concentration of molarity ethanol droplet method for slightly repellent soil was commonly 5 %, supporting this result. . The basic principle of the molarity ethanol droplet method was to determine the severity (critical surface tension), which allowed the lowest ethanol concentration droplet to infiltrate into repellent media within 5s (Moody and Schlossberg, 2010; Doerr et al., 2000; Beatty and Smith., 2014). Moreover, this outcome indicated the 10% aqueous ethanol solution wetted up the slightly repellent sample and showed that the 10 % ethanol in the SL sample reached the critical surface tension but not matched the critical surface tension in the SM sample. Moreover, the hydrophobicity of the soil sample not only resisted the sample being wetted up but also reduced the evaporation and liquid release (Li et al., 2019; Hillel et al., 1975). Therefore, once the repellent sample is wetted up, the aqueous ethanol content at the sample surface would interact with air, and the repellency cannot prevent the liquid content from evaporating. ,

Regarding the strongly repellent sample, the relative differences (7.1 %) between water and aqueous ethanol solutions might suggest that the 30 % ethanol solution matched the critical surface tension of SM samples and the soil cores become fully wetted. Another observation could be supportive; the SM sample did not thoroughly wet up when 10 % and 20 % ethanol solution was applied. When the concentration of testing liquid reached 30 %, the surface of the SM sample wetted immediately. Doerr (1998) suggested the concentration of molarity ethanol solution for strongly repellent soil was 20 %. However, when using 20 % aqueous ethanol

solution to saturate the SM sample, only half of the sample surface got wetted, indicating the 20 % aqueous ethanol solution did not match the critical surface tension of the repellent sample.

This unexpected outcome suggested that the aqueous ethanol solution can be used to detect the severity of soil water repellency. The basic principle behind it was similar to the molarity ethanol droplet method, aiming to reach the critical surface tension of the repellent sample. When the repellent samples were not fully wetted, the relative difference of the wettable sample was higher than the repellent sample, which was caused by the physiochemical properties of aqueous ethanol solution, such as lower surface tension and lower density (Lamparter et al., 2010). Nevertheless, when the aqueous ethanol solution reached critical surface tension of the repellent sample, the relative difference in the wetted sample was lower than the repellent sample (Table 4) because the aqueous ethanol solution eliminated the soil water repellency effects. This outcome indicated that aqueous ethanol solution could be used to determine the severity of soil water repellency while measuring the soil water retention curve in the repellent sample. Although the molarity ethanol droplet method was simple and rapid, it poorly represented the soil wetting behaviour across the sample area ((Moody and Schlossberg, 2010). Compared to the molarity ethanol droplet method, using aqueous ethanol solution as the wetting liquid can wet up the whole soil samples instead of only wet up a droplet size area, which represented

2.4.5 The effect of texture on the water retention curve

The volumetric liquid content at equivalent pressure in the fine sand sample (F) was 1.31 times higher than in the coarse sand sample (CS). The coarse sand samples were a mixture of

fine sand and coarse sand (grain size >1.4 mm), which indicated the finer texture of the soil sample could retain more liquid than coarse texture soil. De Jong et al. (1983) pointed out that the soil texture was the major factor affecting the liquid retention curve of mineral soils. Moreover, McLaren and Cameron (1996) stated that the finer soil texture led to greater water content.

When suction was applied, soils containing large pores did not retain water against the suction and empty with less suction, while increasing suction is needed for emptying smaller pores (McCarty et al., 2016). Compared to coarse sand, fine sand has smaller pores, and therefore fine sand could retain more liquid at equivalent pressure. For example, McCarty et al. (2016) found that the fine sand could retain approximately 36 % of its moisture at the surface, but coarse sand only retains less than 5 % moisture at the surface.

2.4.6 Benefits and drawbacks of using ethanol solutions in coarse sand

There are several benefits and drawbacks when using ethanol solutions as wetting liquid. Due to lower surface tension, ethanol solutions drain faster than water, and it was proven by the result of the water retention curve. Compared to water, ethanol is not affected by the surface properties such as soil water repellency. Moreover, aqueous ethanol solution can detect the degree of soil water repellency by reaching the critical surface tension of the repellent sample. Compared to relative differences between aqueous ethanol content and water content at the same applied pressure, aqueous ethanol solutions from 10 % to 40 % concentration were closer to water.

However, as Beatty and Smith. (2014) suggested ethanol could be sensitive to temperature, evaporation issue cannot be ignored. For future studies, ethanol solutions can be used in cooler temperatures to minimise evaporation losses.

2.5 Conclusion

The relative differences between aqueous ethanol solution and water indicated that ethanol solutions with less than 50 % of ethanol content were suitable for determining liquid retention curve in coarse quartz samples with different wettability and texture. Moreover, by comparing the relative difference between water and ethanol solution in repellent soil samples, 10 % aqueous ethanol solution reached the critical surface tension of SL, and 30 % ethanol solution reached the critical surface tension of SM sample. Therefore, the aqueous ethanol solutions can detect differences between water repellency levels by reaching the critical surface tension of the repellent sample.

However, due to coarse texture and lack of organic matter to improve water retention capability and prevent evaporation of liquid, the evaporation losses in 50 % and 100 % were significantly higher with 11.06 % and 24.6 %. This issue indicated that the 50 % and 100 % ethanol solution was unsuitable for determining the liquid retention curve in coarse sand.

To minimise evaporation losses in the following study, two modifications should be considered. Firstly, change the soil sample from quartz sand to a finer-textured soil sample. Secondly, add organic amendments to the soil to improve liquid retention capability, water holding capacity and minimise evaporation.

Chapter 3

The applicability of using aqueous ethanol solutions on organically amended soil.

3.1 Introduction

In natural soil systems, soil water repellency (SWR) influences soil hydraulic properties by reducing the affinity of soil to water (Diamantopoulos et al., 2013). The implication of SWR includes a reduction in infiltration capacity of soils, acceleration of soil erosion, preferential flow and the leaching of agrochemicals (Doerr et al., 2000). The origin of SWR in natural soils is quite variable; it is commonly accepted that the organic compounds attached to the mineral grains surface resulted in the SWR (Almendros et al., 1988).

Using organic amendments aims to improve soil quality by increasing water infiltration and retention, promoting aggregation, improving aeration, and reducing compaction (Sojka et al., 2007). Moreover, organic amendments could also increase soil microbial and macrofaunal population (Treonis et al., 2010) and improve organic C sequestration (Nicolas et al., 2012).

Organic amendments, such as biochar, improve water retention capability and reduce evaporation losses from the soil surface. Wang et al. (2018) experimented with different application rates (0, 10, 50, 100, and 150 g/kg) of biochar to examine the effect on water retention capability and evaporation loss in loamy and sandy soil. They concluded that biochar reduced soil evaporation losses in all treatment groups, and evaporation losses decreased with increasing biochar application. Besides, Taban and Naeini. (2007) suggested that organic particles could block the soil pores to prevent evaporation. In terms of water retention

capability, Wang et al. (2018) also pointed out that average water content in the soil sample increased by 2.1 % than in the control group. Likewise, Zhang et al. (2016) also found that the biochar could retain 30 % more water than sandy soil itself, and the water content in samples was overall increased by 1.29 %. In terms of evaporation, Zhang et al. (2016) found that the biochar application reduced evaporation when it was mixed with soil instead of mulching on the top.

Shrinking and swelling processes can cause changes in the soil physical and hydrophysical properties, such as density, porosity, hydraulic conductivity and soil water retention (Novak and Hlavacikova 2019). When soil contains clay minerals or organic compounds, changing the soil water content will change the soil volume, and thus the shrinking and swelling process will happen (Novak and Hlavacikova, 2019). Moreover, the hysteresis would also occur when determining the soil liquid retention curve by water (McLaren and Cameron, 1996). The definition of hysteresis is that the equilibrium soil water content at any particular suction is less under wetting conditions than drying conditions (McLaren and Cameron, 1996).

However, many authors concluded that organic compounds could contribute to the development of hydrophobicity (Wijewardana et al., 2016, Doerr et al., 2000, Regalado et al., 2008, Leelamanie and Karube., 2007).

To overcome those problems, ethanol is considered as a completely wetting liquid due to its lower surface tension, and lower capillary pressure acts in the soil pore system (Watson and Letey., 1970; Lamparter et al., 2000). As a completely wetting liquid, the contact angle of ethanol can be considered as 0° (Beatty and Smith., 2014). As discussed in chapter 2, the evaporation losses of 50 % and 100 % ethanol solutions were relatively high. The finer-textured

soil (Templeton silt loam) was chosen to minimise the evaporation losses during the experiment.

Moreover, as Lamparter et al. (2010) suggested, the feasibility of using ethanol to test hydraulic properties on natural soil remains unknown. Additionally, the investigation of using aqueous ethanol solution on organic amendments soil to determine soil hydraulic properties has not been done yet. Therefore, in this chapter, the main aim is to test the applicability and accuracy of aqueous ethanol solution on organically amended treated Templeton silt loam.

The hypotheses are (1) the incorporation of the organic amendments with soil not only increased the liquid retention capability and soil adsorption. (2) organic amendments application could reduce the evaporation losses of the aqueous ethanol solution.

This study aims to determine the soil liquid retention curve on organic amendments treated soil and test the applicability of ethanol and aqueous ethanol in organically amended treated soil.

3.2 Material and method

3.2.1 Soil description

The soil samples were Templeton silt loam which was collected from the Iversen field plot. The soil was initially mixed with different organic amendments (mushroom compost, biochar, dairy effluent, and municipal compost) with a 15 % application rate.

3.2.2 Packing and treatment

For the different organic treatments, the labels are Templeton silt loam (T), Templeton silt loam with mushroom compost (C), Templeton silt loam with Dairy effluent (D), Templeton silt

loam with biochar (B) and Templeton silt loam with municipal compost (M) as shown in Table 6.

Dairy shed effluent was sourced from the Lincoln dairy farm. The biochar was sourced from Bishop Research Ltd in Palmerston North, New Zealand. Mushroom compost (wheat straw) was sourced from Darfield and ground using a plant grinder. Municipal compost was sourced from Living Earth organic compost. All organic materials were air-dried at 25°C for three days and sieved (2 mm sieve), then air-dried at 25°C for another day.

Table 6 below showed the total C and N of the organic amendments. Table 7 showed the sample repacking information of organic amendment treated soil.

Table 6. Total C and N of organic amendments. Retrieved from Esperschutz et al. (2016)

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Table 7. The information for sample packing

Labelling	Treatment	Replicates	Volume of soil (cm ³)	Bulk density (g cm ⁻³)
T	Templeton silt loam	3	26.01	1.1
M	municipal compost	3	26.01	1.1
D	Dairy shed effluent	3	26.01	1.1
C	Mushroom compost	3	26.01	1.1
B	Biochar	3	26.01	1.1

3.2.3 Measurement of hydrophobicity

Before placing the samples into the pressure plate, the samples were tested by the water drop penetration time (WDPT) Method for determining the persistence of soil water repellency.

Five droplets were measured in different locations of the sample surface, and the average time

of water drop penetration was recorded. The classification of severity is cited from Doerr (1998). The severity classification of samples, as shown in Table 8.

Table 8. The WDPT result of each organic treated group

Treatment group	Severity	WDPT
Control (T)	Wettable	1 s
Municipal compost (M)	Wettable	1 s
Dairy effluent (D)	Wettable	7 s
Biochar (B)	Wettable	7 s
Compost (C)	Wettable	5 s

3.2.4 Apparatus set up

The setup of the apparatus was the same as in chapter 2. One bar ceramic pressure plate was used and placed in the container and a plastic tube linked the plate and suction bottle. The bottom container was covered by placing another container on the top, and both containers were sealed with plastic tape. Besides, a cup of testing liquid was also placed inside the chamber to maintain the humidity. To test the evaporation losses, another soil sample was placed beside the ceramic plate, and the weight of this sample was recorded every 24 hours.

The method for minimizing evaporation worked well; the losses from evaporation were around 0.1g (<1 % in total liquid weight) per 24 hours in lower ethanol concentration, which is neglectable. The evaporation losses in 50 % and 100 % ethanols solution were 2.8 % and 2.9 %, respectively.

3.2.5 Ethanol and water retention curve

The concentrations of testing liquid were 10 %, 20 %, 30 % 40 % and 50 % in volume concentration. The DI water and Pure ethanol (100 % in volume) were used as comparison

liquids. The suction level ranged from 2.5 cm to 25 cm, which corresponds to 0.0024 bar to 0.024 bar, respectively.

The samples were saturated with testing liquid for 48 hours within the container. After saturation, the suction bottle was moved to the first suction level (2.5 cm). When the equilibrium reached, the sample weight was recorded and move the suction bottle was moved to the next level.

The adjustment of suction applied was using the capillary rise equation. Table 9 shows the conversion of the suction into pressure, and the pore size that can be emptied under particular suction.

Table 9. The pore size (mm) can be emptied under different suction levels and different fluid properties.

Suction in cm	Pressure (bar)	Ethanol 0 %	Ethanol 10 %	Ethanol 20 %	Ethanol 30 %	Ethanol 40 %	Ethanol 50 %	Ethanol 100 %
2.5	0.0024	0.6	0.4	0.3	0.26	0.25	0.23	0.23
10	0.0096	0.15	0.1	0.079	0.067	0.063	0.06	0.059
15	0.0144	0.1	0.07	0.052	0.044	0.042	0.04	0.039
20	0.0192	0.07	0.05	0.039	0.033	0.032	0.03	0.029
25	0.024	0.06	0.04	0.031	0.027	0.025	0.024	0.023

3.2.6 Statistical analysis

Statistical analyses were conducted using analysis of variance to determine significant differences ($p < 0.05$) in selected parameters measured. Besides, the relative differences of volumetric liquid content between water and aqueous ethanol solution were also compared to determine the proportion of volumetric liquid content change at the same supplied pressure. In addition, the amount of liquid retained at different supplied suction, the relative differences

between water and aqueous ethanol solution and the time for reaching each equilibrium can be seen as the proxy for liquid desorption rate.

3.3 Results

3.3.1 Comparison between organic amendments` effects on liquid retention curve

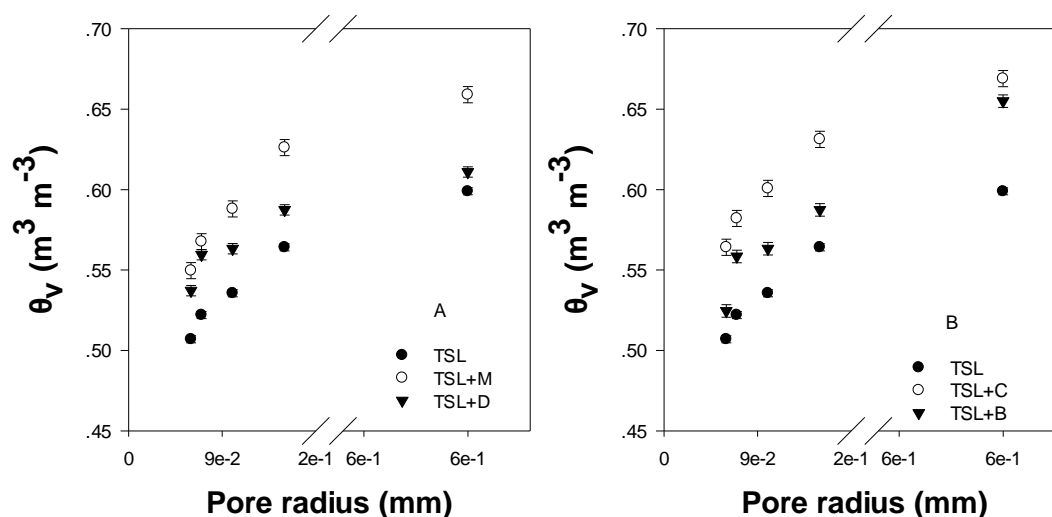


Figure 21. The water retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

Figure 21 showed the water retention curve of Templeton silt loam and Templeton silt loam soil incorporated with municipal compost (M), dairy shed effluent (D), mushroom compost (C) and biochar (B). Compared to TSL, the near-saturated volumetric water content of organically amended treated soil was overall higher at the same supplied pressure. The TSL with mushroom compost treatment increased the average water content by 11.7%. For the other treatments, the average amount of water content increased by 9.6% (M), 4.8% (D) and 5.8% (B), respectively.

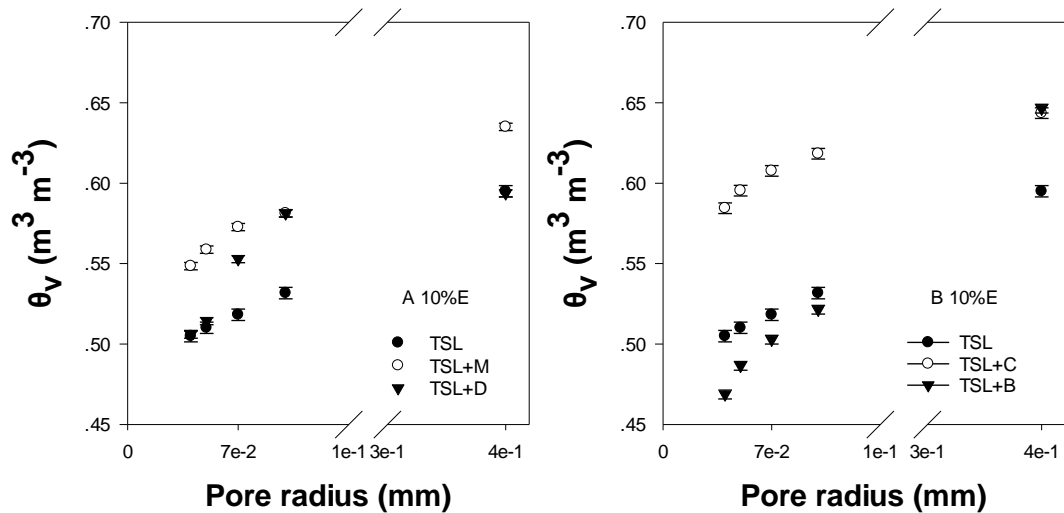


Figure 22. The ethanol (10 %) retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

Figure 22 showed the liquid retention curve of 10 % ethanol solution in TSL and TSL with organic amendments. Compared to TSL, the volumetric liquid content of TSL with organic amendments soil at near-saturation condition was overall higher, but TSL with biochar (B) and dairy shed effluent (D) decreased the residue volumetric liquid content at higher supplied pressure. This outcome was also applied to other concentrations of aqueous ethanol solution. The TSL with mushroom compost treatment increased the average volumetric liquid content by 14.8 %. For other treatments, the average volumetric liquid content increased by 8.9 % (M), 3.4 % (D) and 1 % (B), respectively.

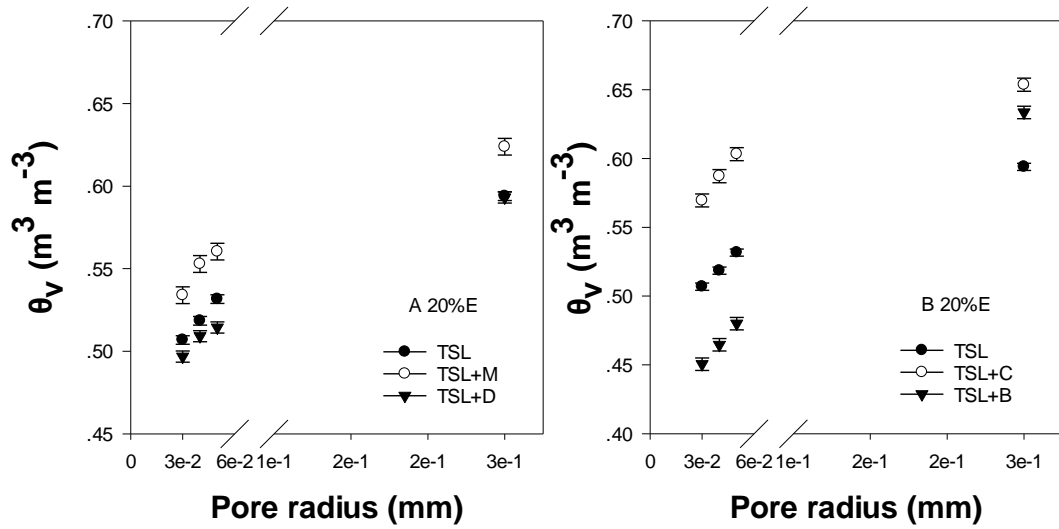


Figure 23. The ethanol (20 %) retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

Figure 23 showed the liquid retention curve of 20 % ethanol solution in TSL and TSL with organic amendments. Compared to TSL, the volumetric ethanol content in TSL with mushroom compost (C) and municipal compost (M) increased by 12.5 % and 5.5 %, respectively. However, the volumetric ethanol content decreased in TSL with biochar (B), and dairy shed effluent (D) by 5.7 % and 1.1 %, respectively.

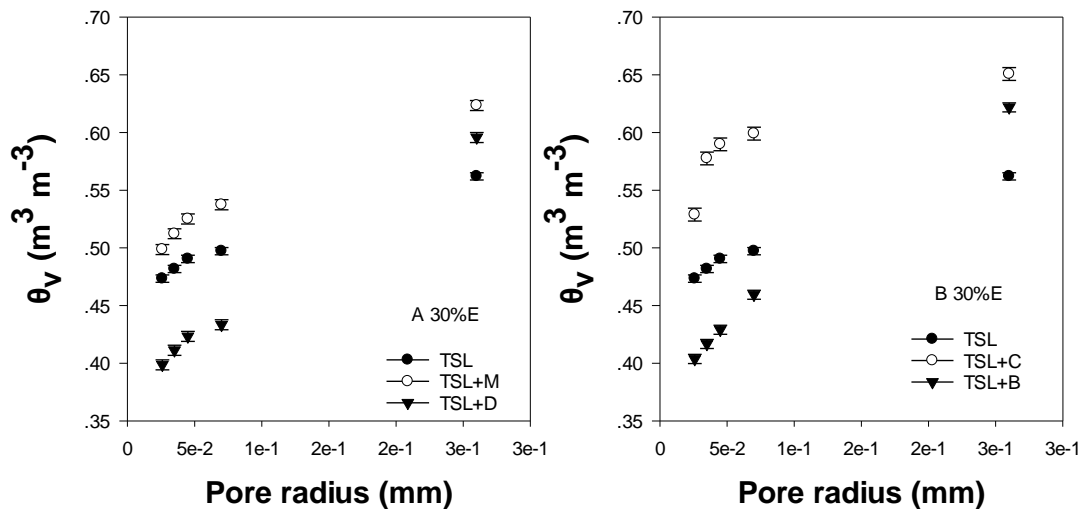


Figure 24. The ethanol (30 %) retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus

TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

Figure 24 showed the liquid retention curve of 30 % ethanol solution in TSL and TSL with organic amendments. Compared to TSL, the volumetric ethanol content in TSL with mushroom compost (C) and municipal compost (M) increased by 17.6 % and 7.6 %, respectively. However, the volumetric ethanol content decreased in TSL with biochar (B), and dairy shed effluent (D) by 7.5 % and 10 %, respectively.

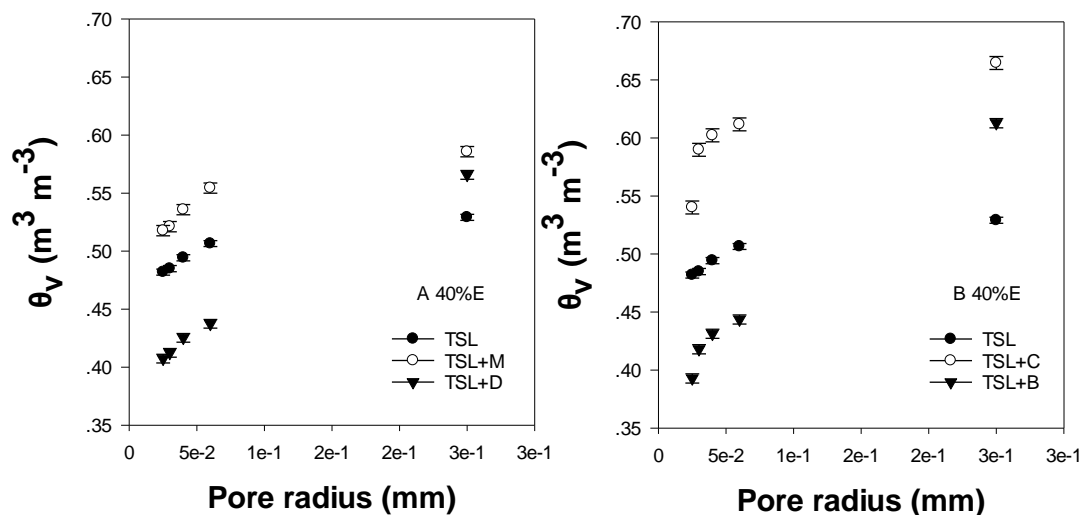


Figure 25. The ethanol (40 %) retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

Figure 25 showed the liquid retention curve of 40 % ethanol solution in TSL and TSL with organic amendments. Compared to TSL, the volumetric ethanol content in TSL with mushroom compost (C) and municipal compost (M) increased by 20.4 % and 8.6 %, respectively. However, the volumetric ethanol content decreased in TSL with biochar (B), and dairy shed effluent (D) by 8.3 % and 10 %, respectively.

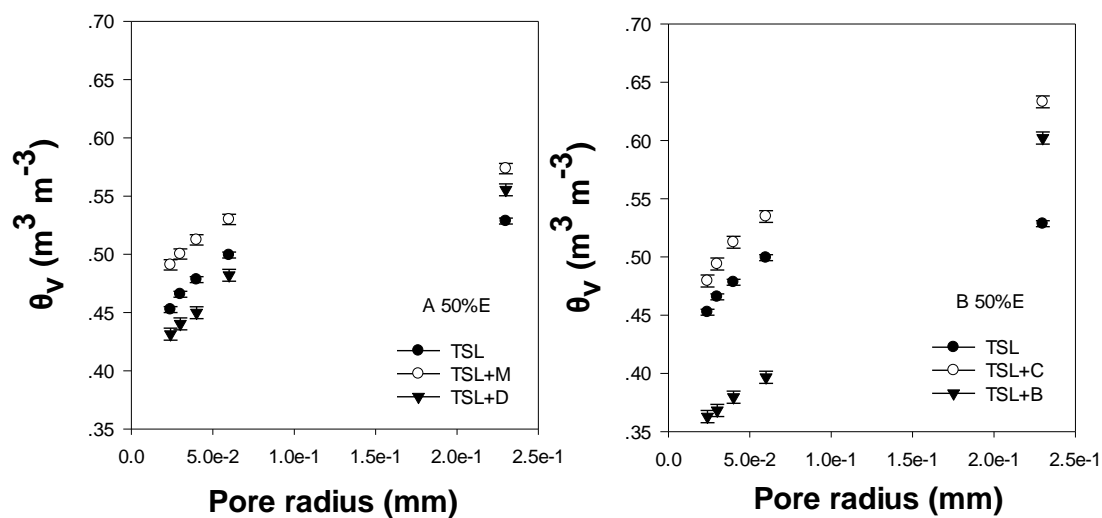


Figure 26. The ethanol (50 %) retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

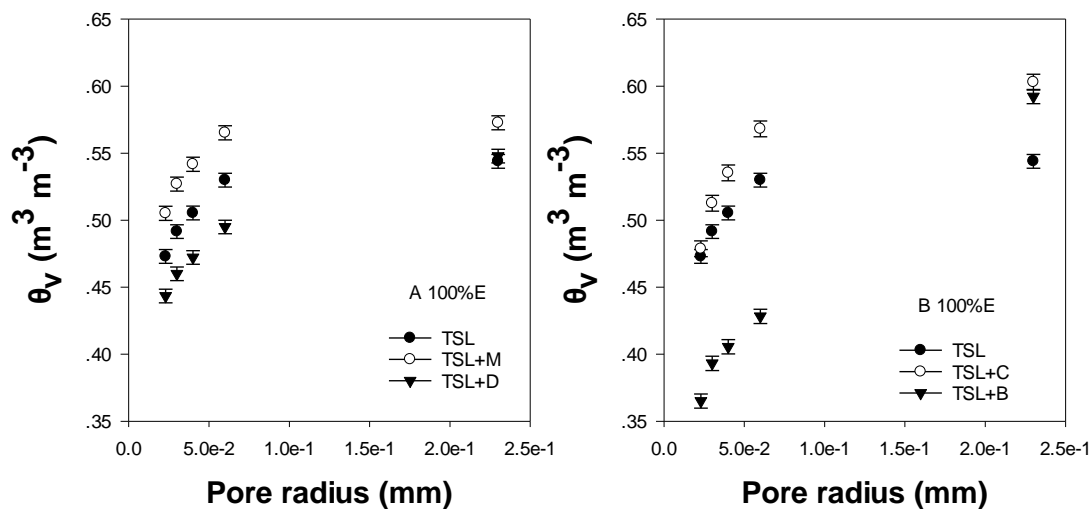


Figure 27. The ethanol (100 %) retention curves of Templeton silt loam (TSL) and TSL incorporation with different organic amendments. The liquid retention curve of TSL versus TSL incorporated with municipal compost (M) and dairy shed effluent (D) in A, and TSL incorporated with mushroom compost (C) and biochar (B) in B. The error bars are obtained from standard error (n=3).

Figure 26 and figure 27 showed the liquid retention curve of 50 % and 100 % ethanol solution in TSL and TSL with organic amendments. Compared to TSL, mushroom compost and municipal compost still increased the volumetric ethanol content by 7 % and 8.2% in 50 % aqueous ethanol solution; 5.8 % and 6.6 % in 100 % aqueous ethanol solution, respectively. The volumetric ethanol content in TSL with biochar (B) and dairy shed effluent (D) was still lower than TSL with 3.1 % and 18.1 % in 50 % aqueous ethanol solution; 14.6 % and 5 % in 100 % aqueous ethanol solution, respectively.

3.3.2 Comparison between testing liquid concentration on liquid retention curve

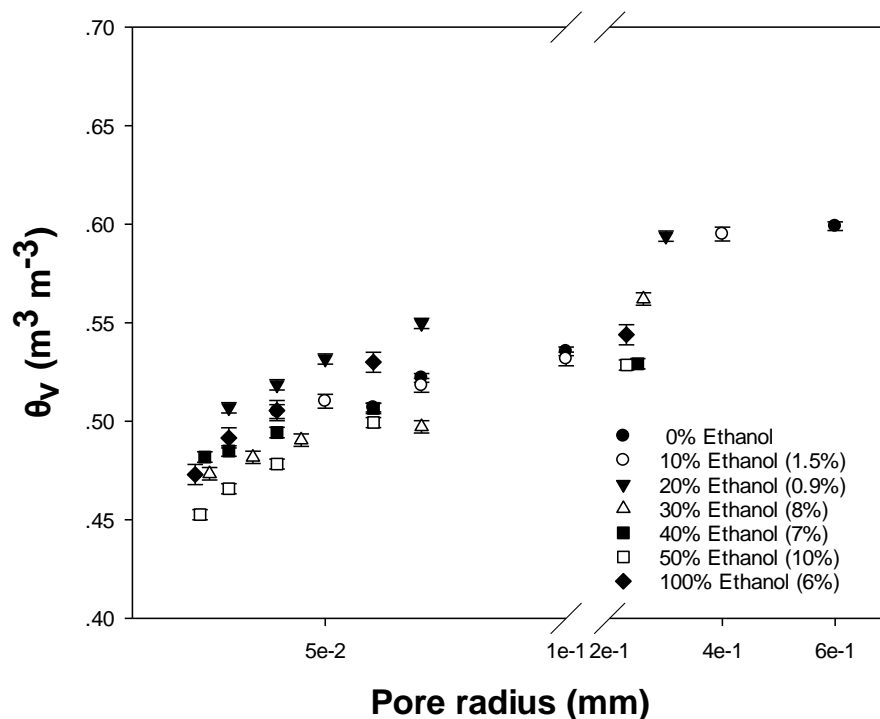


Figure 28. Different concentrations of aqueous ethanol retention curve of T (Templeton silt loam) samples at a different pore radius. The number in the brackets after each testing liquid concentration is the relative difference compared to water. The error bars are obtained from standard error (n=3).

The selected range of pore radius for all figures was less than 0.075 mm (fig 28), corresponding to the pressure between 0.0096 bar (10 cm) to 0.024 bar (25 cm). Water only drained through 0.07 mm and 0.06 mm pores within this range, but 10 % ethanol drained

through 0.05 mm and 0.04 mm. Compared to other solutions at equivalent pressure, 50 % ethanol solution had the lowest volumetric ethanol content (θ_v). There were no significant differences between aqueous ethanol solution ($p > 0.05$) except 20 % ethanol solution versus 50 % ethanol solution ($p = 0.04$). Compared to water, the relative differences of aqueous ethanol solutions in Templeton silt loam ranged from 1.5 % to 10 %. Only the relative difference of 10 % ethanol solution was a positive value.

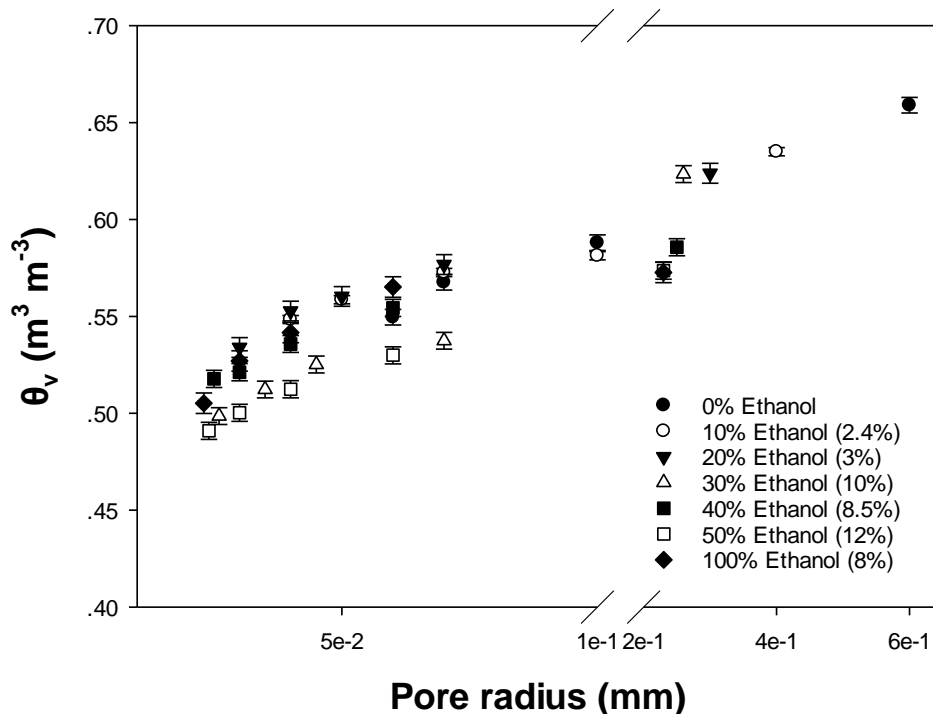


Figure 29. Different concentrations of aqueous ethanol retention curve of M (municipal compost) samples at a different pore radius. The number in the brackets after each testing liquid concentration is the relative difference compared to water. The error bars are obtained from standard error ($n=3$).

Testing liquids behaved similarly in the municipal compost treated soil sample (figure 29) when compared to the Templeton silt loam group. The lowest θ_v appeared in testing liquid with 50 % ethanol concentration. Water and 40 % ethanol started to merge also at a pore size of 0.06 mm. There were no statistically significant differences between all testing liquids ($p = 0.125$).

The relative differences between aqueous ethanol solutions and water in Templeton silt loam with municipal compost were all negative and ranged from 2.5 % to 12.7 %.

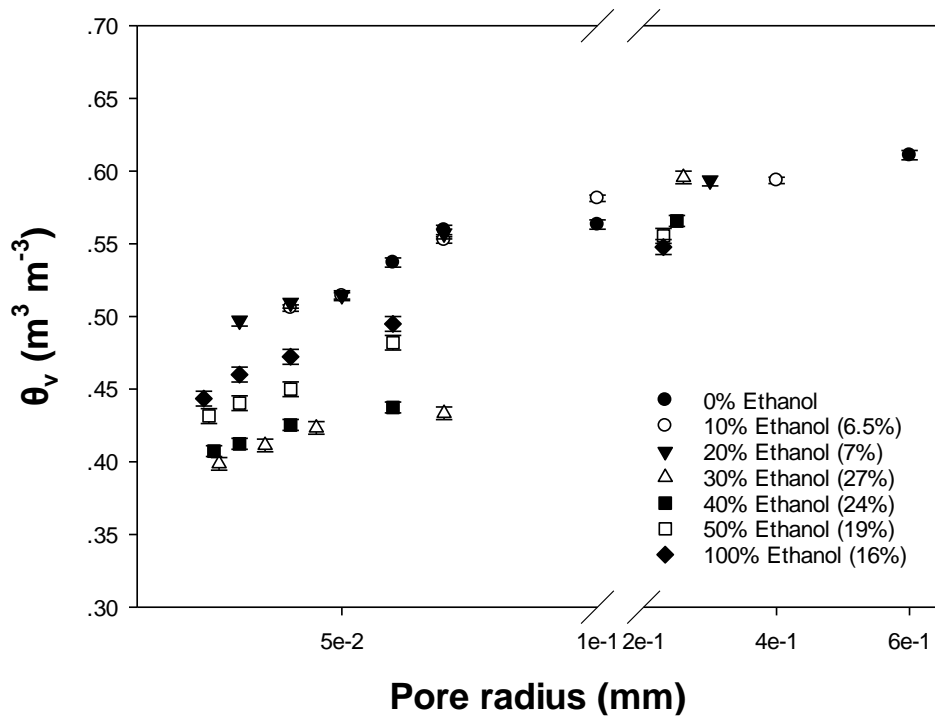


Figure 30. Different concentrations of aqueous ethanol retention curve of D (dairy shed effluent) samples at a different pore radius. The number in the brackets after each testing liquid concentration is the relative difference compared to water. The error bars are obtained from standard error (n=3).

In the dairy effluent treated group (figure 30), testing liquid with 30 % concentration showed the lowest θ_v and was significantly different compared to other concentrations ($p < 0.01$). Likewise, 40 % ethanol solution also showed a significant difference from the other groups ($p < 0.05$). In Templeton silt loam soil with dairy shed effluent sample, the relative differences of aqueous ethanol solutions were negative compared to water, ranging from 6.5 % to 27 %. 30 % ethanol solution showed the highest relative difference with 27 %, followed by the 40 % ethanol solution with 24 %.

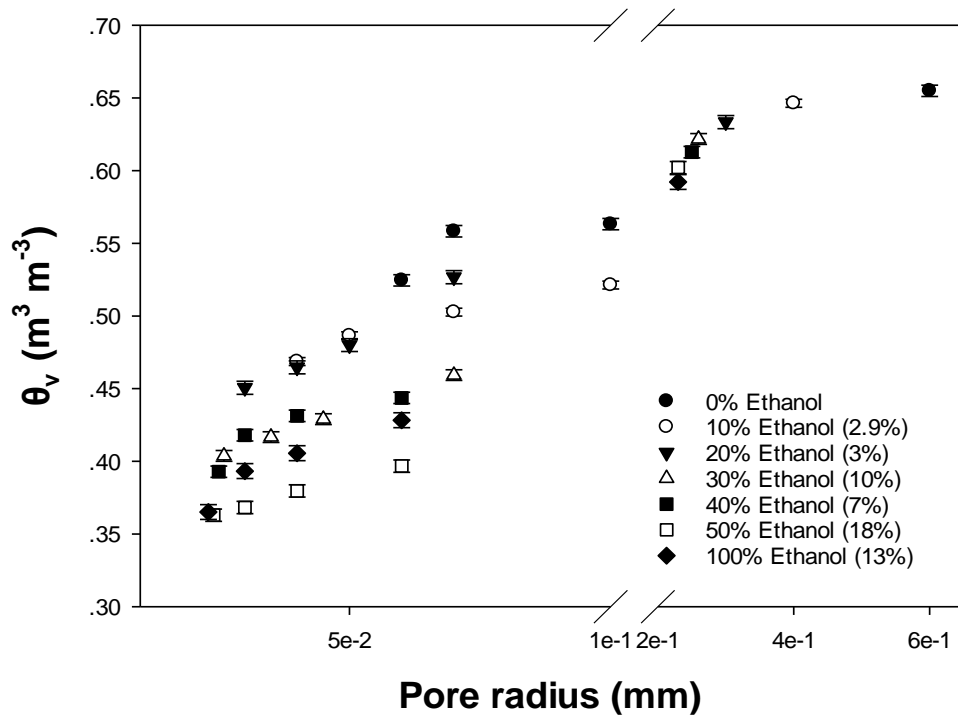


Figure 31. Different concentrations of aqueous ethanol retention curve of the B (biochar) samples at a different pore radius. The number in the brackets after each testing liquid concentration is the relative difference compared to water. The error bars are obtained from standard error ($n=3$).

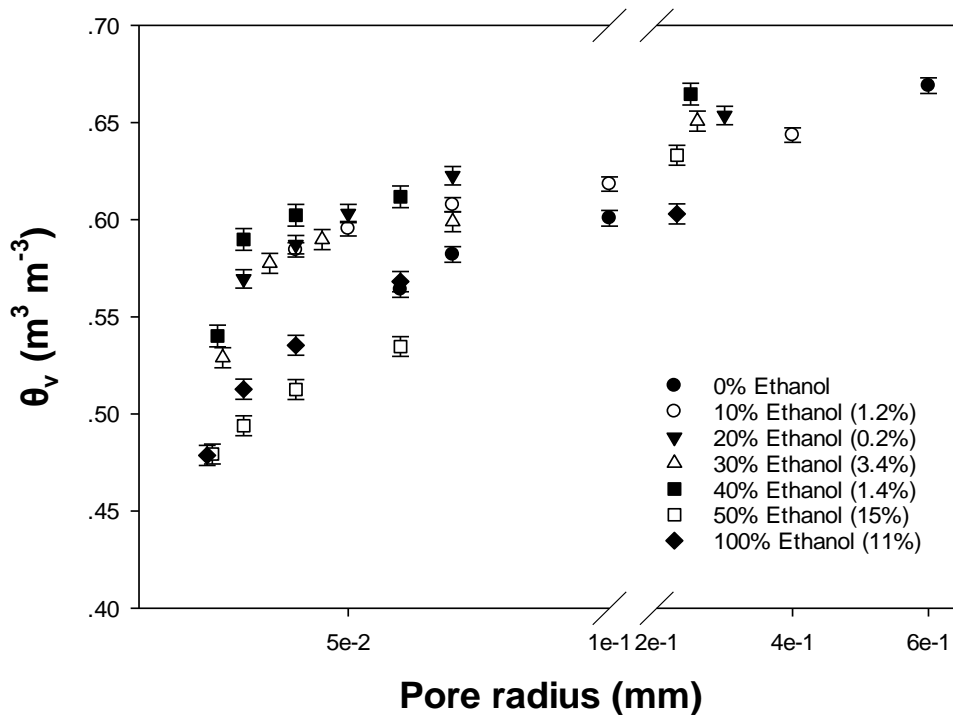


Figure 32. Different concentrations of aqueous ethanol retention curve of the C (mushroom compost) samples at a different pore radius. The number in the brackets after each testing liquid

concentration is the relative difference compared to water. The error bars are obtained from standard error (n=3).

In biochar (figure 31) and mushroom compost (figure 32) treated soil samples, there were no significant differences between testing liquid (p= 0.05). The lowest θ_v appeared in 50 % ethanol solution and followed by 100 % ethanol solution. The relative differences between water and aqueous ethanol solutions in these two organically amended treated soil showed a positive value of 10 % and 20 % ethanol solution with 1.5 % and 2 % in mushroom compost treated sample, and 2.9 % and 3 % in biochar treated sample. As shown in figure 31 and figure 32, 50 % and 100 % ethanol solutions produced the highest negative relative differences value with 15 % and 11 % in mushroom compost treated sample, and 15 % and 11 % in biochar treated sample.

Table 10. The relative difference of aqueous ethanol solutions compared to water in TSL and TSL with organic amendments

Relative difference	water	10% AES	20% AES	30% AES	40% AES	50% AES	100% AES
TSL	1	1.5%	0.9%	8%	7%	10%	6%
TSL+M	1	2.4%	3%	10%	8.5%	12%	8%
TSL+D	1	6.5%	7%	27%	24%	19%	16%
TSL+C	1	1.2%	0.2%	3.4%	1.4%	15%	11%
TSL+B	1	2.9%	3%	10%	7%	18%	13%

Table 10 showed the relative differences of volumetric liquid content between water and aqueous ethanol solution in Templeton silt loam (TSL) and TSL incorporation with organic amendments. Before the concentration of testing liquid reaching 50 % (v/v), the relative differences between water and testing liquid were mainly below 10 %, except TSL with dairy shed effluent. Moreover, compared to the sand sample, the relative difference between water and higher concentration of testing liquid (50% and 100%, v/v) were significantly smaller.

Table 11. Time for testing liquid reaching each equilibrium in TSL samples

Testing liquid	Water	10% AES	20% AES	30% AES	40% AES	50% AES	100% AES
Time for reaching each equilibrium	>24 hours	>24 hours	>24 hours	18 to 22 hours	18 to 22 hours	< 16 hours	< 16 hours

As table 11 shown above, the water took around 24 hours to reach each equilibrium. After the ethanol concentration reached 30 %, the time for equilibrium was approximate 18 to 22 hours. 50 % and 100 % ethanol solution took less than 16 hours to get each equilibrium.

3.4 Discussion

3.4.1 The organic amendments effects on soil liquid retention

Adding organic amendments to the soil improves soil quality, such as soil structure and organic carbon (Sojak et al., 2007; Nicolas et al., 2012). The improvement in soil structure increased the water infiltration and retention (Sojak et al., 2007), and the improvement of soil organic carbon increased soil liquid adsorption properties (Rawls et al., 2004).

According to the liquid retention curve of aqueous ethanol solutions, all organic amendments increased liquid content at the near-saturation condition. When increased applied pressure and ethanol concentration, the volumetric liquid content in TSL with biochar (B) and dairy shed effluent (D) had a greater decrease than other treatments. The reason for this decrease in biochar amendment could be explained by Ouyang et al. (2013), who experimented with biochar application on the sandy loam soil and silt clay soil. Their result suggested that the biochar application increased the water content in both soils within a lower suction range. Moreover, they claimed that the application of biochar decreased the soil bulk density, increased the number of macroaggregates, and decreased the number of microaggregates. These two types of aggregates increased saturated water content and decreased residual water content.

Compared to biochar and dairy shed effluent, the mushroom compost (C) and municipal compost (M) increased the liquid retention capability at near-saturation conditions and increased the liquid holding capacity when the applied pressure and ethanol concentration increased. This increase could be explained by Shiralipour et al. (1992). They reported that the application of compost to soil could enhance the water holding capacity markedly by improving the storage pores (0.5-50 μm). Moreover, Hawke and Summer (2006) also pointed out that the organic amendments such as compost, sawdust and manure to the soils could enhance the total porosity, hydraulic conductivity, and water retention capability.

As another essential factor that contributed to the liquid losses from a soil sample was evaporation. The ratio of evaporation loss through the organically amended treated sample in 50 % and 100 % ethanol solution was lower than in coarse samples. The possible explanation for this reduction was that organic amendments could block soil pores and reduce evaporation (Taban and Naeini, 2007). This statement was also supported by Opara-Nadi and Lal (1987), Naeini and Cook (2000), and Ji and Unger (2001).

TSL samples were natural soils that contained organic material. Organic materials, such as organic carbon, affect the soil structure and adsorption properties (Rawls et al., 2004). Hudson (1994) pointed out that organic carbon increased the volume of water held at field capacity in the sand, silt loam and silty clay loam soil. Moreover, the liquid was attracted to the surface charge of the organic particle leading to the mineral soil with higher organic matter content retaining more liquid (McLaren and Cameron, 1996).

3.4.2 The effect of 50 % and 100 % ethanol solution on Templeton silt loam and organic amendments

In comparison between the volumetric liquid content, the water content in soil samples was higher than ethanol content under the same applied pressure. This value increased with the increasing in ethanol content concentration in the testing liquid. For example, the volumetric water content was 1.02 times higher than 10 % ethanol solution and around 1.18 times higher than 50 % ethanol solution. The volumetric water content was approximately 1.19 times higher than 100 % ethanol solution.

In terms of reducing volumetric liquid content, Sciortino et al. (2010) hypothesized that with the increase in the ethanol content, the liquid retention in the soil would decrease. Moreover, with the increase in ethanol content of the testing solution, the soil absorbed less ethanol (Sciortino et al., 2010). With regard to liquid properties, 100 % ethanol solution has lower surface tension and density than 50 % ethanol, which reduced the soil liquid content at a particular soil pressure head (Sciortino et al., 2010).

Besides, the degradation of soil organic material when applying the ethanol onto samples could also result in the inaccuracy of the measurement. Lamparter et al. (2010) suggested that ethanol can degrade the soil organic matter and consequently change the soil pore system. The dry weight of soil samples was reduced by approximately 10.8 % after treating 50 % and 100 % ethanol solutions. This loss in the dry weight of soil samples indicated that aqueous ethanol solution (above 50 % concentration) dissolved the soil organic solid. Jonsson et al. (2010) suggested that ethanol was commonly used to remove pollutants in soil, and ethanol solutions provided higher extraction efficiencies. For example, 50 % (v/v) ethanol solution could extract

15 % of contaminants attached to the organic matter and finer aggregates, and 95 % (v/v) could remove 23 % of pollutants in 15 minutes (Jonsson et al., 2010).

Besides, it is commonly accepted that the organic materials from dead plant tissues and microorganisms caused soil water repellency (Doerr et al., 2000). The degradation of organic compounds might reduce the degree of soil water repellency. It is also necessary to study the potential degradation of hydrophobic compounds in either testing liquid is water or aqueous ethanol solutions.

3.4.3 Evaporation of 50 % and 100 % ethanol solution in Templeton silt loam soil

The ratio of evaporation losses in 50 % and 100 % ethanol solution in TSL samples were 2.8 % and 2.9 %, respectively, compared to the evaporation losses in the coarse sand sample (11.06 % in 50 % ethanol solution and 24.6 % in 100 % ethanol solution). The reasons for this reduction were related to the pore size and organic matters. Sandy soil usually has larger pores, such as macropores (pore size over 0.08 mm) (Vittum, 2009). Macropores promoted evaporation and water drainage (Easton and Book., 2016). In contrast, a silt loam soil contains medium size to smaller pores (Vittum, 2009). In an unsaturated condition, the liquid is held in smaller pores under higher suction (McLaren and Cameron, 1996), and thus reduced the evaporation losses.

3.4.4 Benefits and drawbacks of using ethanol solutions in natural soil

As discussed above, lower surface tension results in ethanol solutions draining faster than water. Although, soil organic matter and organic amendments improve soil structure, water retention capability and reduce the evaporation in Templeton silt loam. The risk of dissolving organic matter should be considered. The dry weight of soil samples reduced approximately

10.8 % after testing, indicating solid matter losses through the drainage process, which could be due to organic matter loss. Lamparter et al. (2010) also suggested that ethanol could dissolve organic material in natural soil. For future research, more analyses need to be done to indicate the dynamic change of the amount of organic matter after applying aqueous ethanol solutions.

Additionally, the increase in ethanol content results in decreasing hydraulic conductivity because the viscosity of ethanol solution will reach its maximum at 45 % on a weight basis (Sciortino et al., 2010; Beatty and Smith., 2014). Moreover, Sciortino et al. (2010) pointed out when the concentration of ethanol solution reached 45 % on a weight basis, the viscosity of solution reached the maximum, and any further increase or decrease in concentration would increase hydraulic conductivity by reducing the viscosity of the solution.

3.5 Conclusion

The speed of desorption using aqueous ethanol solution was quicker than water because it required lower pressure or suction for emptying liquid from smaller pores. Especially, 50 % and 100 % ethanol solution took less time than other solutions to reach the equilibrium, and the desorption speed was 1.8 times and 1.9 times faster than water, respectively. The organic amendments improve the soil liquid retention capability and reduce the evaporation, leading to more ethanol content retained in the soil samples, especially the mushroom compost and municipal compost. Those two types of compost could increase water holding capacity markedly by improving the storage pores and liquid adsorption properties. Especially, Templeton silt loam incorporated with mushroom compost increases the highest amount of volumetric liquid content compared to other organic amendments. This increase is observed in all concentrations of testing liquid.

On the other hand, compared to the coarse sand sample, the Templeton silt loam contains organic materials and fewer large pores, resulting in more liquid retained in smaller pores, thus reducing liquid losses through evaporation.

Moreover, the aqueous ethanol solutions with less than 50 % ethanol content could be considered an alternative option for determining the soil liquid retention curve due to its faster desorption rate. However, the risk of dissolving organic materials should be taken into consideration when using an aqueous ethanol solution with more than 50 % ethanol content. Additionally, the dissolution of organic compounds would reduce the hydrophobicity of the soil samples. Therefore, it is also necessary to study the potential degradation of hydrophobic material in the wetting and drying process.

Chapter 4 Summary

The objectives of this study are to test the applicability of aqueous ethanol solution on soil liquid retention curve in soils with different organic amendments, wettability, and particle size. To achieve this goal, two experiments were conducted: (1) The feasibility of using aqueous ethanol solutions to determine soil liquid retention curve on the homogeneous porous system with different wettability and texture; (2) The applicability of using aqueous ethanol solutions on organically amended soil.

The result of the sand experiment showed that under the same supplied pressure, the desorption rate of aqueous ethanol solutions in sand samples was overall faster than water by approximately 1 to 3x based on the liquid content at the same applied pressure and the time for reaching each equilibrium. For example, under the equivalent pressure, the volumetric water content in samples was around 1.5 times higher than 50 % ethanol solution and 3 times than 100 % ethanol solution. In addition, the separation of the water retention curve and ethanol retention curve in the hydrophobic sand samples indicating the existence of soil water repellency. Moreover, the results from the sand experiment suggested that when the concentration of aqueous ethanol solution was below 50%, the losses via evaporation was less than 1 %, and the relative differences between water and the testing liquid were lower than 10 %. However, the evaporation losses were 11.06 % and 24.6 %, and the relative differences in 50 % and 100 % ethanol solution were around 15 % and 30 %, respectively. Therefore, 0 to 40 % aqueous ethanol solutions were suitable in the sand samples due to less evaporation.

In the second experiment, the overall desorption speed of aqueous ethanol solution was still faster than water. The organic amendments in the Templeton silt loam soil not only

increased the water retention capability but also reduced the evaporation losses. The evaporation losses in TSL soil and TSL with organic amendments soil were with 1 % in solutions with less than 50 % ethanol content. The evaporation losses of 50 % and 100 % ethanol solution were 2.8 % and 2.9 %, respectively. When compared the liquid content to water at equivalent pressure, the relative differences between water and aqueous ethanol solutions were similar to the sand experiment when the concentrations of ethanol solutions were below 50 %. However, the relative differences in 50 % and 100 % ethanol solution were smaller than in the sand sample with around 10 % and 15 %, respectively. In the comparison between organic amendments effects on soil liquid retention capability, the mushroom compost and municipal compost increased the amount of liquid in the TSL sample by approximately 13.4 % and 6.8 %, respectively. However, the biochar and dairy shed effluent only increased the amount of liquid retention at the near-saturation condition (all less than 5 %).

Hence, 0 to 40 % of ethanol solutions could be used as an alternative wetting liquid for determining soil liquid retention curve due to the faster desorption rate. Additionally, the first benefit of using aqueous ethanol solutions is the fast desorption rate compared to water. The second benefit is eliminating the effect of soil water repellency. Aqueous ethanol solutions with certain concentrations are not affected by the soil water repellency and can thoroughly wet up repellent soil samples. The third benefit is detecting the degree of soil water repellency by reaching the critical surface tension of the repellent sample. However, evaporation is an issue in coarse-textured soil, and the risk of dissolving organic matter cannot be ignored. Moreover, increasing ethanol concentration results in a hydraulic conductivity decrease until the concentration of ethanol solution is above 45 % on a volume basis.

For future studies, more analyses need to be done to indicate the dynamic change of the amount of organic matter and the potential degradation of hydrophobic compounds after applying either aqueous ethanol solutions or water

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Appendix A

The changes in hydrophobicity and the movement of hydrophobic material during the continuous wetting and drying cycle

A.1 Introduction

The coating of soil particles by hydrophobic substances delayed the water infiltration into the soil and consequently lowers the wettability of the soil (Muller et al., 2018). Many authors suggested that the increase in soil water repellency increases the risk of surface runoff and overland flow (Ferreira et al., 2016; Gomi et al., 2008b; Keizer et al., 2005; Miyata et al., 2010). Doerr et al. (2000) also pointed out that the soil water repellency caused preferential flow and could result in the leaching of repellent substances through the finger pathways. However, the understanding of the breakdown process of soil water repellency is still poor (Doerr et al., 2000).

. For example, Muller et al. (2018) studied runoff and nutrient loss from repellent soil. According to their outcomes, surface runoff had minor impacts on the breakdown of soil water repellency. Besides, Bisdom et al. (1992) reported that the soil water repellency could be reduced by decomposition of organic matter or dissolving organic matter in hydrogen peroxide. Moreover, it is widely accepted that the soil water repellency degree was closely related to the soil moisture (Li et al., 2018; Doerr and Thomas., 2000). During the wetting and drying cycles, with the increase in soil moisture content, the hydrophobicity decreases. However, when the soil moisture content dropped below the critical point, the hydrophobicity will re-appear (Doerr

and Thomas., 2000). Moreover, many studies used the liquids that could dissolve the hydrophobic substances to study the breakdown process of soil water repellency (Clothier et al., 2000; Muller et al., 2018; Bisdom et al., 1992). The outcome of those studies indicated the breakdown of repellency associated with the dissolution of hydrophobic material.

A rainfall simulation experiment was suitable for study soil processes under the controlled water input (Meyer, 1994). This concept was intensively used in the field trial on soil water repellency (Muller et al., 2018). However, many researchers conducted rainfall simulation in the studies of runoff and erosion in water repellent fields (Gomi et al., 2008b; Leighton-Boyce et al., 2007; Muller et al., 2018). The water input for generating runoff must exceed the infiltration rate (Muller et al., 2018). However, the rainfall simulation for the runoff experiment cannot fit into the natural conditions if the precipitation amount is not enough to generate runoff (Jordan et al., 2009). Therefore, to study the dynamic of hydrophobicity under the continuous wetting and drying event, the concept of rainfall simulation will be used.

In this study, extremely and strongly repellent soil was used to identify the dynamic changes of hydrophobicity under the wetting and drying event. The main objectives were (i) to quantify the hydrophobicity changes after the wetting and drying cycles, (ii) to generate an insight into the movement of hydrophobic material within the soil under the wetting and drying event.

A.2 material and method

A.2.1 Soil description

In this study, TW and R series of soil were collected in 2019 by Bayad et al. (2020), and MB samples were collected in 2014 by Whitley. (2018). The soil order of the R samples was

Pallic soil, TW sample was Pumice soil, and the MB samples were Brown, Pallic and Pumice soil. Table 12 showed the soil order, soil type and chemical detail of samples, and Table 13 showed the soil texture information.

Table 12. The information about soil samples. Retrieved from Bayad et al., 2020 and Whitley, 2018

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Table 13. The soil texture information Retrieved from Bayad et al., 2020.

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The soil cores were oven-dried and ground, then disturbed soil sample passed through a 2-mm sieve. The actual persistence of soil water repellency was measured by WDPT method and carried out through every wetting and drying cycle.

A.2.2 Set up

Whatman No.2 110 mm diameter papers were used. The filter paper was widely used for liquid adsorption and solid and liquid separation (Du et al., 2014). The filter paper was folded to fit the shape of the funnel. Then, soil samples were placed in the funnels, which were covered by filter paper. The water input amount was 15 mm per square meter, equal to 29 ml for 0.00196 m². The water was applied in the middle part of the sample surface to allow the soil samples to wet up. Samples were left in the laboratory draining freely and air drying at 25 degrees. After the drying process, the WDPT result was recorded, and the wetting process was reapplied.

Diagram of apparatus setup

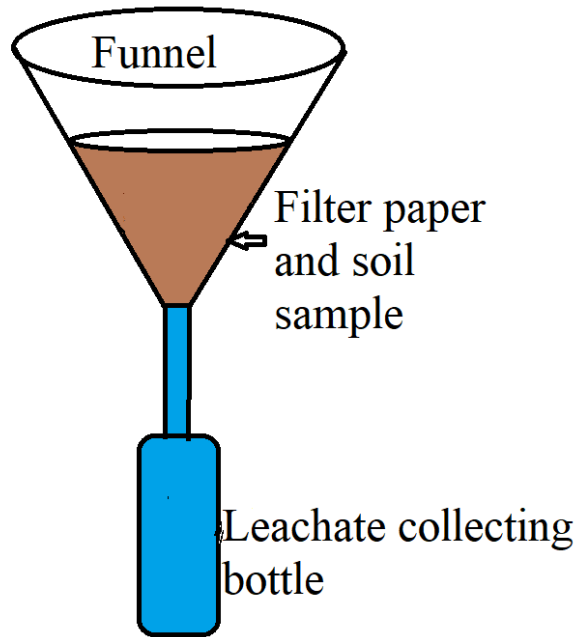


Figure 33. The diagram of the leaching experiment setup

A.3 Result

Table 14 showed the initial and final WDPT results. It was indicated that after ten times wetting and drying events, the decreased rate of hydrophobicity in all samples ranged from two times to thousands of times.

Table 14. The initial WDPT result and Final WDPT result

Sample	Initial WDPT	Classification	Final WDPT	Classification
MB2	5248s	Extreme	1 s	Wettable
MB3	5888s	Extreme	83.2 s	Slight
MB6	691s	Strong	1 s	Wettable
MB7	7762s	Extreme	1 s	Wettable
MB8	72.44s	Slight	38.8 s	Wettable
TW4	467.7s	Slight	168.2 s	Slight
R3	3548s	Extreme	94.8 s	Slight
R4	1288.2s	Strong	37.8 s	Wettable
R6	138s	Slight	75.6 s	Slight
R7	58.88s	Slight	9.2 s	Wettable

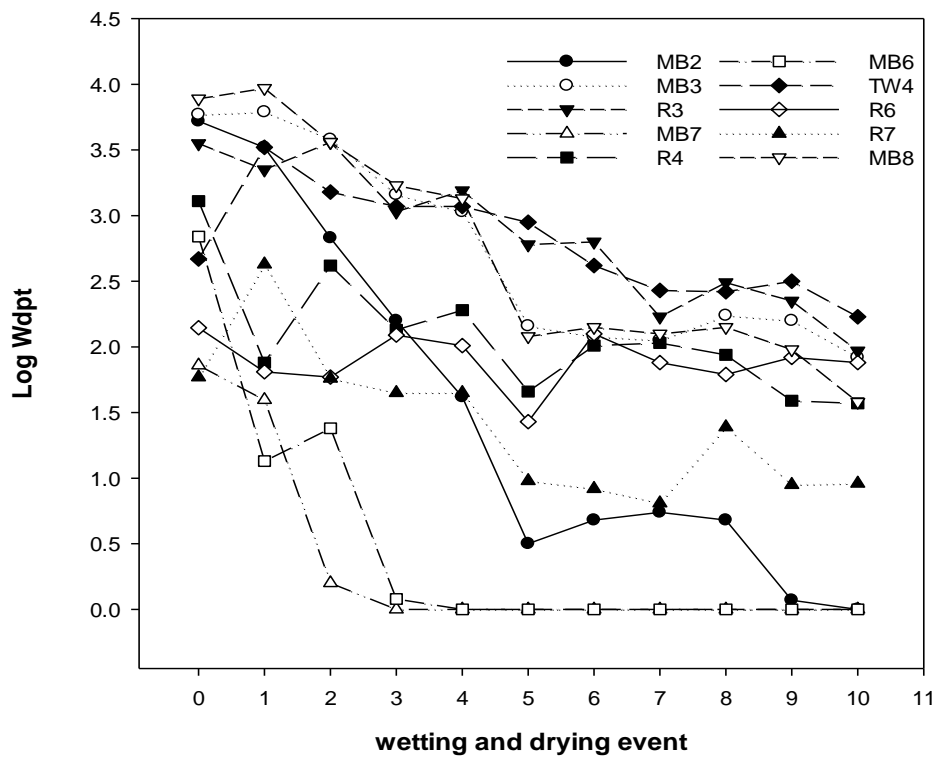


Figure 34. The WDPT change after 10 times of wetting and drying events.

Figure 34 showed hydrophobicity of all samples during ten times wetting and drying cycle. After ten times of water input, the hydrophobicity of all the soil decreased. The hydrophobicity in R3, R4 and MB 2 dramatically reduced to 0, which meant the WDPT result was equal to 1s or less after ten times of wetting and drying event. The hydrophobicity of the rest samples descended to a lower level after ten times of events (the highest WDPT was 318 s).

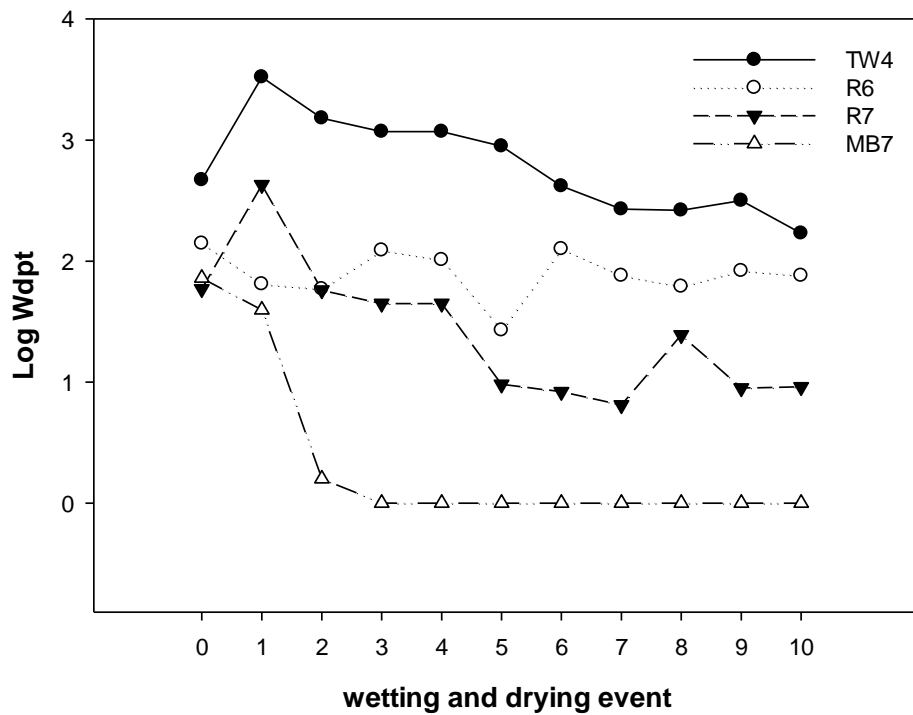


Figure 35. The hydrophobicity changes within the strongly repellent soil sample after 10 times wetting and drying events.

The actual hydrophobicity of the most strongly repellent soil MB7 decreased from 7762 s to 1 s (figure 35). The R7 has the lowest initial WDPT value with 58.88 s after ten times of wetting and drying cycle, and this value decreased to 9.2 s. The final WDPT (after ten times of event) of R6 and TW4 were almost half of the initial WDPT result with 75.6 s and 168.2 s, respectively.

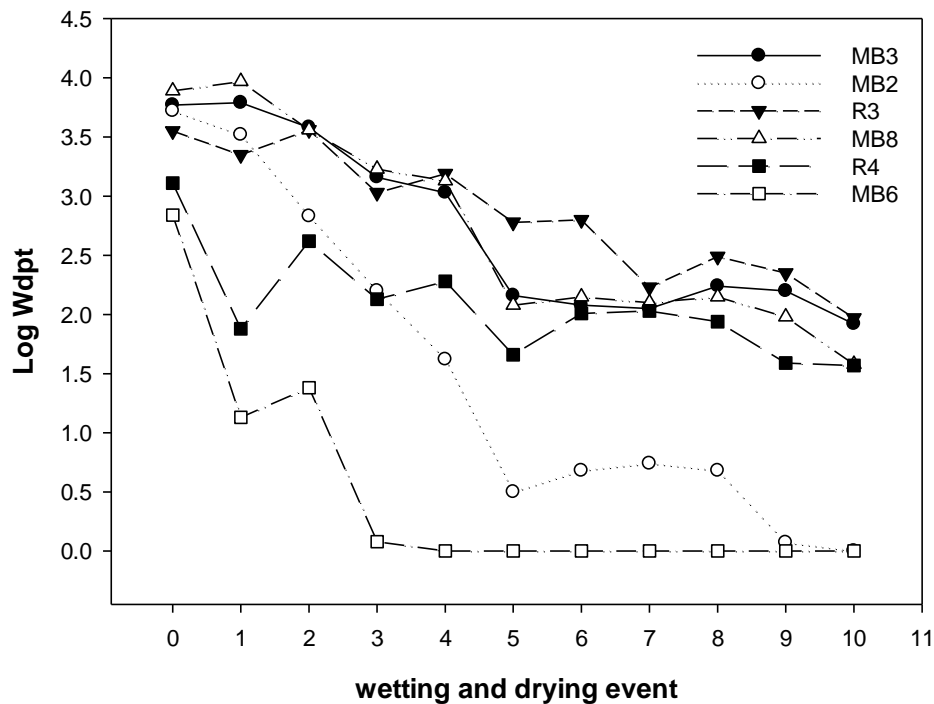


Figure 36. The hydrophobicity changes within extremely repellent soil samples after 10 times wetting and drying events.

The most significant change of hydrophobicity appeared in extremely repellent samples (figure 36). After ten wetting and drying cycles, three soil samples (MB6, MB7 and MB2) became hydrophilic, and the WDPT result was 1 s. Furthermore, other repellent samples' actual degree of hydrophobicity descended from extreme to strongly class (WDPT result less than 600 s).

A.4 Discussion

A.4.1 The movement of hydrophobic substance

The overall change of wettability within repellent samples was due to the leaching of hydrophobic material. Muller et al. (2018) theorized that the hydrophobic material was leached and consistently lowered after all runoff events during the rainfall event. Furthermore, Doerr et al. (2000) stated that the water-repellent substances could leach through the finger pathways

and speculated by Ritsema et al. (1998a). The latter have observed the rewetting of existing flow pathways or fingers in repellent soil was because of the leaching of hydrophobic substances from the pores along the finger flow pathways. One of the observations of this study also found that the surface of filter paper used to filter soil samples showed hydrophobic behaviour after drying.

Moreover, this observation and the runoff result from Muller et al. (2018) indicated that the movement of hydrophobic material during the wetting period was vertical. In vertical flow, the leaching of hydrophobic substances through finger flow pathways leads to the development of permanent flow pathways (Hardie et al., 2012). However, Muller et al. concluded that there was no direct link between the breakdown of repellency and washout of hydrophobic material during the repeated runoff events. The higher persistence of soil water repellency caused a longer delay in infiltration leading to longer water ponding (Doerr and Moody., 2004). The water ponding would result in the reconfiguration, leaching or washing out of hydrophobic substances (Urbanek et al., 2015).

A.4.2 The relationship between the breakdown of repellency and soil texture

Soil texture and organic content played an essential role in the development of soil water repellency (Doerr et al., 2000). Coarse textured soil typically was considered to be easier for developing soil water repellency due to its smaller surface area of particles (Debanno, 1991; Doerr et al., 2000). However, when the soil water repellency was overcome, the coarse-textured soil could be highly permeable (Urbanek et al., 2015). According to the present results, three sandy soil samples (MB6, MB7 and MB2) reached the thoroughly wettable class. After four wetting and drying events, the WDPT result of sandy texture samples MB6 and MB7 become

1s. In contrast, the hydrophobicity of the MB2 sample with a clay loam texture reduced gradually and after nine times wetting and drying event became fully wettable. Hardie et al. (2010) reported that the hydrophobic substances leached during the sequential leaching experiment, and the repellency level did not return.

Sand and clay content could also affect the soil water repellency. DeBano (1991) concluded that the soil water repellency was prone to develop in soil contained less than 10 % clay content. Additionally, adding dispersible clay to a sandy soil can reduce water repellency effectively (Cann and Lewis, 1994; Carter and Hetherington, 1994). Mckissick et al. (2002) also concluded that some clay became mobilised during the wetting and drying cycle and coated the sand grains, and eventually reduced the soil water repellency. Those findings might explain the MB2 with extreme hydrophobicity but could be wettable after ten times of wetting.

A.4.3 The effect of wetting and drying cycle on water repellency

Besides, the wetting and drying event could reduce water repellency alone. Table A.3 showed an exact comparison between the initial and final WDPT results. The wetting and drying cycle tended to reduce the hydrophobicity of fine sand than coarse sand (Mckissick et al., 2002). In the field condition, the water repellency tended to be seasonal and decrease in winter due to the heavy rainfall and higher soil moisture content (Doerr et al., 2000).

Another important reason for reducing soil water repellency during the wetting and drying phase could be the changes in the conformation of organic molecules that render them hydrophilic (Mckissick et al., 2002). Additionally, some soluble organic matter also contributed to the breakdown of soil water repellency. Horne and McIntosh (2000) reported that when they

added some water-soluble humic components extracted from repellent soil into repellent sand, the hydrophobicity of repellent sand was reduced.

A.5 Conclusion

During the continuous wetting and drying cycle, the hydrophobicity of soil samples declined due to the vertical movement of hydrophobic substances. After the wetting and drying process, the hydrophobic substances accumulated on the surface of filter paper and the extremely repellent clay loam sample (MB2) reached full wettable, indicating the clay content also plays a significant role in the breakdown process of soil water repellency. Although other repellent samples did not become wettable, the tendency of the hydrophobicity reduction showed that the hydrophobic compounds could leach during the wetting phase.

A further experiment is required to analyse leachate from repellent soil during the wetting phase to generate a better understanding of the breakdown of water repellency in the chemical aspect.

A.6 References

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