

**INFLUENCE OF VARIOUS WETTING AGENTS ON WATER
STATUS IN USGA GREENS AS DETERMINED BY THEIR
PHYSICAL PROPERTIES**

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By
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dissertation entitled:

**INFLUENCE OF VARIOUS WETTING AGENTS ON WATER
STATUS IN USGA GREENS AS DETERMINED BY THEIR
PHYSICAL PROPERTIES**

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a candidate for the degree of Doctor of Philosophy,
and herby certify that, in their opinion, it is worthy of acceptance.

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DEDICATION

First and foremost, I would like to thank and dedicate this dissertation to my mom and dad. Throughout my life you have always been my greatest supporters in all of my endeavors. When no one believed in my abilities or intelligence, I could always count on you both to be there for me. At any time, I could call you and count on your wisdom and motivation to push me through the difficult times and keep me striving to achieve my goals. Even when I debated quitting, you pushed me to continue pressing on to achieve a goal that no one thought I could ever do. I can never repay you for your unwavering compassion, strength and motivation over the past 10 years of my college career and throughout my life. Thank you, mom and dad, for being the who I look up to and strive to be day in and day out.

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DISSERTATION ABSTRACT

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Soil hydrophobicity is an increasing issue in sandy soils, affecting agricultural land and golf courses. This phenomenon causes water repellency and bypassing of hydrophobic root zones, limiting water accessibility. Due to golf course putting greens utilizing a sand-based rootzone, soil water repellency commonly occurs, leading golf course superintendents to apply wetting agents to mitigate its effects. Over 75% of the wetting agents currently on the turfgrass market do not list their active ingredients, which limits the predictability of their performance in the rootzone.

These studies investigated how various wetting agents influence water's physical properties, such as surface tension (γ), to predict the effect of wetting agents on water infiltration or retention. The determination of the γ of 23 different wetting agents led to the hypothesis that wetting agents with γ values ≤ 30 mN m⁻¹ have greater influence on water infiltration; those between 30 to 40 mN m⁻¹ influence both water infiltration and retention; and those ≥ 40 mN m⁻¹ have greater influence on water retention. Three studies were conducted based on the surface tension categories to determine a correlation between: 1) selected wetting agents' water infiltration and rewettability into water-repellent sand; 2) to evaluate selected wetting agents' influence on water infiltration and retention under field conditions; and 3) to determine selected wetting agents' influence on water movement and leaching through water-repellent sand utilizing a soil water tracer. Our results contradicted our original hypothesis that γ alone cannot be utilized to predict a

wetting agent's functionality, however demonstrated that other factors need to be assessed.

Abbreviations and key words: infiltration; leaching; rewettability; soil hydrophobicity; soil water tracer; γ , surface tension; water movement; water repellency; water retention; wetting agent

CHAPTER I

Literature Review

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Introduction

Over the last century, golf course superintendents and soil scientists found that they needed to address the gradually worsening issue of soil hydrophobicity (Dekker et al., 2005). Research efforts have been increasing since 1980, as publications on soil water repellency have nearly doubled worldwide (Dekker et al., 2005). Soil water repellency has been cited in the United States, New Zealand, Europe, Canada, and Australia, where over 5 million hectares of agricultural land have developed soil water repellency, reducing the overall crop yield (Dekker et al., 2005; Franco et al., 2000; Roper, 2006). In addition to agricultural land, soil water repellency affects golf courses, coastal land and pastures (Wallis & Horne, 1992; Doerr et al., 2006).

Soil water repellency is the inability of water to wet a soil due to hydrophobic organic coatings covering the surface of a soil particle. Research has shown that these hydrophobic organic materials can originate from many sources, including plant root and soil microbe exudates, or degradation of waxy cuticles from the leaf surface (Mainwaring et al., 2004; Hallett et al., 2006). Soil hydrophobicity has developed into a reoccurring issue for golf course superintendents due to the 12-inch sand rootzone found under most United States Golf Associations (USGA) putting greens (Hummel, 1993). Sandy soils

are most prone to develop soil hydrophobicity due to the low specific surface area of sand, which allow hydrophobic molecules to completely cover the soil particle, resulting in a water repellent soil (Woche et al., 2005; Hallett, 2008). Additionally, water repellent soils tend to develop irregular infiltration patterns (Wang et al., 2000). These irregular infiltration patterns create preferential flow or fingering, a process where water moves unevenly and faster throughout the soil profile (Wang et al., 2000). Together, these factors contribute to localized dry spot (LDS), which is a major problem for golf courses (Karnok & Beall, 1995). LDS leads to non-uniform patches of wilted or dead turfgrass that causes poor playability and is visually unappealing (Tucker, 1990). Soil hydrophobicity is the underlying cause of these issues.

Different remediation methods have been implemented to relieve hydrophobicity in soil media (Hallett, 2008). These include biological control methods, such as the addition of wax-degrading bacteria to consume hydrophobic materials on soil particles or physical control methods by tilling the soil and removing the hydrophobic coatings from a soil particle (Buczko et al., 2006; Roper, 2006). In addition to biological and physical control, wetting agents are a chemical technique that have quickly become widespread in ameliorating soil water repellency. It is estimated that approximately 80% of golf course superintendents have adopted the use of wetting agents to alleviate soil hydrophobicity and consequently increase soil water infiltration and retention (Franklin et al., 2005; Karnok et al., 2004). However, there is still a gap in the understanding of the principles surrounding wetting agents and their effect on soil water repellency, infiltration and water retention.

Physical Characteristics of Water

To understand the origin of water repellency, it is necessary to understand the concept of water relations. Molecules are either polar, having either a positive or negative charge, or non-polar, having zero positive or negative charge. Water molecules are comprised of two hydrogen atoms and one oxygen atom held together by covalent bonds. In addition, water is a dipolar molecule, which refers to having both a partial positive and negative electrical charge (Parker, 1987). This dipolar configuration is responsible for the essential physical property of water known as hydrogen bonding (Doerr et al., 2000). Hydrogen bonding results from the attraction of the positively charged hydrogen end to the negatively charged portion of another molecule, such as the negatively charged oxygen end of another water molecule. Water is attracted to other water molecules by a cohesive attraction, while water is either attracted or repelled from a solid surface by an adhesive attraction. Water will adhere to a variety of solid surfaces as they consist of positively and negatively charged ions attracting the polar water molecule (Doerr et al., 2000). Due to this dipole attraction, when a water molecule is surrounded by other water molecules, there is a net zero charge within the liquid. When the boundary of the liquid is reached, the surface water molecules are strongly attracted toward the other interior molecules which reduces the overall surface area of water. This strong attraction to the interior water molecules causes a strain on the attraction between the surface water molecules, referred to as surface tension (Parker, 1987). Water has an exceptionally high surface tension value of 72.8 mN m^{-1} . The concept of surface tension results in the classic spherical droplet shape seen on a solid surface (Doerr et al., 2000).

For a water droplet to spread on a solid, the adhesive forces between the solid and the water need to exceed the cohesive forces present within the water itself. The surface

tension of a solid needs to be greater than 72.8 mN m^{-1} , making most surfaces naturally hydrophilic (Doerr, 2000; Parker, 1987). Surface tension values of most solids range from 500 to 5000 mN m^{-1} (Zisman, 1964). However, organic polymers and waxes that may coat a solid surface have naturally lower surface tension values than water, less than 72.8 mN m^{-1} . If a surface is coated with these organic polymers or waxes, the cohesive forces within the water droplet are not broken and the water molecule will not spread across the solid surface (Zisman, 1964). Resulting in the once naturally hydrophilic solid surface becoming an altered hydrophobic surface, leading to the concept of water repellency.

Origin of Water Repellency

Soil water repellency (SWR) is the inability of a water molecule to naturally wet a soil particle due to a monolayer or multiple monolayers of hydrophobic organic molecules coating the surface of the soil particle (Doerr et al., 2000; Tucker et al., 1999; Wilkinson and Miller, 1978). These organic coatings consist of amphiphilic molecules which contain both a polar, hydrophilic water loving region and a non-polar, hydrophobic water repellent region (Karnok et al., 2004; Müller & Deurer, 2011). These organic molecules adhere their polar, hydrophilic region to the naturally hydrophilic soil particle, thereby orienting their non-polar, hydrophobic region into the soil pore. Due to the lack of an attractive charge, soil water molecules are repelled from the soil particle, resulting in the phenomena of SWR.

When SWR is seen in soils, it is mostly associated with more sandy soils. This is due to sand particles having the lowest specific surface area, causing hydrophobic organic materials to have a much greater impact and induce SWR more easily,

particularly when compared to silt or clay particles (Woche et al., 2005). A study by Ma'shum et al. (1988) found that to induce SWR in a sandy soil, only 0.35 g of hydrophobic materials were needed to induce severe water repellency in 1000 g of medium-sized sand displaying that very little organic material needs to be present in a sandy soil type to induce SWR.

In the early 1940's to the 1950's, soil water repellency started gaining recognition throughout the world (Dekker et al., 2005). Jamison (1947) described how sandy soil under his citrus trees resisted wetting and decreased the yield in his orchard. From then, reports began to arise about difficult-to-wet soils in the Netherlands and New Zealand, presumably due to organic coatings on soil particles which reduced the wettability of the soils (Domingo, 1950; Van't Woudt, 1959). Bond (1964) discovered that sandy soils in Australia developed water repellency due to filamentous algae and fungi production from *Basidiomycetea*. This disease causes uniform rings of increased grass growth due to nutrient accumulation, but is also accompanied by a zone of water repellency due to the fungi spreading throughout the soil (Scheffer and Schachtschabel, 1989). These fungi have also been associated with the decomposition of plant litter, resulting in the excretion of hydrophobic compounds as it moves through the soil profile (Scheffer and Schachtschabel, 1989). As the fungal hyphae expand, they excrete exudates containing non-polar hydrophobic molecules, which bind to the soil particle and render it hydrophobic (Hallett, 2007). Due to the lack of charge from non-polar hydrophobic coatings surrounding a sand particle, a polar water molecule would not adhere to the soil particle and be utilized by the plant (Spindler, 2016). The USGA putting greens are extremely prone to develop water repellency due to the use of a sand-based rootzone

(Hallett et al., 2001a). Due to the small specific surface area and resulting pore sizes of sand rootzones, growing conditions are much better for fungi than bacteria, allowing the fungi to thrive (Hallett, et al, 2001a).

Water repellency has also been associated with the decomposition of plant tissue and surface wax of leaves (Doerr et al., 2000; Hallett, 2007). As plant matter degrades, such as leaf tissue or root biomass, hydrophobic materials from the surface waxes are incorporated into the soil, becoming a potential source of water repellency. Plants most associated with causing water repellency in soils are evergreen trees due to the abundant amount of resins, waxes and aromatic oils that are present (Doerr et al., 2000). Grasslands and turfgrasses have also been shown to develop SWR. Intensely managed turfgrass, such as creeping bentgrass (*Agrostis* spp.), commonly display SWR which is attributed to decomposing plant tissues, fungal, root or microbe exudates (Karnok et al., 1993; York, 1993).

Plant root and microbial exudates have been attributed to contribute toward the development of SWR (Mainwaring et al., 2004). Within the rhizosphere, the roots and microbes can release exudates to increase surrounding nutrient availability (Hallett et al., 2003; Hallett, 2007). In addition, plant roots release hydrophobic substances in the soil, such as allelopathic chemicals, which suppress competing vegetation from germinating and induce hydrophobicity at the soil surface. Leading to the reduction of evapotranspiration, driving water deeper in the soil due to preferential flow pathways, which adds to the hydrophobicity of the soil (Moore and Blackwell, 1998; Scott, 1992). Doerr et al. (1998) conducted a study looking at the effects of eucalyptus (*Eucalyptus globulus*) roots on the development of hydrophobicity in sandy loam or loamy sand soils.

Hydrophobicity was assessed at 15 locations where root networks had developed and 15 locations where the soil was root free to test the resulting level of SWR based on the molarity of ethanol droplet test (MED) values. All locations were deep-plowed, generally resulting in hydrophilic soils. Soils that did not contain roots produced an average soil MED of 3, or slightly hydrophobic, while soil containing roots produced an average soil MED of 6, or very strongly hydrophobic (Doerr et al., 1998). Root and microbial exudates are hydrophilic in wet soil until the soil dries past the critical moisture content. This forces the hydrophilic molecules to bind with adjacent hydrophilic molecules on the soil particle. This orients the hydrophobic region of the molecule toward the soil pores, causing the soil particle to become hydrophobic (Dekker et al., 1998). In this process, water is repelled from the hydrophobic soil particles and SWR inevitably develops. Therefore, shifts in the water content of a soil greatly affects the wettability of a soil (Dekker et al., 2001).

Soil organic matter (SOM) and soil organic carbon (SOC) content within a soil have also been associated with the development of SWR. The SOC is the representative carbon fraction in the soil that is derived from the organic compounds and comprise roughly 58% of the SOM mass (Hoyle, 2013). A major fraction of SOC that has been associated with the development of SWR is humic organic carbons (HOC). This fraction of SOC consists of older, decayed organic compounds which have resisted decomposition (Hoyle et al., 2006) and are partially comprised of humic and fulvic acids (Miller and Wilkinson, 1977; Robers and Carbon, 1972). Humic acids (HA) are large carbon molecules that are soluble in water under alkaline conditions, while fulvic acids (FA) are smaller carbon molecules that are soluble regardless of the pH in the soil (Sutton and

Sposito, 2005). These organic acids contain carboxyl (-COOH), and phenolic hydroxyl (-OH) functional groups, making these primarily hydrophilic (Chen and Schnitzer, 1978; Karnok et al., 1993). However, when this humic matter undergoes dehydration in the soil, protons are shared with the adjacent -COO and -OH groups, creating a nonpolar, hydrophobic surface which induces SWR (Karnok et al., 1993; Tan, 1982).

Water Repellency Classification

In 1962, research describing procedures to measure the liquid-solid contact angle of sand and soil was reported. These procedures describe the influence of liquid-solid contact angle on the movement of water through soil, which became a way to characterize water repellency (Letey et al., 1962 a & b). Since then, the relationship between liquid-solid contact angle and water infiltration has become a point of interest (Carrillo et al., 1999).

With the interest in SWR growing globally, the first international meeting on soil repellency was held in 1968 at the University of California, Riverside (DeBano, 1969; Letey, 1969). Topics related to water movement through soil, the distribution of SWR through environments and the effect of wetting agents on SWR were all discussed to better understand the growing interest in SWR (DeBano, 1969; Letey, 1969). To date, characterizing water repellency is still a large area of interest for researchers.

To characterize water repellency more effectively, a relationship between the liquid-surface tension and liquid-solid contact angle were established (Watson and Letey, 1970; Watson et al., 1971). Other methods developed for quantifying the severity of water repellency included the water drop penetration test (WDPT) and the molarity of ethanol droplet test (MED), both of which are still utilized today (King, 1981; Letey,

1969; Wessell, 1988). The WDPT determines water repellency by placing 40 μ L droplets of water on a soil surface and timing how long it takes to penetrate the soil surface. King (1981) described a longer droplet penetration time, and indicates a higher level of water repellency, ranging on a scale from not significant to moderate. King (1981) only measured for 4 minutes after the droplets were placed on the soil surface, not allowing him to classify higher severity levels of water repellency. This differed from Letey (1969), who initially developed the WDPT to separate soils into groups having a contact angle either below or above 90°, while King's (1981) method classifies different levels of severity. Bisdom et al. (1993), based his work off King (1981) and Letey (1969), classifying higher levels of water repellency using WDPT beyond 4 minutes. Using a sandy soil, five classifications for water repellency were created: wettable (<5 s), slightly water repellent (5-60 s), strongly water repellent (60-600 s), severely water repellent (600-3600 s), and extremely water repellent (> 3600 s) (Bisdom et al., 1993). This WDPT classification of water repellency is still used today.

Similarly, King (1981) adapted the MED method Watson and Letey (1970) developed by creating ethanol concentrations that increased by intervals of 0.2 M in a range between 0 and 5 M. The levels of water repellency can then be determined by placing 40 μ L droplets of the various ethanol concentrations on the soil surface and increasing the concentrations until the droplet penetrated into the soil. The MED value of a soil is determined by the lowest concentration of ethanol that penetrates the soil within 5 seconds. King (1981) then created MED classifications: not significant or very low (0 MED), low (0 to 1.0 MED), moderate (1.2 to 2.2 MED), severe (2.4 to 3.0 MED) and very severe (≥ 3.2 MED). As WDPT and MED use different classifications, comparison

of water repellency between the two methods can be difficult and inaccurate (Doerr, 1998). King (1981) made correlations between the WDPT and MED values he derived. However, due to King (1981) not performing the WDPT past 4 minutes, MED values above 1.6 M had no correlation. King (1981) determined that 8 to 53 seconds correlated to the 0 to 1.0 M MED values, and 85 to 260 seconds correlated to MED values 1.2 to 1.6 M. Doerr (1998) then standardized both methods to increase the comparability between the two methods. He took 176 soil samples which were collected from sandy soils and soils afforested by pine (*Pinus pinaster*) and eucalyptus (*Eucalyptus globulus*) trees and conducted a laboratory study comparing WDPT and MED values. Both WDPT and MED were conducted on the same soil sample and on the same day to maintain environmental conditions. A correlation coefficient of 0.73 ($p < 0.01$, $n = 176$, Spearman Rank correlation) determined higher MED values and higher WDPT values strongly correlated with each other (Doerr, 1998). The MED values of 3.4 to 4.4 M correlate to >1 hr or severely water repellent, and MED values of >4.6 M correlate to >5 hr or extremely water repellent (Doerr, 1998; King, 1981). Correlation is inconsistent for a WDPT time between 600 to 3600 s, due to variability in samples collected (Doerr, 1998). A disadvantage to using the WDPT is the time intensive procedure to determine more severe water repellent soils (Hallett, 2007).

Another method of measuring water repellency is the intrinsic sorptivity method created by Tillman et al. (1989). Sorptivity is the effect of liquid movement into a porous material, like soil, due to capillarity (Culligan et al., 2005). This method compared the sorptivity of water, affected by repellent soil, to the sorptivity of ethanol, which is not affected by repellent soil. This method determines a water repellency index based on the

sorptivity difference of the two liquids using a physically meaningful measurement, while bypassing the need for a geometric measurement of contact angle. However, unlike the previous methods, the limiting factor of this test is the difficulty in measuring sorptivity in the field (Tillman et al., 1989).

Alternative Amelioration

Through the years, different amelioration methods to amend SWR were assessed. Indirect strategies, including physical solutions such as tillage, have been used to reduce SWR. Research has shown that disruption of soil particles by tilling can physically remove hydrophobic coatings from soil particles (Buczko et al., 2006). Soil aeration also can be implemented to reduce soil water repellency. Aeration assists in the breakdown of thatch, potentially removing some hydrophobic soil, and consequently improving water infiltration (Müller & Deurer, 2011). In addition, by adding clay to the soil, the overall surface area of the soil profile can be increased. Increasing the surface area of the soil decreases the effect of hydrophobic molecules, reducing the overall soil water repellency (Lichner et al., 2002).

Wax degrading bacteria are known to produce biosurfactants, which can break down waxes that coat soil particles (Roper, 2005). McKenna et al. (2002), attempted to utilize actinomycetes biosurfactant production to reduce SWR, as they are able to consume a wide range of organic material as a source of carbon for energy and growth (Müller and Deurer, 2011; Williams et al., 1989). This led Roper (2004) and Dunkelberg et al. (2006), to isolate wax degrading bacteria from natural water repellent sandy soils and expose these bacteria to a variety of hydrophobic compounds, such as wool wax, sewage sludge, and animal fats (Müller and Deurer, 2011). In these Australian soils, 37

different wax degrading bacteria were identified. Four of the cultures were inoculated into bags in a high concentration of 10^{10} cells kg^{-1} of soil, containing grey sand with a 3.9 MED water repellency (Roper, 2004). Over a period of 250 days, the MED was measured throughout to assess the effectiveness of the wax-degrading bacteria treatments. Three of the treatments resulted in a reduction in MED value, with a *Rhodococcus* spp. isolate reducing the MED value by 74.4% to a value of 1 over 150 days (Roper, 2004). Two other isolates, another *Rhodococcus* spp. and a *Mycobacterium* sp., resulted in a 61.5% reduction in MED values, to <1.5 after 250 days (Roper, 2004). However, the last isolate, a *Nocardia* sp., did not significantly reduce the water repellency of the grey sand when compared to the control, which only had deionized water added (Roper, 2004).

Roper (2007) investigated the mechanisms by which these wax degrading bacteria reduce the overall SWR and determined two underlying mechanisms. One mechanism relating to bacteria with hydrophobic cell surfaces, such as *Streptomyces* spp. and *Mycobacterium* spp., while the other is related to bacteria that produce biosurfactants, such as *Rhodococcus* spp. (Müller and Deurer, 2011). She explained the first mechanism, which occurs from bacteria with hydrophobic cell surfaces, relates to when sands are wet. These bacteria live at the air-water interface as compared to hydrophilic cell surface bacteria which are suspended in the aqueous soil solution (Roper, 2007). When the wet sands undergo drying, the hydrophilic bacteria are moved to the pore spaces, while the hydrophobic bacteria, such as actinobacteria, are drawn to the soil particle surface and go into a resting period where spores are formed to allow them to survive the hot dry conditions. During these hot and dry conditions, new waxes are formed, either by organic matter or plant material, which adhere to the soil particles and induce SWR, creating

preferential flow patterns in the soil. Once these soils are rewet and water reaches these hydrophobic bacteria adhering to the soil surface, they are reactivated and utilize the hydrophobic wax coatings as a source of carbon for energy. They then continue to consume these hydrophobic coatings and result in the amelioration of SWR (Müller and Deurer, 2011; Roper, 2007). The second mechanism described by Roper (2007) which related to the production of bacterial biosurfactants from *Rhodococcus* spp., is based on these bacteria's response to non-polar alkanes on the soil surface. These bacteria will produce a biosurfactant to improve their ability to utilize hydrophobic materials as a growth substrate (Lang and Philp, 1998; Müller and Deurer, 2011; Roper, 2007; Walter et al., 1991). The biosurfactant production leads to an increase in the aqueous solubility of hydrophobic compounds, releasing the waxy hydrophobic coatings from the sand particle surface (Müller and Deurer, 2011; Roper, 2007). The bacteria produced biosurfactant is composed of trehalose-based glycolipids, which are among the most potent biosurfactants known (Lang and Philp, 1998; Müller and Deurer, 2011). However, the ability of these various wax degrading bacteria to be effectively utilized as a bioremediation source of SWR relies on the population sizes present in the soil (Roper and Gupta, 2005).

Application of lime to soil has also been found to reduce SWR. It is postulated that increasing the soil pH to a more favorable level would increase the activity and population of soil microbial communities, and hence facilitate break-down of the organic coatings that cause water repellency (Kennedy et al., 2004; Lupwayi et al., 2009). Roper (2005) also found that the addition of lime to soils will decrease SWR over time due to an increase in microbial activity. The addition of lime to a white sand soil increases the soil pH, leads to the increase of wax degrading bacteria and decreases SWR. Before

application of treatments, the soil tested had severe water repellency (MED ~4.0). Varying rates of lime (laboratory grade CaCO_3) were applied at 0, 5, 10, and 15 (t/ha). Applications of lime at higher rates resulted in a 10-fold increase in population of wax degrading bacteria within the soil, determined by a Most Probable Number (MPN) assay, resulting in a reduction in the MED value within treated plots from 4.0 to <2.0. In addition, all application rates of lime increased the soil pH from ~4.7 to >6.8. Roper (2005) reported effects of the lime addition was a two-phase response; first being the rapid interaction of the lime with the hydrophobic surfaces of the sand particles, followed by the increase of wax degrading bacteria which increased the degradation of hydrophobic compounds coating the sand particles (Müller and Deurer, 2011). Her research suggested that the application of lime could be used as a biological technique to reduce water repellency in soils due to the lime's ability to increase the amount of wax degrading bacteria present in the soil (Roper, 2005).

Roper (2006) supported her laboratory results by performing a similar field experiment, where plots were exposed to the inoculation of various actinomycete strains (*Rhodococcus* spp.) only or by the inoculation of the same actinomycete strains with the addition of lime and controls. In plots with inoculation of actinomycetes and addition of lime at rates between 3 to 15 t ha⁻¹, a significant reduction of SWR occurred, as compared to the non-limed, bacteria inoculated plots. This was due to the significant interaction between the addition of lime and the increase of wax degrading bacteria populations (Roper, 2005). Certain actinomycete strains were able to reduce the MED value by 8.4% or greater when the addition of lime was present versus absent (Roper, 2005).

The use of a strong inorganic alkali, such as sodium hydroxide (NaOH), which potentially dissolves and flushes out the organic coatings, such as FA, from the soil has been studied (Karnok et al., 1993). Karnok et al. (1993) was the first to report applying a 0.1 M NaOH solution to a 'Penncross' creeping bentgrass (*Agrostis stolonifera* L.) turf. Consecutive applications of NaOH flushed with water or water only at 3, 6, and 9 days after treatment (DAT) were evaluated to determine the reduction of water repellency within the soil. After applying NaOH for 6 to 9 consecutive days, the MED values were reduced by 82% or greater, and in some cases were completely eliminated. However, the risk associated with this approach is the phytotoxicity that the inorganic alkali could have on creeping bentgrass on putting greens or tee boxes, limiting the number of superintendents who would utilize this technique (Karnok et al., 1993). Although Karnok et al., 1993 did not rate phytotoxicity throughout his study, however, he theorized it could be a potential negative effect.

Another amendment tests the addition of clay during the construction of the sand-based rootzone to increase the overall surface area of the soil (Dlapa et al., 2004; Wallis & Horne, 1992). Clay reduces SWR by masking the hydrophobic coating effects, due to most clay minerals being naturally hydrophilic, and having a large specific surface area (Blackwell, 2000; Tschapek, 1984). Dlapa et al. (2004), described adding different percentages of kaolinite or Ca-montmorillonite clays to water repellent sand and assessed their ability to reduce water repellency. Clays were added at 1, 2, and 3% of the water repellent silica sand mass and mixed on a shaker table before performing the WDPT to measure the level of water repellency. Results showed that the addition of kaolinitic clay at all percentages, reduced the WDPT by 7-fold or greater from the control (Dlapa,

2004), while the addition of Ca-montmorillonite increased the WDPT by a maximum of 24.5% (Dlapa, 2004). This research signified that correct utilization of clay amendments, such as kaolinite, can be effective in reducing water repellency in a sandy soil, while other clay amendments, such as Ca-montmorillonite, can increase water repellency in a hydrophobic sand rootzone (Dlapa, 2004; McKissock et al., 2000). Theories by Ma'shum et al. (1989) suggested that efficacy of clay amendments on SWR is dependent on the ability of the clay to disperse in a soil, crystal structures and particle shape. Clays with high surface charges tend to flocculate, while low charge clays remain more evenly dispersed on sand surfaces (Müller and Deurer, 2011). Certain clay minerals that disperse when wet, such as kaolinite and illite, are able to expose a larger surface area, when compared to clays that aggregate when wet, such as montmorillonite and smectite, which reduce the overall surface area available to mitigate the hydrophobic sands present in the soil (McKissock et al., 2000; Müller and Deurer, 2011). However, conflicting results have been seen, such as by Ward and Oades (1993), who found the inverse effect where the addition of montmorillonite more effectively reduced SWR of artificial hydrophobic sand, made with cetyl alcohol, as compared to kaolinite. Ward and Oades (1993), explained that these contradictory effects are due to flocculation and dispersion of clays affected by the exchangeable cations that are present in the soil solution (Müller and Deurer, 2011). As flocculation of clays will increase as the cationic charge increases (Ward and Oades, 1993).

Earthworms can also aid in reducing SWR (Müller and Deurer, 2011). As they move through soil, earthworms consume and mix water repellent and non-water repellent soils together, reducing the amount of water repellent soil (Müller & Deurer, 2011). In

addition, earthworms leave castings behind that enhance the surrounding microbial populations and activity, leading to increased rates of organic matter decomposition, such as hydrophobic coatings. Finally, as earthworms move through soil, they will create burrows which help increase water infiltration and reduce surface water ponding (Müller & Deurer, 2011).

The use of wetting agents to ameliorate water repellency is preferred by many golf course superintendents due to their ability to improve infiltration and enhance soil water movement into water repellent soil (Watson et al., 1969). Golf courses started to use wetting agents based on research showing improvement of turfgrass growth and irrigation within a water repellent soil (Letey et al., 1962c; Morgan et al., 1967). Some researchers studied other remediation methods, such as adding loamy soil cores to water repellent sand to increase infiltration rates, but the use of wetting agents still draws the most attention globally (Bond, 1978). Developing an understanding of wetting agents' functions were assessed by evaluating factors to increase the wetting agents' effect on ameliorating water repellency, water movement and its effect on pesticide mobility through the soil to ground water (Huggenberger et al., 1973; Miller et al., 1975; Mustafa and Letey, 1970).

Wetting Agents

Wetting agents are a subcategory of a chemical class known as surfactants, which influence the surface tension of a liquid. There are many different categories of surfactants, including wetting agents, emulsifiers, spreaders, penetrants or detergents. Surfactants, or surface-active agents, physically alter the surface of a liquid by reducing the attraction of molecules at the liquid-air interface by the molecules at the center of the

liquid, lowering the overall liquid surface tension (Karnok et al., 2004). Surface tension is the attraction of molecules at the surface layer of a liquid by the molecules in the bulk of the liquid (Karnok et al., 2004; Müller and Deurer, 2011). Water's surface tension, having a value at 72.8 mN m^{-1} , can be dramatically decreased when mixed in solution with wetting agents. Due to the reduction of the liquid surface tension by the addition of wetting agents, the adsorption of water by hydrophobic soils will increase due to the decreased contact angle between water and a solid surface, such as soil (Müller & Deurer, 2011). All surfactants perform differently, but the basic chemical structure is the same. Surfactants consist of amphipathic molecules, meaning they contain a strong polar hydrophilic head group, and a long non-polar, hydrophobic hydrocarbon chain group (Karnok et al., 2004; Müller & Deurer, 2011). When wetting agents are applied to a soil, soil water will repel the hydrophobic region, which orients and binds the region towards the hydrophobic coatings on the sand particle through hydrophobic bond relations. This then orients the hydrophilic region toward the soil pore, attracting water to adhere to the wetting agent molecule on the sand particle, changing the once non-wettable sand particle into a wettable, sand particle (Kostka, 2000; Kostka and Bially, 2005)

Within soil wetting agents, different types of chemistry were developed: anionic, cationic, nonionic and amphoteric (Karnok et al., 2004; Spindler, 2016). Anionic blends are negatively charged surfactants which can increase the rate of soil wetting. However, this group of wetting agents can potentially be phytotoxic to turf and disperse clay particles, due to the negative charge, which in turn negatively impacts the soil structure (Zontek & Kostka, 2012). Anionic wetting agents were introduced to turf markets in the 1950's and are referred to as old chemistries (Zontek & Kostka, 2012). Cationic blends

are positively charged, but tend to not be used as soil wetting agents. Due to the positive charge of the surfactant, it will bind with soil particles and potentially increase the water repellency present in the soil. Additionally, application of cationic surfactants has shown a potential to cause severe damage to plant tissues (Zontek & Kostka, 2012). Anionic and cationic wetting agents can react with different ions in solution, due to their charge, causing them to precipitate once in solution (Karnok et al., 2004).

In the turfgrass industry, nonionic surfactants are the most widely utilized soil wetting agents. Nonionic wetting agents do not ionize in water and have low phytotoxicity to plant tissue (Karnok et al., 2004). The group of nonionic surfactants are separated into six subgroups based on their different chemical structures: polyoxyethylene (POE), block co-polymers, modified methyl capped block co-polymers, alkyl polyglucoside (APG), humic substance redistribution molecules and multibranch regenerating wetting agents. First, the group of POE surfactants are derived from older chemistry and were originally developed to remedy LDS. Entering the turf market in 1954, they enhanced soil water movement, but could potentially cause phytotoxicity on finer turfgrass, limiting their use on golf greens (Zontek & Kostka, 2012). Wetting agents in this subgroup include Surfside[®] 37, E-ZWet, Lesco[®] Wet and PenMax[®] (Zontek & Kostka, 2012).

The most predominant group of nonionic surfactants on the market is the block co-polymer surfactants. This group of chemistry is known to alleviate soil water repellency, improve soil water content and plant available water, but is also not phytotoxic to finer turfgrass species. Block co-polymer wetting agents are broken down into three subgroups: straight block co-polymers, reverse block co-polymers, and blends

of straight and reverse block co-polymers (Zontek & Kostka, 2012). Straight block co-polymers have been shown to improve soil water movement and limit leaching of pesticides in field studies (Zontek & Kostka, 2012). They can either be applied through a commercial sprayer, such as Capacity[™], Cascade Plus[™] or Hydro-Wet[®], or injectable formulations through a sprinkler system, such as Duplex[™] and InfilTRx[®]. Reverse block co-polymers have been shown to enhance water retention throughout the rootzone, particularly in soils that have a low water holding capacity (Zontek & Kostka, 2012). Reverse block co-polymers which are commercially available include Primer Select[®], Magnus[™], TriCure AD[™] and Retain (Zontek & Kostka, 2012). Lastly, companies have started to create blends of straight and reverse block co-polymers as well, trying to achieve a wetting agent that contains characteristics from both subgroups. Aquatrols[®], one of the top wetting agent producers, tested a blend of straight and reverse block co-polymers and concluded that it dramatically increased the effects from both subgroups, improve turf quality and remedied the LDS present (Zontek & Kostka, 2012). These blends of straight and reverse block co-polymers include Aqueduct[®] and Resurge[®], and are now becoming a standard when producing new experimental formulations (Zontek & Kostka, 2012).

The APG surfactants, which are formed by reacting a sugar molecule with a fatty acid, are considered to be naturally derived surfactants (Zontek & Kostka, 2012). This group of chemistry has shown an ability to improve water infiltration into water repellent soils. However, when APGs are blended with a block co-polymer, the effects of both wetting agents are enhanced. When blended together, the APG and block co-polymer wetting agents improved water penetration, water availability in the rootzone and

increased irrigation efficiency in a water repellent soil (Zontek & Kostka, 2012). A university study showed that applying a blend of APG and block co-polymers, even at 50% evapotranspiration (ET) replacement, improved plant-available water and turf quality. Introduced in 2000, commercial APG and straight block co-polymer wetting agents include Dispatch[®] Injectable and Dispatch[®] Sprayable (Zontek & Kostka, 2012). Additionally, a commercial APG, straight and reverse block co-polymer is Tournament-Ready[®], which utilizes multiple modes of action (Zontek & Kostka, 2012).

The modified methyl capped block co-polymer wetting agent, as the name implies, utilizes similar chemistry to block co-polymers, but the hydroxyl (–OH) terminal groups are replaced by methyl (–CH₃) caps. This replaces the more hydrophilic –OH groups with a more hydrophobic –CH₃ group, altering how the wetting agent will interact with the water repellent soil particles (Zontek & Kostka, 2012). As a result, a more thin, continuous film of water forms around the surface of the soil particle and organic matter, allowing for enhanced water availability and limiting turf stress from LDS. Revolution[®] is currently the only wetting agent with methyl capped block co-polymer chemistry on the market (Zontek & Kostka, 2012).

Humic substance redistribution molecules will disperse the supramolecular humic substances in the upper centimeters of the soil profile, then allow for enhanced water infiltration into the hydrophobic soil (Zontek & Kostka, 2012). These wetting agents reduce the size of the hydrophobic molecules to smaller, more soluble structures, which allow these molecules to move from the surface layers of the soil, where SWR is commonly found, to deeper in the profile where they can potentially aid moisture control

(Zontek & Kostka, 2012). Commercial wetting agents that fall into this subgroup include OARS[®] and Matador.

Multibranched regenerating wetting agents utilize higher molecular weight branches, which create multiple sites of interaction, leading to increased interaction between the wetting agent and hydrophobic soil particle. Due to the branches higher molecular weight, the biodegradation in the soil is affected. Higher molecular weight branches will be degraded first, allowing lower molecular weight branches to regenerate, maintaining long-term water management in the soil profile (Zontek & Kostka, 2012). Use of these molecules was patented in 2005 by Milliken & Co, and commercially available wetting agents include PBS-150[®] and OARS[®] (Zontek & Kostka, 2012).

Hydrophilic-lipophilic balance (HLB) and Critical micelle concentration

HLB concept and classification

The concept of the HLB value was initially derived by an Atlas Powder Company chemist named William Griffin to establish a standard classification for the proportional balance between the hydrophilic polar head group and hydrophobic non-polar tail group (Griffin, 1949; Pasquali et al., 2008). Creation of this classification aided in predicting the potential behavior of a surfactant and reduced the amount of time and effort involved in selecting the most effective emulsifier, wetting agent or detergent for the issue at hand (Griffin, 1949; Griffin, 1954). Surfactants are molecules constructed with a hydrophilic polar head group and are generally composed of water-soluble functional groups and a lipophilic nonpolar tail group that is composed of fatty acids or fatty alcohols (Davies, 1957; Gadhawe, 2014; Griffin, 1949; Luan et al., 2009).

The HLB number of a surfactant revolves around the combination of hydrophilic and lipophilic functional groups into a singular molecule, where the proportional weight difference between these groups can potentially indicate the expected behavior of that surfactant (Griffin, 1949; Griffin, 1954). Griffin determined these values after years of laboratory experiments through a number of oil in water (O/W) and water in oil (W/O) emulsification studies (Griffin, 1949). It was understood that surfactants which tend to be more soluble in water make O/W emulsions and surfactants more soluble in oil tend to make W/O emulsions (Davis, 1994). Griffin based his method around the molecular structure of the surfactant molecule and the affinity of a surfactant to a particular solvent (Griffin, 1949; Yamashita and Sakamoto, 2016). Based on a surfactant emulsifying and solubilizing characteristics, Griffin (1949) developed a scale to define the functionality of a surfactant based on its HLB value. Surfactants with lipophilic characteristics were assigned a lower HLB value and surfactants containing hydrophilic characteristics were assigned a higher value, with 10 representing the approximate midpoint (Griffin, 1949). Griffin's (1949) surfactant classification ranges from 3.5 to 6 representing W/O emulsifiers, 7 to 9 representing wetting agents, 8 to 18 representing O/W emulsifiers, with 13 to 15 being detergents and 15 to 18 being solubilizers (Griffin, 1949).

The development of Griffin's HLB scale sparked interest throughout the surfactant community with the aim of developing simpler methods to determine HLB numbers without the rigorous and time-consuming laboratory methods. This led to surfactant chemists, including Griffin, to develop theoretical equations and experimental procedures to aid in a more precise determination of HLB values for surfactants.

Theoretical and experimental determination of HLB

In 1954, Griffin developed a theoretical equation (Eq. 1.1) based on the structural balance between the hydrophilic and lipophilic groups in a POE surfactant, where the surfactant was given a numeric index from 0 to 40 based on the emulsification seen when testing various POE surfactants (Griffin, 1954; Yamashita et al., 2016). This equation utilized the hydrophilic weight fraction within the POE molecule,

$$HLB = \frac{POE(wt\%)}{5} \quad \text{Eq. 1.1}$$

being POE (wt%), to determine the HLB value for the surfactant (Eq. 1.1) (Gadhav, 2014; Griffin, 1954; Yamashita et al., 2016). Equation 1.1, which was determined by empirical emulsification, was widely utilized throughout the surfactant industry and during the formulation of a surfactant (Yamashita et al., 2016). However, this equation only utilized a POE surfactant, which limits its application to the various types of surfactants and surfactant mixtures available. Due to this limitation, Griffin then developed another equation (Eq. 1.2) to calculate the HLB value for fatty acid esters chemically bonded with polyalcohols:

$$HLB = 20 \times \left(1 - \frac{S}{A}\right) \quad \text{Eq. 1.2}$$

where S is the saponification number and A is the acid numbers of the esters (Gadhav, 2014; Griffin, 1954; Yamashita et al., 2016). Saponification is a hydration reaction, where free hydroxide breaks the ester bonds between the fatty acids and glycerol of a triglyceride, producing free fatty acids and glycerol which are both soluble in aqueous solutions (Prabu et al., 2015). Hence, the saponification number represents the number of milligrams of either potassium hydroxide (KOH) or sodium hydroxide (NaOH) necessary to hydrolyze one gram of fat to form soap and glycerol (Prabu et al., 2015). The acid number is a measure of the number of carboxylic acid groups in compounds, such as fatty

acids, and is determined by the number of milligrams of KOH necessary to neutralize one gram of said compound (Patel and Shah, 2015).

Equation 1.1 and 1.2 can be applied to most non-ionic surfactants; however, some non-ionic surfactants do not represent the behavior which is expected based on the HLB value determined, due to the specific chemical composition of the surfactant (Griffin, 1954). Eq 1.1 and 1.2 cannot be applied to ionic surfactants or surfactant mixes. Ionic surfactants have the ability to ionize, which puts greater emphasis on the hydrophilic portion of the molecule and results in a more hydrophilic surfactant than calculated by the equations (Griffin, 1954). Additionally, Eq 1.1 and 1.2 can only be applied to the HLB value of a singular amphiphilic molecule and does not express how a mixture of structurally different amphiphilic molecules would affect the overall HLB value of surfactant mixtures (Yamashita et al., 2016). Due to this, Davies developed a formula based on giving each functional group, hydrophilic and hydrophobic, a value to describe the amphiphilic molecule as a whole (Eq. 1.3) (Davis, 1994; Davies, 1957; Yamashita et al., 2016).

$$HLB = 7 + \Sigma (\text{unit value of hydrophilic group}) + n(\text{unit value of lipophilic group}) \quad \text{Eq. 1.3}$$

Where n is the number of $-\text{CH}_3$, or lipophilic groups, in the surfactant molecule. The unit values were determined from studies conducted by Griffin (1954) and Davies (1957) which gave molecular functional groups, such as $-\text{SO}_4\text{Na}$, $-\text{COONa}$, $-\text{OH}$ and $-\text{CH}_2$, HLB values (Becher, 1984; Kanicky et al., 2001). These functional groups, either hydrophilic or lipophilic, HLB values are utilized as the unit values in Eq 1.3 to then determine the

overall HLB value of a surfactant mixture. This equation utilizes both entities of the amphiphilic molecule in the calculation of the HLB instead of just the hydrophilic portion as in Griffin's formula. Equation 1.3 is more versatile and allows for the calculation of non-ionic and ionic surfactants. However, the HLB value might not precisely predict the functional properties of the surfactant solution (Yamashita et al., 2016).

Still, the issue with these theoretical determinations of the HLB value is that significantly different values are produced depending on which equation is used, creating a critical problem when trying to apply these equations to predict the function of a surfactant (Yamashita et al., 2016). Additionally, theoretical equations are also unable to determine the true HLB value of a surfactant mixtures, which are widely available and utilized, as the combined effects of mixed surfactants with differing HLB values can alter overall HLB value and performance of the mixture (Pawignya et al., 2016; Yamashita et al., 2016).

Experimental determination of HLB values

To create a more accurate determination of a surfactant's HLB value, various experimental methods were developed to accurately determine HLB values and create a standardized method which could be applied throughout industrial production (Kumar et al., 2004; Yamashita et al., 2016). Greenwald et al. (1956) utilized a titration method with a dioxane-benzene surfactant and determined the water number (WN) of two surfactant families of polyhydric alcohol esters, being ethylene oxide adducts and those without ethylene oxide, to then correlate this value to known HLB values determined by Griffin (1949) (Pasuali et al., 2009). The surfactant is dissolved in a benzene-dioxane mixture containing 4% v/v of benzene and the solution is then titrated with distilled water until

turbidity, or cloudiness, of the solution was reached (Greenwald et al., 1956; Nagy et al., 2015). The amount of water added to the solution is determined as the WN of the surfactant. The determined WN of the 18 different surfactants tested were correlated to the known HLB value determined by Griffin (1949) to find a relationship (Greenwald et al., 1956; Nagy et al., 2015). Greenwald et al. (1956) found that a linear regression for each surfactant family could be created. This indicated that the WN of a surfactant would give a fair indication of the HLB number and performance of a surfactant (Greenwald et al., 1956). However, the main issues with this method are that it would overestimate the HLB value for a single surfactant and surfactant mixtures, and had a low overall safety, due to the carcinogenic benzene effects (Nagy et al., 2015). This method has since been altered and is currently utilized in laboratories by incorporating spectrophotometric methods and an alternative, safer solvent to improve this methodology, which will be discussed later.

Chun & Martin (1961) utilized an interfacial tension method to determine HLB values for surfactants. Ten percent of an aqueous surfactant solution was overlaid with toluene and the solution's interfacial tension was measured and correlated to HLB values (Pasquali et al., 2009). A linear relationship was seen when the interfacial tension values were plotted against the known HLB values, hence potentially being able to utilize this method to determine the HLB of unknown surfactants (Chun & Martin, 1961; Pasquali et al., 2009). Another method which utilized the polarity of surfactants was developed based on the retention times of methanol and various hydrocarbons in a surfactant and analyzed in a gas-liquid chromatography column (Huebner, 1962). Several years later, a linear relationship between the polarity index and the HLB value of ethylene oxide surfactants

was determined (Fineman, 1969). Becher & Birkmeier also utilized gas-liquid chromatography to determine the different retention times for polar and non-polar liquids in a surfactant (Pasquali et al., 2009). This method was significant because it allowed for the determination of an HLB value for a single surfactant or a surfactant mixture by gas-liquid chromatography (Becher & Birkmeier, 1964; Pasquali et al., 2009). Various methods have been developed to determine the HLB value of surfactants, but still the biggest challenge was developing a method to determine the HLB value of a surfactant mixture with varying HLB values.

In recent years a novel experimental method has been developed based on the Greenwald et al. (1956) method which utilized the WN of a surfactant (Kothencz et al., 2017; Nagy et al., 2015; Nagy et al., 2016). Nagy et al. (2016) determined a method which utilizes a safer solvent, cyclohexane-dioxane, that correlated closely to Griffin's theoretical method of HLB calculation (Kothencz et al., 2017; Nagy et al., 2015; Nagy et al., 2016). In a series of papers and experiments done by Nagy et al. (2015; 2016) their novel titrimetric method was compared to the Greenwald et al. (1956) previous method and Griffin's theoretical HLB value determination to assess the accuracy of their novel method. Following similar procedures to the Greenwald et al. (1956) method, a non-ionic surfactant was dissolved in cyclohexane-dioxane, at 4% v/v cyclohexane, and the surfactant solution was titrated with distilled water until permanent turbidity was reached and transmittance within the solution could not decrease any further from the addition of distilled water (Kothencz et al., 2017). Measuring the transmittance of the titrated solution with a fiber-optic spectrophotometer (AvaSpec 2048) allowed the determination of an accurate WN for the surfactant solution (Nagy et al., 2015). Transmittance values

were represented as a function of the distilled water volume added and the equivalence point was determined, based on the curve created. The equivalence point corresponded to the relative solubility value or WN of the surfactant (Kothencz et al., 2017; Nagy et al., 2015; Nagy et al., 2016). To test this novel method for accuracy of HLB determination, Nagy et al. (2015) tested the novel method against the Greenwald et al (1956) experimental method and the Griffin (1949) method based on the estimated molecular structure. Based on the Nagy et al. (2015) results, the novel method either exactly matched or differed by a maximum of 7.6% from the Griffin (1949) method based on molecular structure. As compared to the Greenwald et al. (1956) method, which varied 11.8% to 65.0% when compared to Griffin (1949) method (Nagy et al., 1957). Through these experiments and applying a linear regression to the determined HLB values, an equation was developed utilizing WN to determine the HLB of non-ionic and anionic surfactants (Eq. 1.4) (Kothencz et al., 2017).

$$HLB = \frac{WN}{0.6524} - 0.6339 \quad \text{Eq. 1.4}$$

Another equation was developed using the same method, but for surfactant mixes based on its WN (Eq. 1.5) (Kothencz et al., 2017).

$$HLB = \frac{WN}{1.206} - 10.5 \quad \text{Eq. 1.5}$$

This novel method addressed the issue of determining the HLB values of either non-ionic, anionic or a surfactant mix accurately and calculated a HLB value related to the chemical structure (Kothencz et al., 2017). Due to the high correlation to HLB values determined by the Griffin (1949) method, it can easily be applied to industrial practices that use Griffin's HLB scale as a standard. With the development of this novel titrimetric method, accurate HLB values can be calculated for non-ionic, anionic and surfactant

mixes with an unknown chemical composition. This procedure could potentially be applied to surfactants with unknown chemical makeup, such as soil wetting agents, to predict the surfactants' possible function within the soil.

Predictability of Soil Wetting Agent Functions by the HLB value

Different chemistries are utilized within the broad category of non-ionic surfactants, such as POE, block co-polymer, APG, and modified methyl capped block co-polymer which all function differently in the soil (Zontek & Kostka, 2012). Non-ionic surfactants are physically adsorbed onto soil particles, unlike ionic surfactants which electrostatically bind (Paria & Khilar, 2004). The HLB value of these surfactants directly affect how they adsorb and function within the soil, but due to the lack of Environmental Protection Agency (EPA) regulation and information on the chemical composition, the HLB values of these surfactants are usually not known. This limits the ability to infer the potential effect of the soil surfactant when applied to a hydrophobic soil. Non-ionic surfactants tend to adsorb to a soil surface in a 4 step Langmuir isotherm (Paria & Khilar, 2004; Zhang & Somasundaran, 2006). Surfactant molecules slowly adsorb to the soil surface, due to the van der Waals interactions, and therefore heavily rely on the ratio of the hydrophobic and hydrophilic portions of the surfactant molecule (Paria & Khilar, 2004). A monolayer is slowly formed on the soil surface and then adsorbate-adsorbate interactions between the surfactant molecules will add more molecules to the soil surface. These adsorbate-adsorbate interactions usually depend on the HLB value within the surfactant (Paria & Khilar, 2004; Pasquali et al., 2008). When the hydrophilic or hydrophobic group portion is weakly adsorbed to the soil surface, it can easily be displaced from the surface due to interactions with surrounding water molecules or other

surfactant molecules in the soil solution (Paria & Khilar, 2004). These interactions allow surfactants to infiltrate water through the soil, by the surfactant binding with water molecules and then displacing from the soil surface and infiltrating into the soil profile (Kumar et al., 2004; Paria & Khilar, 2004). When a strong hydrophilic association is present on the soil surface, this causes the hydrophobic portion to protrude in the soil pore and away from the soil particle (Paria & Khilar, 2004; Zhang & Somasundaram, 2006). Hydrophobic ends of surfactant molecules within the soil solution will bind to the adhered surfactant's hydrophobic tail and create a bilayer of surfactant molecules around the soil particle (Paria & Khilar, 2004; Zhang & Somasundaram, 2006). This bilayer allows the hydrophilic portions on the outside of the bilayer to bind with water particles to maintain a wet and hydrated soil profile (Kumar et al., 2004). These relationships between the soil surface and surrounding surfactant molecules are directly influenced by the surfactant's HLB value, leading to surfactants functioning differently based on their HLB relationship. When surfactants interact with a hydrophobic surface, a lower HLB value surfactant has a higher portion of hydrophobic groups which allows for increased surface-activity and molecule density of the hydrophobic surface (Kumar et al., 2004). Surfactants with a higher HLB value, having a larger hydrophilic group, are less surface active and have lower molecule density on the hydrophobic surface, due to limited binding ability from the reduced hydrophobic tail group (Kumar et al., 2004). Demonstrating how the HLB value directly affects the surfactants function in the soil and on a hydrophobic soil surface.

The functionality and effectiveness of a surfactant is also directly influenced by its critical micelle concentration (CMC), which is related to the HLB value of the

surfactant. The CMC is a concentration at which surfactant molecules start to self-assemble, due to a reduction of surfaces to bind to, by interactions between the hydrophobic tails, creating a hydrophobic core micelle with an outer hydrophilic head shell (Patist et al., 2000; Hait & Moulik, 2001; Pawignya et al., 2016). When these micelles are formed in the soil solution, they are not able to actively bind with the soil surface which reduces their functionality and limits their ability to aid in reversing the hydrophobic soil effects. The CMC value varies depending on the ratio of the hydrophobic and hydrophilic groups (Hait & Moulik, 2001; Pawignya et al., 2016). Not knowing the HLB value, and its potential relation to CMC, could lead to applying a surfactant at too high of a concentration and increasing the formation of micelles in the soil solution, ultimately decreasing the overall effect of the surfactant applied. There are multiple methods to determine the CMC value of a surfactant. Most commonly, tensiometry, fluorimetry and spectrophotometry are utilized to determine the CMC (Hait & Moulik, 2001). Tensiometry determines the surface tension of a surfactant at different concentrations. Above the CMC value, the surface tension will decrease with increasing concentration, until reaching the CMC concentration, where the surface tension will remain consistent, even if the surfactant concentration is increased (Moulik, 1996). By accurately determining the CMC and HLB value of wetting agents with unknown chemical compositions, this could help in understanding at what concentration to apply a wetting agent and could lead to potentially understanding their interaction and function in the soil. Hait and Moulik (2001) observed a correlation between CMC and HLB values for nonionic surfactants. When plotting the natural log (ln) of CMC vs. HLB values of known surfactants, the trend was linear. Hence, determining the CMC of a surfactant

could help determine the HLB value of a surfactant if it is unknown, potentially leading to a better understanding of the performance of a surfactant.

Infiltration

Water repellent soils can limit water infiltration and movement, which in turn affects plant growth and water distribution in the soil (Bauters et al., 1998; DeBano, 1969a). Wettability, being the ability of a liquid to spread and wet a solid surface, relates to the infiltration and water retention of a soil due to hydrophobic coatings present on the outside of soil particles (Hallett, 2007). Infiltration drew major interest in areas that had been exposed to wildfires or agricultural fields with sandy soils, due to these soils' ability to form SWR (Scott and Burgy, 1956). When soils become water repellent, the soil can resist water infiltration into the surface of the soil (Bauters et al., 1998; Brandt, 1969).

As interest in SWR grew throughout the 1970's, models for soil infiltration and water movement were developed and the concept of unstable wetting fronts arose (Bachmat and Elrick, 1970; Hillel, 1972). Preferential flow pathways, or fingering bypass flow, are unstable wetting fronts moving through soil causing non-uniform infiltration into the soil profile (Bauters et al., 1998; Dekker and Ritsema, 1994). This leads to variability of soil moisture and increased leaching from the soil profile, which ultimately leads to hindering plant growth (Dekker and Ritsema, 1994; Scotter, 1978). Preferential flow also leads to increased contamination of groundwater, due to a faster flow of water and pesticides through the soil (Bauters et al., 1998). Unstable wetting fronts occur when the soil water flux, which is the volume of water passing through a soil cross-sectional area in a unit of time, is less than the unsaturated conductivity (Wang et al., 2000). Infiltration rates of a soil relate to the speed at which water enters into a soil (Feng et al.,

2002). These infiltration rates into wettable soils are typically higher initially, but over time, infiltration rates decrease due to a decrease in hydraulic gradient in the soil (Feng et al., 2002). In contrast, infiltration rates into a water repellent soil are initially slow, they increase over time (Feng et al., 2002). Infiltration into water repellent soils does not spontaneously occur due to the hydrophobicity within the soil (Song et al., 2014b). This can be overcome by applying a positive water entry pressure head, h_p , to force water into the repellent soil (Feng et al., 2002). At high ponding depths, the infiltration rate increases initially and then decreases over time, because the water repellent soil is converting to a wettable soil, and infiltration rates naturally decrease with time (Feng et al., 2002). However, this concept is very impractical for the management of a golf course putting green, because water ponded on a golf green would be antagonistic for the playability on the green (Song et al., 2014b).

To overcome unstable infiltration on a golf putting green, many superintendents incorporate the use of wetting agents (Karnok, 2006). Wetting agents, a category of surfactants, when added with water and applied to soil, reduce the surface tension of water and decrease the h_p required to enter the water repellent soil, allowing the water to penetrate more easily (Feng et al., 2002). This is based on the assumption that soil pores are related to capillary tubes, and the capillary equation (Eq. 1.6):

$$h_p = -2\gamma\cos\theta/pgr \quad \text{Eq. 1.6}$$

can be applied, where h_p is the liquid entry pressure head, γ is the liquid surface tension, θ is the liquid-solid contact angle, p is the liquid density, g is the gravitational constant and r is the capillary radius. For Eq. 1.6, when the θ is $>90^\circ$ then the h_p is positive due to the $\cos \theta$ being negative, while in contrast, when the θ is $<90^\circ$, the value of h_p is negative

due to the $\cos \theta$ being positive (Feng et al., 2002). Based on this, for a greater infiltration rate to occur, a high absolute numeric value, or a more negative value, of h_p is desired (Feng et al., 2002). Additionally, if the h_p value is positive, a lower positive value is desired for greater infiltration rates (Feng et al., 2002). Due to this, there can be beneficial and negative affects when utilizing wetting agents to lower the γ based on the value of h_p (Feng et al., 2002). When the value of h_p is positive, lowering the γ by the addition of wetting agents is desirable when trying to increase the infiltration rate, as this will reduce the h_p value (Feng et al., 2002). Comparatively, when the h_p value is negative, lowering the γ will reduce the absolute numeric value or become less negative, of h_p , which theoretically would reduce the infiltration rate (Feng et al., 2002). Due to this, when wetting agents are added to water, the γ will be lowered, which lowers the θ and ultimately lowers the h_p and increases the infiltration rate into water repellent soils (Feng et al., 2002). However, for an already wettable soil, the reduction in γ by a wetting agent can positively or negatively affect the infiltration rate into the soil depending on what the θ value of the wettable soil is (Feng et al., 2002).

Water infiltration rates of soils can be determined through both laboratory and field methods. Direct measurement of water infiltration rates can be determined in a laboratory utilizing soil columns uniformly packed with soil (DeBano, 1971; Nektarios et al., 2002). A consistent ponding depth (h_o) is applied and maintained by utilizing a Mariotte bottle siphon system, which is placed on an elevated scale, to deliver water or a solution to the infiltration column. Infiltration rate (i) is determined utilizing equation 1.7:

$$i = \frac{\Delta v}{r^2 \pi \Delta t} \quad \text{Eq. 1.7}$$

where the change in the mass of the liquid in the Mariotte bottle (Δv) over a consistent period of time (Δt) is determined, with r being the radius of the infiltration column (Song et al., 2014a). When the infiltration rate through the column reaches a steady flow rate, the hydraulic conductivity (K) can be determined (Eq. 1.8) by dividing the steady flow rate by the hydraulic head gradient across the sand column:

$$K = \frac{i_c L}{\Delta h} \quad \text{Eq. 1.8}$$

where i_c is the steady infiltration rate, Δh is the change in hydraulic head across the column and L is the length of the column (Reynolds and Elerick, 2002; Song et al., 2014a). Additionally, when infiltration rate is determined in a laboratory utilizing a soil column, the seepage time (T_s), is the amount of time necessary for water or liquid to exit the bottom of the sand column. Various researchers have utilized this soil column system to determine the influence of wetting agent solutions on infiltration rates into water repellent soils, as there is more control over experimental conditions, such as the water repellency value of the sand (Feng et al., 2001; Nektarios et al., 2002; Song et al., 2014a). Artificial hydrophobic sand (AHS) has been utilized, due to the ability to control the level of water repellency, in laboratory studies to determine wetting front instability, preferential flow and the relationship with ponding depth (h_o), or water entry pressure head (h_w) (Carrillo et al., 2000; Feng et al., 2001; Nektarios et al., 1999; Ritsema et al., 1993; Song et al., 2014a; Wang et al., 2000).

In a field setting, double-ring infiltrometers are widely utilized by turfgrass managers and soil scientists to measure the infiltration rate (ASTM, 2003; Gregory et al., 2005). Infiltration rate in a field directly affects surface runoff and soil erosion. Double-ring infiltrometers consist of a small cylinder concentrically positioned inside a larger

cylinder. There are two techniques utilized when using a double-ring infiltrometer to measure the infiltration rate of a soil. The first is a constant head, where the pressure head in the inner cylinder is maintained at a fixed level throughout the experiment and the infiltration rate is based on the amount of water necessary to maintain the fixed pressure head (Bouwer, 1986; Gregory et al., 2005). The second method utilizes a falling pressure head, where the water level of the inner cylinder is allowed to decrease in a set period of time (Gregory et al., 2005). For both methods, the outer ring is filled and water level is maintained throughout the measurement to mitigate the lateral movement of water from the inner cylinder (ASTM, 2003; Bouwer, 1986; Gregory et al., 2005). This allows for the infiltration rate determined from the inner cylinder to represent the true measure of the vertical infiltration rate into the soil (Bouwer, 1986; Gregory et al., 2005). However, the use of double-ring infiltrometers is time-consuming and complicates the ability to accurately determine infiltration rates into a water-repellent, sand-based putting green (Gregory et al., 2005; Lai and Ren, 2007; Song et al., 2014a).

Song et al. (2014b) demonstrated that different wetting agents, at varying concentrations, can affect infiltration into hydrophobic soil. Most wetting agents tested showed infiltration curves similar to that of a water repellent soil, being an initial increase in infiltration rate until reaching a constant plateau or steady flow rate (Feng et al., 2001, 2002; Song et al., 2014b; Wang et al., 2000). Application of other wetting agents displayed infiltration curves that closely resemble a change from a water repellent soil to a wettable soil, demonstrating a peak in infiltration rate within 5 minutes and then slowly decreasing until reaching a steady flow rate (Feng et al., 2001; Song et al., 2014b; Wang et al., 2000). Even though wetting agents have become the chosen method to ameliorate

water repellency, limited research is available on the effect of different wetting agents on water infiltration into water repellent USGA sand-based greens (Song et al., 2014a; Throssell, 2005).

Rewettability

An important soil property affecting the development of water repellency is consistent soil moisture content over time (Doerr et al., 2000). It is largely accepted that SWR is seasonally dependent, where a low or absent SWR is found under prolonged wet periods and more severe SWR is found during prolonged dry periods (Crockford et al., 1991; Imerson et al., 1992; Ritsema and Dekker, 1994). A soil particle will remain hydrophobic until the organic layer surrounding the particle is altered by either water or a wetting agent. When water is not present in the soil, the polar ends of amphiphilic organic molecules will interact with hydrogen bonds, forcing these molecules to reorient themselves, with the polar hydrophilic portion toward the soil particle and non-polar hydrophobic portion oriented into the soil pores (Doerr et al., 2000; Ma'shum and Farmer, 1985; Tschapek, 1984; Valat et al., 1991). Rewettability of a soil refers to the ability of a soil to wet after undergoing a drying period. To enhance the rewettability of a water-repellent sand-based putting green, surfactants are incorporated into a soil to maximize these properties (Feng et al., 2002).

Minimal laboratory studies have been conducted to determine the influence of wetting agents to allow rewettability of a water-repellent soil (Baird and Calhoun, 1999; Feng et al., 2001; Song et al., 2014a). Baird and Calhoun (1999) observed significantly lower rewetting times in cores treated with wetting agents as compared to untreated cores. Song et al. (2014a) applied six different wetting agent solutions to an AHS

column, to determine the influence on initial infiltration through the column. Following the completion of the infiltration event, the columns were oven dried at 55°C until reaching a constant weight, then only water was reapplied to these AHS columns treated with various wetting agent solutions to determine the influence on rewettability properties (Song et al., 2014a). They found that different wetting agents influenced rewettability differently after three dry-wet cycles. Of the six, only two wetting agents, Cascade Plus™ and LescoFlo™ Ultra, maintained rewettability of the soils after three dry-wet cycles (Song et al., 2014a). Two of the wetting agents applied, Hydro-Wet® and Surfside® 37, were unable to allow water infiltration after two dry-wet cycles (Song et al., 2014a). In contrast, two other wetting agents, Revolution® and Tournament-Ready®, demonstrated an inability to allow water infiltration after the third dry-wet cycle (Song et al., 2014a). Wetting agents applied varied in their ability to rewet a hydrophobic soil after multiple dry-wet cycles. During these rewettability studies, Song et al. (2014a) saw water infiltration rates that resembled the initial infiltration rates of the wetting agent solutions, where a rapid increase occurred before reaching a steady flow rate. These results differed from Feng et al. (2002), who reported that water infiltration rates into the pretreated wetting agent sand resembled infiltration rates for a wettable soil, decreasing over time. Regardless, wetting agents overall have shown the ability to convert water repellent soils into wettable soils while still maintaining wettability within the soil over time (Feng et al., 2002; Song et al., 2014a). Wetting agents soil longevity will vary based on their chemical structure and their application intervals (Song et al., 2014a).

Water Retention

Water retention is the capacity of a soil to hold water within the pores after gravitational water has drained (Leinauer et al., 2001). Various soil properties relate to the ability of a soil to retain water, such as capillary porosity, air-filled porosity and organic matter (O.M.) content. Capillary pores are known to represent a soil's ability to hold and retain water in a soil profile (Amer, 2002). Additionally, studies have shown that an addition of organic matter resulted in between 144% to 434% greater total available water in a USGA sand-based putting green, compared to no addition of organic matter (Wesseling et al., 2009). Studies performed by de Jonge et al. (1999) determined that the severity of soil water repellency is affected by the water content in the soil. Soils which are previously wettable can develop water repellency when a lower soil water content is reached. However, water repellency then diminishes when higher soil water contents occur. In contrast, other soils initially are water repellent, but as the soil water content increases, soils convert to a wettable media (de Jonge et al., 1999). The determination of water retention in sand-based putting greens is based on the volumetric water content (VWC) measured through time-domain reflectance (TDR) meters. This is an indirect method to measure the VWC of a soil, which measures the propagation of electromagnetic (EM) signal through a transmission line into a soil media (Topp et al., 1980). The TDR unit emits the EM signal as a step voltage pulse and the travel time of the signal is measured along the transmission line or probes (Topp and Ferre, 2002). The travel time is utilized to calculate the permittivity, or dielectric constant, of the soil which strongly relates to the water content present in the soil (Topp et al., 1980). The dielectric constant of water is 80, while soil has a value between 2 and 7, and air has a value equal

to 1 (Topp et al., 1980). The dielectric constant of the soil is then directly converted to the VWC of the soil (Topp et al., 1980).

The application of wetting agents has become a tool utilized by golf course superintendents to either enhance water infiltration or water retention. However, due to wetting agents resulting in a lower γ water and reduced θ between the solid-liquid interface, the influence on water retention of the soil can vary with wetting agent application (Karagunduz et al., 2001). Conflicting results have been demonstrated. Wiecko and Carrow (1992) saw a decrease in the water retention of plots treated with wetting agents (Leinauer et al., 2001). In contrast, several studies reported a significant increase in soil water content when wetting agent treatments are applied (Blogdgett et al., 1993; Karnok et al., 1989; Leinauer et al., 2001).

Leinauer et al. (2001) determined the water retention of a sandy soil when two different wetting agents were applied throughout a growing season. They concluded that both wetting agents showed increased water retention regardless of soil medium. No significant difference in VWC was seen in the upper 50 mm of soil depth between either wetting agent or control treatment (Leinauer et al., 2001). However, the application of Primer 604[®], at 2.5 ml m⁻², significantly increased VWC throughout the season, at a soil depth of 150 mm when compared to Midorich and control, regardless of rate applied, by 15.1% or greater (Leinauer et al., 2001). However, application of Midorich, at 10 ml m⁻², increased VWC by 10.3% throughout the season compared to the control, at a soil depth of 150 mm (Leinauer et al., 2001). Application of both wetting agents showed an increase in water retention compared to the control. Similarly, Karnok and Tucker (2001) saw significantly greater VWC in wetting agent treated plots compared to the untreated

control. When VWC was pooled for both years of the study, the wetting agent treatment significantly increased VWC by 8.3% and 3.5%, as compared to the control (Karnok and Tucker, 2001). Conversely, Karagunduz et al. (2001) reported that water retention decreased when a surfactant was present as compared to the untreated control where only water was applied. The application of Triton® X-100, at 0.750 g L⁻¹, decreased the VWC of Ottawa sand by 45.5% compared to the absence of the surfactant (Karagunduz et al., 2001). Additionally, other studies have shown the presence of wetting agent applications neither increased or decreased the VWC compared to the untreated control (Barton and Colmer, 2011; Ruemmele and Amador, 2008).

Soldat et al. (2010) reported that a wetting agent's effect on VWC can also be impacted by the preexisting VWC and O.M. content in the soil. They found that putting greens treated with Aqueduct®, Primer 604® and Revolution® all had lower VWC under wet soil conditions early in the growing season when compared to the control. However, later in the season, when dryer soil conditions were present, all wetting agent treatments maintained a greater VWC than the control (Soldat et al., 2010). Additionally, Soldat et al. (2010) tested a wetting agent, Revolution®, in low and high O.M. rootzones. He found that in low O.M. rootzones, application of Revolution® significantly reduced the VWC throughout the season compared to the untreated control (Soldat et al., 2010). In contrast, in high O.M. rootzones, no difference in VWC between Revolution® or the untreated control was seen (Soldat et al., 2010). This leads to the question; are soil water characteristics affected differently based on which wetting agent is applied? Ultimately, the effects of wetting agents on the water retention of a water repellent soil are still in question.

Soil Water Tracers

Soil water tracers have been widely utilized by soil scientists to follow the movement and velocity of soil water in laboratory or field studies for many years (Bowman, 1984; Davis et al., 1980). The determination of the proper soil water tracer is dependent on three factors: the tracer should not be significantly sorbed by the soil being tested, the tracer should be unnatural or present at very low concentrations in the soil, and the tracer should not be significantly degraded either chemically or biologically throughout the duration of the study (Bowman, 1984; Davis et al., 1980). Additionally, the ideal soil water tracer should be nontoxic, mobile in water, easy to detect at low quantities, inexpensive, and should not alter the natural flow pattern of the water (Davis et al., 1980). Even though the perfect soil tracer does not exist, many tracers are better suited for use than others (Bowman, 1984; Davis et al., 1980). When tracer studies fail, many times that failure is dependent on the tracer that is chosen. Many tracers are easily sorbed onto soil particles and do not move through the soil, while others are quickly decomposed in the soil, not allowing them to be detected (Davis et al., 1980).

A variety of tracers are available for soil scientists, depending on the desired purpose, such as ionized substances, radioactive molecules, organic dyes and fluorocarbons (Davis et al., 1980). There are advantages and disadvantages to each of these tracers, as well as appropriate and inappropriate situations for each. Ionized substances are popular due to their low cost, ease of detection and low sorption. When these salts ionize in solution, they increase the electrical conductivity of the water, which could be utilized as a method of detection. However, rather high concentrations need to be utilized to create a significant change in the electrical conductivity, which would

increase the density of the solution and could potentially alter the natural flow pathway of the soil water (Davis et al., 1980). The most popular ion types are chloride (Cl^-) and bromide (Br^-), while lithium (Li^+), ammonia (NH_4^+), and magnesium (Mg^{++}) have been used (Bowman, 1984; Davis et al., 1980). However, Br^- generally is utilized for soil water studies due to its relatively low natural abundance in soil, lack of sorption on soils and low toxicity compared to the other tracers mentioned (Bowman, 1984; Davis et al., 1980). The concentration of Br^- is roughly 0.0033% less than that of Cl^- in natural soil water, with background concentrations of Br^- being less than 1 mg L^{-1} (Davis et al., 1980). Detection of Br^- is also relatively easy by a specific ion electrode or high-pressure liquid chromatography (HPLC) (Abdalla and Lear, 1975; Bowman, 1984; Clothier et al., 2000; Kasteel et al., 2002; Kurwadkar et al., 2011; Onken et al., 1975; Ritsema et al., 1998; Wang et al., 2007). Detection of Br^- through a specific ion electrode has a detection limit of 0.05 mg L^{-1} , meaning that if a Br^- tracer is utilized at a concentration of $1,000 \text{ mg L}^{-1}$ a 4-fold dilution of the tracer is possible before being masked by natural background concentrations (Davis et al., 1980). In addition, studies conducted by Onken et al. (1977), Parta and Rego (1994), and Smith and Davis (1974), determined the movement of Br^- is similar to nitrate (NO_3^-) under field conditions, potentially aiding in determination of NO_3^- movement or leaching in a soil. Radioactive soil tracers during the late 1950's to early 1960's dramatically increased due to the availability of radioactive concentration prediction methods (Davis et al., 1980). In recent years, increased awareness of radiation hazards has limited the utilization of radioactive tracers in field studies due to potential negative environmental effects. For laboratory studies, radioactive tracers can still be utilized as the potential for environmental contamination is reduced (Wagner, 1977).

Commonly used radionuclides for soil water movement studies are tritium (^3H) or carbon-14 (^{14}C) (Davis et al., 1980). Of these, ^3H has been more widely utilized due to its ability to form part of a water molecule and travel with the ground water (Kaufman, 1961). If choosing to utilize a radionuclide as a soil water tracer, the half-life needs to be considered based on the duration of the experiment. Detection can be completed through the utilization of a liquid scintillation counter.

Multiple organic dyes have been utilized as soil water tracers, however due to most being sorbed to soil particles, these are best utilized when shorter distances of soil water movement are being evaluated (Bowman, 1984; Davis et al., 1980). Advantageous features of organic dyes are the low toxicity, multitude of methods for detection, high sensitivity and low cost (Davis et al., 1980). However, organic dyes can be affected by photodegradation, pH changes and temperature fluctuations (Davis et al., 1980).

Commonly used organic dyes include fluorescein, Brilliant Blue FCF, rhodamine WT and lissamine FF (Bowman, 1984; Davis et al., 1980; Forrer et al., 2000; Kasteel et al., 2002; Mooney and Morris, 2008). Dyes are most useful due to their ability to be visually detected either by researchers or spectrophotometers in very low concentrations, such as parts per million and parts per billion, respectively (Davis et al., 1980; Forrer et al., 2000; Kasteel et al., 2002; Mooney and Morris, 2008).

Fluorocarbons have been increasing in popularity due to their ability to resist chemical breakdown and extreme nonreactivity in soils (Bowman, 1984; Davis et al., 1980). Additionally, these are easily detectable in a wide range of concentrations, between 1 to 100 parts per trillion, through HPLC (Bowman, 1984; Davis et al., 1980). This would allow for 1 g of fluorocarbon tracer to label roughly 2.6 million gallons of

water (Davis et al., 1980). These tracers are also beneficial as they have very low toxicities and their sorptivity to soils are relatively similar to those seen by Br⁻ tracers (Bowman, 1984; Davis et al., 1980). Fluorobenzoates, such as *o*-trifluoromethyl benzoic acid (*o*-TFMBA), pentafluorobenzoic acid (PFBA) and 2,6-difluorobenzoic acid (2,6-DFBA), have been utilized in a study performed by Bowman (1984) evaluating new soil water tracers and it was found they move similarly to Br⁻, indicating that their utilization will increase in future studies. However, due to the conservative nature of Br⁻, it is still more preferred as a soil water tracer.

Various studies have been conducted utilizing soil water tracers to assess water and solute transport through preferential flow pathways in a soil, due to underlying SWR (Clothier et al., 2000; Larsson et al., 1999; Mooney and Morris, 2008; Ritsema and Dekker, 2000; Wessolek et al., 2009). These studies have either been performed in a laboratory, utilizing soil columns, or in a field setting. The quantification of soil water movement through preferential flow pathways is critical in determining the effect these pathways have on leaching from the soil profile (Mooney and Morris, 2008; Larsson et al., 1999; Ritsema and Dekker, 2000). When fertilizer and pesticides are more rapidly moved through a soil profile due to preferential flow pathways, a reduction in the efficacy is found, as well as an increase in groundwater contamination. When preferential flow pathways are present, the ability of the soil matrix to adsorb, immobilize and degrade potential pollutants is reduced and therefore, increases the risk that chemicals will leach from the soil profile. Hence, soil tracers, such as Br⁻, are utilized to assess and model preferential flow pathways in soils, to predict the potential impact on leaching and to aid in the development of an applicable simulation tool to understand these processes

and their impact (Ritsema and Dekker, 2000). In addition, a novel technique to measure the potential impact wetting agents have on water, potential nitrate, and agrochemical movement in a water repellent sandy soil could be done through the utilizations of Br⁻ soil water tracers.

Objective

For golf course superintendents to effectively utilize wetting agents in a maintenance program, it is crucial to understand how they function. However, even with wetting agents being utilized in the turf industry for many years, over 75% of their active ingredients are not listed on the label. This limits the predictability of a wetting agents influence on water infiltration or retention. However, understanding various wetting agents influence on waters physical properties, such as surface tension, could potentially predict their functionality and influence on water infiltration or retention prior to their application.

Hence, this dissertation study was conducted to investigate: 1) the influence of selected wetting agents on waters liquid surface tension and liquid-solid contact angle, in correlation with water infiltration and rewettability into water-repellent sand; 2) evaluate selected wetting agents influence on water infiltration and retention under field conditions, based on their resulting surface tension values; and 3) assess the influence of selected wetting agents, with differing surface tension values, on water movement and leaching through water-repellent sand by utilization of a soil tracer.

Reference

- Abdalla, N.A., and B. Lear. 1975. Determination of inorganic bromide in soils and plant tissues with a bromide selective-ion electrode. *Commun. Soil Sci. Plant Anal.* 6: 489-494.
- Amer, A.M. 2002. Drainable and water-filled pores as related to water storage and conductivity in agricultural soils of the Nile Delta. *Verh. Internal Verein. Limnology*, Vol.28, part 4, p.1912-1919 Stuttgart-Germany, 28th SIL Congress.
- ASTM. 2003. Standard test method for infiltration rate of soils in field using double-ring infiltrometer. *Annual Book of ASTM Standards* 04.08. Amer. Soc. Testing Materials, West Conshohocken, PA.
- Bachmann, J., S.K. Woche, M.O. Goebel, M.B. Kirkham, and R. Horton. 2003. Extended methodology for determining wetting properties of porous media. *Water Resources Research*. 39(12).
- Bachmat, Y., and D.E. Elrick. 1970. Hydrodynamic instability of miscible fluids in a vertical porous column. *Water Resources Research* 6: 156–171.
- Baird, J.H., and R.N. Calhoun. 1999. Wetting agents for localized dry spots [Online]. [http:// www.msu.edu/user/turf/misc/misc2.html](http://www.msu.edu/user/turf/misc/misc2.html)
- Bancroft, W.D. 1912. Applied colloid chemistry: general theory. *Journal of Physical Chemistry*. pp. 17, 345, 475, 739.
- Barton L., and T.D. Colmer. 2011. Granular wetting agents ameliorate water repellency in turfgrass of contrasting soil organic matter content. *Plant Soil*. 348: 411-424.
- Bauters, T.W.J, D.A. DiCarlo, T.S. Steenhuis, and J.Y. Parlange. 1998. Preferential flow in water-repellent sands. *Soil Sci. Soc. J.* 62: 1185-1190.

- Becher, P. 1984. HLB – a survey, in surfactants in solution. Vol. 3, Mittal, K.L., (Ed.), Plenum, New York. 1925-1946.
- Becher, P., and R.L. Birkmeier. 1964. The determination of hydrophile-lipophile balance by gas-liquid chromatography. *Journal of the American Oil Chemists*. 41: 196-172.
- Ben-Et, G., and D. Tatarsky. 1972. Application of NMR for the determination of HLB values of nonionic surfactants. *Journal of the American Oil Chemists*. 49: 499-500.
- Blackwell, P.S. 2000. Management of water repellency in Australia, and risks associated with preferential flow, pesticide concentration and leaching. *J. Hydrol.* 231-232: 384-395.
- Blodgett, A.M., D.J. Beattie, and J.W. White. 1993. Hydrophilic polymers and wetting agents affect absorption and evaporative water loss. *Hort. Sci.* 28(6): 633-635.
- Bond, R.D. 1964. The influence of the microflora on the physical properties of soils. II. Field studies on water repellent sands. *Australian Journal of Soil Research* 2: 123–131.
- Bond, R.D. 1978. Addition of cores of loam to overcome dry patch in turf on sandy soils. *Modification of Soil Structure* 8: 285.
- Bouwer, H. 1986. Intake rate: Cylinder infiltrometer. p. 825-843. In: *Methods of Soil Analysis*. A. Klute, ed. ASA Monograph 9. ASA. Madison, WI.
- Bowman, R.S. 1984. Evaluation of some new tracers for soil water studies. *Soil Sci. Soc. Am. J.* 48: 987-993.

- Brandy, G.H. 1969. Water movement in hydrophobic soils. p. 91-115. *In Proc. Symp. Water Rep. Soils*, Riverside, CA. 6-10 May 1968. Univ. of Calif., Riverside.
- Buczko, U., O. Bens, and R.E. Hüttl. 2006. Tillage effects on hydraulic properties and macroporosity in silty and sandy soils. *Soil Sci. Soc. J.* 70: 1998-2007.
- Carrillo, M.L.K., J. Letey, and S.R. Yates. 1999. Measurement of initial soil-water contact angle of water repellent soils. *Soil Sci. Soc. J.* 63: 433-436.
- Carrillo, M.L.K., J. Letey, and S.R. Yates. 2000. Unstable water flow in a layered soil: I. Effects of a stable water-repellent layer. *Soil Sci. Soc. Am. J.* 64: 450-455.
- Chen, Y., and M. Schnitzer. 1978. The surface tension of aqueous solutions of soil humic substances. *Soil Sci.* 125:7-15.
- Chun, A.H.C., and A.N. Martin. 1961. Measurement of hydrophile-lipophile balance of surface-active agents. *Journal of Pharmaceutical Science.* 50: 732-736.
- Clothier, B.E., I. Vogeler, and G.N. Magesan. 2000. The breakdown of water repellency and solute transport through a hydrophobic soil. *Jour. Hydro.* 231-232: 255-264.
- Crockford, S., S. Topalidis, and D.P. Richardson. 1991. Water repellency in a dry sclerophyll forest – measurements and processes. *Hydrological Processes.* 5: 405-420.
- Culligan, P.J., V. Ivanov, and J.T. Germaine. 2005. Sorptivity and liquid infiltration into dry soil. *Advances in Water Resources.* 28(10):1010-1020.
- Davies, J.T. 1957. A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent. *Gas/Liquid and Liquid/Liquid Interfaces. Proceedings of 2nd International Congress Surface Activity.* pp. 426-438.

- Davis, H.T. 1994. Factors determining emulsion type: hydrophile-lipophile balance and beyond. *Colloids and Surfaces*. 94: 9-24.
- Davis, S.N., G.M. Thompson, H.W. Bentle, and G. Stiles. Ground water tracers – a short review. *Ground Water*. 18(1): 14-23.
- De Jonge, L.W., O.H. Jacobsen, and P. Moldrup. 1999. Soil water repellency: effects of water content, temperature and particle size. *Soil Science Society of America J.* 63: 437-442.
- DeBano, L.F. 1969. Water movement in water-repellent soils. *Proceedings Symposium Water-Repellent Soils*, University of California, May 1968. Pp. 61-89.
- DeBano, L.F. 1969a. Water repellent soils; A world-wide concern in management of soil and vegetation. *Agro. Sci. Rev.* 7: 11-18.
- DeBano, L.F. 1971. The effect of hydrophobic substances on water movement in soil during infiltration. *Soil. Sci. Soc. Am. J.* 35: 340-343.
- Dekker, L.W., and C.J. Ritsema. 1994. How water moves in a water repellent sand soil. 1. Potential and actual repellency. *Water Resour. Res.* 30: 2507-2517.
- Dekker, L.W., and C.J. Ritsema. 1996a. Variation in water content and wetting patterns in Dutch water repellent peaty clay and clayey peat soils. *Catena* 28: 89-105.
- Dekker, L.W., C.J. Ritsema, K. Oostindie, and O.H. Boersma. 1998. Effect of Drying Temperature on the Severity of Soil Water Repellency. *Soil Science* 163(10): 780–796.
- Dekker, L.W., C.J. Ritsema, K. Oostindie, and O.H. Boersma. 1998. Effect of drying temperature on the severity of soil water repellency. *Soil Sci.* 163:780-796.

- Dekker, L.W., K. Oostindie, and C.J. Ritsema. 2005. "Exponential Increase of Publications Related to Soil Water Repellency." *Soil Research* 43(3): 403–41.
- Dekker, L.W., K. Oostindie, and C.J. Ritsema. 2005. Exponential increase of publications related to soil water repellency. *Soil Res.* 43(3): 403–441.
- Dekker, L.W., S.H. Doerr, K. Oostindie, A.K. Ziogas, and C.J. Ritsema. 2001. Water repellency and critical soil water content in a dune sand. *Soil Sci. Soc. J.* 65: 1667-1674.
- Doerr, S.H., R.A. Shakesby, and R.P.D. Walsh. 1998. Spatial variability of soil water repellency in fire-prone eucalyptus and pine forests. *Soil Science* 163: 313-324.
- Doerr, S.H., R.A. Shakesby, and R.P.D. Walsh. 2000. Soil water repellency: its causes, characteristics and hydro-geomorphological significance. *Earth-Science Reviews* 51(1–4): 33–65.
- Doerr, S.H., R.A. Shakesby, L.W. Dekker, and C.J. Ritsema. 2006. Occurrence, prediction and hydrological effects of water repellency amongst major soil and land-use types in a humid temperate climate - Doerr - 2006 - *European Journal of Soil Science* - Wiley Online Library. *European Journal of Soil Science* 57: 741–754.
- Domingo, W.R. 1950. Some notes on irreversibly dried difficultly wettable soils. *Landbouwkund Tijdschr* 62: 252–260.
- Dunkelberg, E., U. Boeckelmann, B. Braun, D. Diehl, G.E. Schaumann, and E. Grohmann. 2006. DO wax-degrading bacteria influence water repellency of soil. In 1st International Biohydrology Conference, Prague, Czech Republic. pp. 20-22.
- Feng, G. L., J. Letey, and L. Wu. 2001. Water ponding depths affect temporal infiltration rates in a water repellent sand. *Soil Sci. Soc. Am. J. Soil Res.* 1: 9-16.

- Feng, G.L., J. Letey, and L. Wu. 2002. The Influence of Two Surfactants On infiltration into a Water-Repellent Soil. *Soil Science Society of America Journal* 66(2): 361–367.
- Forrer, I., A. Papritz, R. Kasteel, H. Flühler, and D. Luca. 2000. Quantifying dye tracers in soil profiles by image processing. *Euro. J. Soil Sci.* 51:313-322.
- Franco, C.M., P. Michelsen, and J. Oades. 2000. Amelioration of water repellency: application of slow-release fertilisers to stimulate microbial breakdown of waxes. *Journal of Hydrology* 231–232: 342–351.
- Franklin, M. K., S. E. McCann, and S. J. Kostka. 2005. Evaluating turfgrass performance after surfactant application in a wettable and a non-wettable soil. *Intl. Turfgrass Soc. Res. J.* 10: 85-86.
- Gadhav, A. 2014. Determination of hydrophilic-lipophilic balance value. *International Journal of Science and Research.* 3: 573-575.
- Greenwald, H.L., G.L. Brown, and M.N. Fineman. 1956. Determination of hydrophile-lipophile character of surface-active agents and oils by water titration. *Analytical Chemistry.* 28: 1693-1697.
- Gregory, J.H., M.D. Dukes, G.L. Miller, and P.H. Jones. 2005. Analysis of double-ring infiltration techniques and development of a simple automatic water delivery system. *Applied Turfgrass Sci.* Online.
- Griffin, W.C. 1949. Classification of surface-active agents by HLB. *Journal of the Society of Cosmetic Chemists.* pp. 311-326.
- Griffin, W.C. 1954. Calculation of HLB values of non-ionic surfactants. *Journal of the Society of Cosmetic Chemists.* pp.249-256.

- Hait, S.K., and S.P. Moulik. 2001. Determination of critical micelle concentration (CMC) of nonionic surfactants by donor-acceptor interaction with Iodine and correlation of CMC with hydrophile-lipophile balance and other parameters of the surfactants. *Journal of Surfactants and Detergents* 4(3): 303–309.
- Hallet, P.D., K. Ritz, and R.E. Wheatley. 2001a. Microbial derived water repellency in golf course soil. *Intl. Turgrass Soc. Res. J.* 9: 518-524.
- Hallet, P.D., N.A. White, and K. Ritz. 2006. Impact of basidiomycete fungi on the wettability of soil contaminated with a hydrophobic polycyclic aromatic hydrocarbon. *Biologia* 61: S334-S338.
- Hallett, P.D. 2007. An introduction to soil water repellency. *International Society for Agrochemical Adjuvants*.
- Hallett, P.D. 2008. A brief overview of the causes, impacts and amelioration of soil water repellency – a review. *Soil and Water Research* 3(Special Issue No. 1): S21–S29.
- Hallett, P.D., D.C. Gordon, and A.G. Bengough. 2003. Plant influence on rhizosphere hydraulic properties: direct measurements using a miniaturized infiltrometer. *New Phyt.* 157: 597-603.
- Hillel, D.E. 1972. Unstable flow in layered soils: a review. *Hydrological Processes* 1: 143–147.
- Hoyle F.C., D.V. Murphy, and I.R.P. Fillery. 2006. Temperature and stubble management influence microbial CO₂-C evolution and gross transformation rates. *Soil Biology and Biochemistry*. 38: 71-80.
- Huebner, V.H. 1962. Determination of the relative polarity of surface-active agents by gas liquid chromatography. *Analytical Chemistry*. 34: 488-491.

- Huggenberger, F., J. Letey, and W.J. Farmer. 1973. Effect of two nonionic surfactants on adsorption and mobility of selected pesticides in a soil-system. *Soil Science Society of America Proceedings* 37: 215–219.
- Hummel, H. 1993. Rationale for the Revisions of the USGA Green Construction Specifications. *USGA Green Section Record* 32(2): 7-21.
- Imerson, A.C., J.M. Verstraten, E.J. Van Mullingen, and J. Sevink. 1992. The effects of fire and water repellency on infiltration and runoff under Mediterranean type forests. *Catena*. 19:345-361.
- Jamison, V.C. 1947. Resistance of wetting in the surface of sandy soils under citrus trees in central Florida and its effect upon penetration and the efficiency of irrigation. *Soil Science Society of America Proceedings* 11: 103–109.
- Kanicky, J.R., J.C. Lopez-Montilla, S. Pandey, and D.O. Shah. 2001. Surface chemistry in the petroleum industry. *Applied Surface and Colloid Chemistry*. 251-267.
- Karagunduz, A., K.D. Pennell, and M.H. Young. 2001. Influence of a nonionic surfactant on the water retention properties of unsaturated soils. *Soil Sci. Soc. Am. J.* 65: 1392-1399.
- Karnok, K.J. 2006. Which wetting agent is best? *Golf Course Manage.* 74: 82-83.
- Karnok, K.J., and Beall, M. 1995. Localized dry spots caused by hydrophobic soil: what have we learned?. *Golf Course Management* 8: 57-59.
- Karnok, K.J., and K.A. Tucker. 2001. Wetting agent treated hydrophobic soil and its effect on color, quality and root growth of creeping bentgrass. *Int Turfgrass Soc.* 9: 537-541.

- Karnok, K.J., E.J. Rowland, and K.H. Tan. 1993. High pH treatments and the alleviation of soil hydrophobicity on golf greens. *Agron. J.* 85: 983-986.
- Karnok, K.J., G. Wiecko, and R.M. Beall. 1989. The use of time domain reflectometry for determining the effectiveness of various wetting agents on hydrophobic soils. *Agron. Abs.* pp. 160.
- Karnok, K.J., K. Xia, and K. Tucker. 2004. Wetting agents: What are they, and how do they work? *Golf Course Management*: 84–86.
- Kasteel, R., H.J. Vogel, and K. Roth. 2002. Effect of non-linear adsorption on the transport behaviour of brilliant blue in a field soil. *Eur. J. Soil Sci.* 53: 231-240.
- Kaufman, W.J. 1961. Tritium as a ground-water tracers. *Am. Soc. Civil Eng. Trans. Paper.* 3202: 436-446.
- Kennedy, N., E. Brodie, J. Connolly, and N. Clipson. 2004. Impact of lime, nitrogen and plant species on bacterial community structure in grassland microcosms. *Environ. Microbiol.* 6: 1070-1080.
- King, P. 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect its measurement. *Soil Research* 19(3): 275.
- Kostka, S.J. 2000. Amelioration of water repellency in highly managed soils and the enhancement of turfgrass performance through the systematic application of surfactants. *J. Hydrol.* 231-232: 359-368.
- Kostka, S.J., and P.T. Bially. 2005. Synergistic surfactant interactions for enhancement of hydrophilicity in water repellent soils. *Int. Turfgrass Soc. Res. J.* 10: 108-114.

- Kothencz, R., R. Nagy, and L. Bartha. 2017. Determination of HLB values of some nonionic surfactants and their mixtures. *Studia UBB Chemia*. 4: 451-458.
- Kumar, N., S. Garoff, and R. Tilton. 2004. Experimental Observations on the scaling of adsorption isotherms for nonionic surfactants at a hydrophobic solid-water interface. 20: 4446-4451.
- Kunieda, H., and K. Shinoda. 1985. Evaluation of the hydrophile-lipophile balance (HLB) of nonionic surfactants. *Journal of Colloid and Interface Science*. 107: 107-121.
- Kurwadkar, S.T., C.D. Adams, M.T. Meyer, and D.W. Kolpin. 2011. Comparative mobility of sulfonamides and bromide tracer in three soils. *J. Environ. Manag.* 92: 1874-1881.
- Lai, J., and L. Ren. 2007. Assessing the size dependency of measured hydraulic conductivity using double-ring infiltrometers and numerical simulation. *Soil Sci. Soc. Am. J.* 71: 1667-1675.
- Lang, S., and J.C. Philp. 1998. Surface-active lipids in rhodococci. *Antonie van Leeuwenhoek*. 74:59-70.
- Larsson, M.H., N.J. Jarvis, G. Torstensson, and R. Kasteel. 1999. Quantifying the impact of preferential flow on solute transport to tile drains in a sandy field soil. *J. Hydro.* 215: 116-134.
- Leinauer, B., P.E. Rieke, D. VanLeeuwen, R. Sallenave, J. Makk, and E. Johnson. 2001. Effects of soil surfactants on water retention in turfgrass rootzones. *Int. Turfgrass Soc.* 9: 542-547.

- Letey, J. 1969. 'Measurement of contact angle, water drop penetration time, and critical surface tension', *Proceedings of the Symposium on Water-Repellent Soils* 6(10): 43-47.
- Letey, J., J. Osborn, and R.E. Pelishek. 1962a. The influence of the water-solid contact angle on water movement in soil. *Int. Ass. Sci. Hydrol. Bull* 3: 75-81.
- Letey, J., J. Osborn, and R.E. Pelishek. 1962b. Measurement of liquid-solid contact angles in soils and sand. *Soil Sci.* 93(3): 149-153.
- Letey, J., N. Welch, R.E. Pelishek, and J. Osborn. 1962c. Effect of wetting agents on irrigation of water repellent soils. *California Agriculture* 16 (12): 12-13.
- Li, J.L., and B.H. Chen. 2002. Solubilization of model polycyclic aromatic hydrocarbons by nonionic surfactants. *Chemical Engineering Science* 57(14): 2825–2835.
- Lichner, L., N. Babejova, and L.W. Dekker. 2002. Effects of kaolinite and drying temperature on the persistence of soil water repellency induced by humic acids. *Rostlinna Vryoba* 48: 2003-2007.
- Luan, F., H. Liu, Y. Gao, Q. Li, X. Zhang, and Y. Guo. 2009. Prediction of hydrophile-lipophile balance values of anionic surfactants using a quantitative structure-property relationship. *Journal of Colloid and Interface Science.* 336: 773-779.
- Lupwayi, N., M.A. Arshad, R.H. Azooz, and Y.K. Soon. 2009. Soil microbial response to wood ash or lime applied annual crops and perennial grass in an acid soil of northwestern Alberta. *Can. J. Soil Sci.* 89: 169-177.
- Ma'shum, M., and V.C. Farmer. 1985. Origin and assessment of water repellency of a sandy Australian soil. *Australian J. Soil. Res.* 23:623-626.

- Ma'shum, M., J.M. Oades, and M.E. Tate. 1989. The use of dispersible clays to reduce water-repellency of sandy soils. *Aust. J. Soil Res.* 27: 797-806.
- Ma'shum, M., M.E. Tate, G.P. Jones, and J.M. Oades. 1988. Extraction and characterization of water-repellent material from Australian soils. *Soil Science*. 39: 99-110.
- Mainwaring, K.A., C.P. Morley, S.H. Doerr, P. Douglas, C.T. Llewellyn, G. Llewellyn, I. Matthews, and Stein B.K. 2004. Role of heavy polar organic compounds for water repellency of sandy soils. *Env. Chem. Letters*. 2: 35-39.
- McKenna, F., K.A. El-Tarabily, S. Petrie, C. Chen, and B. Dell. 2002. Application of actinomyces to soil to ameliorate water repellency. *Lett. Appl. Microbiol.* 35:107-112.
- McKissock, I., E.L. Walker, R.J. Gilkes, and D.J. Carter. 2000. The influence of clay type on reduction of water repellency by applied clays: a review of some West Australian work. *J. Hydrol.* 231-232: 323-332.
- Miller, R.H., and J.F. Wilkinson. 1977. Nature of the organic coatings on sand grains of nonwetttable golf greens. *Soil Sci. Soc. Am. J.* 41:1203-1204.
- Miller, W.W., N. Valoras, and J. Letey. 1975. Movement of two nonionic surfactants in wettable and water-repellent soils. *Soil Science Society of America Proceedings* 39: 11-16.
- Miyamoto, S., and J.B. Bird. 1978. Effects of two wetting agents on germination and shoot growth of some southwestern range plants. *Journal of Range Management* 31: 74-75.

- Mooney, S.J., and C. Morris. 2008. A morphological approach to understanding preferential flow using image analysis with dye tracers and x-ray computed tomography. *Catena*. 73: 204-211.
- Moore, G., and P. Blackwell. 1998. Water repellence. In: Moore, G. (Ed.), *Soil Guide. Agriculture Western Australia*, pp. 53-63.
- Morgan, W.C., J. Letey, S.J. Richards, and N. Valoras. 1967. Using physical soil amendments, irrigation, and wetting agents in turfgrass management. *California Agriculture* 21(1): 8–11.
- Moulik, S.P. 1996. Micelles: Self-Organized Surfactant Assemblies. *Current Science* 71:5.
- Müller, K., and M. Deurer. 2011. Review of the remediation strategies for soil water repellency. *Agriculture, Ecosystems & Environment* 144(1): 208–221.
- Mustafa, M.A., and J. Letey. 1970. Factors influencing effectiveness of two surfactants on water-repellent soils. *California Agriculture* 24(6): 12–13.
- Nagy, R., R. Kothencz, C. Varga, and L. Bartha. 2016. Titrimetric characteristics of the solubility properties of various surfactants. *Fiatal Muszakiak Tudományos Ulesszaka*. pp. 297-300.
- Nagy, R., R. Kothencz, R. Sallai, and L. Bartha. 2015. An improved method for the determination of HLB properties of nonionic surfactants. *International Journal of Scientific & Engineering Research*. 6: 580-583.
- Nektarios, P.A., A.M. Petrovic, and T.S. Steenhuis. 2002. Effect of surfactant on fingered flow in laboratory golf greens. *Soil Sci.* 167: 572-579.

- Onken, A.B., C.W. Wendt, R.S. Hargrove, and O.C. Wilke. 1977. Relative movement of bromide and nitrate in soils under three irrigation systems. *Soil Sci. Soc. Am. Proc.* 41: 50-52.
- Onken, A.B., R.S. Hargrove, C.W. Wendt, and O.C. Wilke. 1975. The use of a specific ion electrode for determination of bromide in soils. *Soil Sci. Soc. Am. Proc.* 39: 1223-1225.
- Paria, S., and K.C. Khilar. 2004. A review on experimental studies of surfactant adsorption at the hydrophilic solid-water interface. 110: 75-95.
- Parker, S.D. 1987. *Encyclopedia of Science and Technology*. McGraw-Hill, New York.
- Parta, A.K., and T.J. Rego. 1994. Modified procedure for bromide estimation with ion-selective electrode for predicting nitrate movement in soil. *Current Sci.* 67(7): 545-546.
- Pasquali, R.C., M.P. Taurozzi, and C. Bregni. 2007. Some considerations about the hydrophilic-lipophilic balance system. *International Journal of Pharmaceutics.* 356: 44-51.
- Pasquali, R.C., N. Sacco, and C. Bregni. 2009. The studies on hydrophilic-lipophilic balance (HLB): sixty years after William C. Griffin's Pioneer work. *Latin American Journal of Pharmacy.* 2: 313-317.
- Patel, N.K., and S.N. Shah. 2015. Biodiesel from plant oils. *Food, Energy, and Water.* 277-307.
- Patist, A., S.S. Bhagwat, K.W. Penfield, P. Aikens, and D.O. Shah. 2000. On the measurement of critical micelle concentrations of pure and technical-grade nonionic surfactants. *Journal of Surfactants and Detergents.* 3: 53-58.

- Pawignya, H., A. Prasetyaningrum, E.R. Dyartanti, T.D. Kusworo, and B. Pramudono. 2016. Estimation hydrophilic-lipophilic balance number of surfactants. Nanoscience and Nanotechnology Symposium. pp. 1-7.
- Prabu, S.L., T.N.K Suriya Prakash, and R. Thirumurugan. 2015. Cleaning validation and its regulatory aspects in the pharmaceutical industry. *Developments in Surface Contamination and Cleaning*. 7:129-186.
- Reynolds, W.D., and D.E. Elerick. 2002. Constant head soil core (tank) method. In: J.H. Dane and G.C. Topp, editors, *Methods of soil analysis. Part 4. Physical methods*. SSSA Book Ser. 5. SSSA, Madison, WI. p. 804-808.
- Ritsema, C.J. and L.W. Dekker. 1994. How water moves in a water repellent sandy soil: 2. Dynamics of fingered flow. *Water Resources Res.* 30: 2519-2531.
- Ritsema, C.J. and L.W. Dekker. 2000. Preferential flow in water repellent sandy soils: principles and modeling implications. *Jour. Hydro.* 231-232: 308-319.
- Ritsema, C.J., J.L. Nieber, L.W. Dekker, and T.S. Steenhuis. 1998. Stable or unstable wetting fronts in water repellent soils – effects of antecedent soil moisture content. *Soil & Tillage Res.* 47: 111-123.
- Ritsema, C.J., L.W. Dekker, J.M.H. Hendrickx, and W. Hamminga. 1993. Preferential flow mechanism in a water repellent sandy soil. *Water Resour. Res.* 29: 2183-2193.
- Robbers, J.E., and V.N. Bhatia. 1961. Technique for the rapid determination of HLB and required HLB values. *Journal of Pharmaceutical Science*. 50: 708-709.

- Roberts, F.J., and B.A. Carbon. 1972. Water repellence in sandy soils of south-western Australia: II. Some chemical characteristics of the hydrophobic skins. *Aust. J. Soil. Res.* 10:35-42.
- Roper, M.M. 2004. The isolation and characterization of bacteria with the potential to degrade waxes that cause water repellency in sandy soils. *Australian Journal of Soil Research.* 42: 427-434.
- Roper, M.M. 2006. Potential for remediation of water repellent soils by inoculation with wax-degrading bacteria in south-western Australia. *Biologia.* 61(19).
- Roper, M.M., 2005. Managing soils to enhance the potential for bioremediation of water repellency. *Aust. J. Soil Res.* 43, 803–810.
- Roper, M.M., and V.V.S.R. Gupta. 2005. Enumeration of wax-degrading microorganisms in water repellent soils using a miniaturized Most-Probable-Number method. *Aust. J. Soil Res.* 43: 171-177.
- Ruemmele, B.A., and J.A. Amador. 1998. Turfgrass and soil responses to soil wetting agents. *Jour. Turfgrass Manag.* 2(4): 71-82.
- Scheffer, F., and P. Schachtschabel. 1989. *Soil Science*. Enke, Stuttgart, 491 pp.
- Schott, H. 1969. Hydrophile-lipophile balance and cloud points of nonionic surfactants. *Journal of Pharmaceutical Sciences.* 58: 1443-1449.
- Scott, D.F. 1992. The influence of vegetation type on soil wettability. *Proceedings of the 17th Congress of the Soil Science Society of South Africa*, University of Stellenbosch, 28-30th Jan. 1992. Pp. 10B21-10B26.

- Scott, V.H., and R.H. Burgy. 1956. Effects of heat and bush burning on the physical properties of certain upland soils that influence infiltration. *Soil Science* 82: 63–70.
- Scotter, D.R. 1978. Preferential solute movement through larger soil voids: I. Some computations using simple theory. *Australian Journal of Soil Research* 16: 257–267.
- Smith, S.J., and R.J. Davis. Relative movement of bromide and nitrate through soils. *Jour. Environ. Qual.* 3(2): 152-155.
- Soldat, D.J., B. Lowery, and W.R. Kussow. 2010. Wetting agents affect soil moisture uniformity in sand putting greens. *Golf Course Management*. 78(8): 76-82.
- Song, E., J.G. Schneider, S.H. Anderson, K.W. Goyne, and X. Xiong. 2014a. Wetting agent influence on water infiltration into hydrophobic sand: I. Rewettability. *Agron. J.* 106(5): 1873-1878.
- Song, E., J.G. Schneider, S.H. Anderson, K.W. Goyne, and X. Xiong. 2014b. Wetting agent influence on water infiltration into hydrophobic sand: II. Physical Properties. *Agron. J.* 106(5): 1879-1885.
- Spindler, J. 2016. The relations between water and soils. *Sports Turf*: 34-37.
- Stone, E.L., and L. Thorp. 1971. *Lycopodium* fairy rings: effect on soil nutrient release. *Soil Science Society of America Proceedings* 35: 991–997.
- Suzuki, H. 1990. Interface and Surface-Active Agent. *Sangy-otosho*. pp. 38.
- T'schapek, M. 1984. Criteria for determining the hydrophilicity-hydrophobicity of soil. *Zeitschr. Pflanzenern. Bodenk.* 147: 137-149.
- Tan, K.H. 1982. Principles of soil chemistry. Marcel Dekker, New York.

- Throssell, C. 2005. GCSAA-USGA wetting agent evaluation. *Golf Course Management*: 52-59.
- Tillman, R.W., D.R. Scotter, M.G. Wallis, and B.E. Clothier. 1989. Water-repellency and its measurement by using intrinsic sorptivity. *Aust. J. Soil Res.* 27: 637-644.
- Topp, G.C., and P.A. Ferre. 2002. Time domain reflectometry. P. 434-446. *In* J.H. Dane and G.C. Topp (eds.) *Methods of soil analysis. Part 4. Physical Methods*. SSSA Book Ser. 5. SSSA, Madison, WI.
- Topp, G.C., J.L. Davis, and A.P. Annan. 1980. Electromagnetic determination of soil water content: measurement in coaxial transmission lines. *Water Resources Research*. 16: 574-582.
- Tucker, K.A., K.J. Karnok, D.E. Radcliffe, G. Landry, R.W. Roncadori, and K.H. Tan. 1990. Localized dry spots as caused by hydrophobic sand on bentgrass greens. *Agronomy Journal* 82: 549-555.
- Valat, B., C. Jouany, L.M. Riviere. 1991. Characterization of the wetting properties of air-dried peats and composts. *Soil Science*. 152:100-107.
- Van't Woudt, B.D. 1959. Particle coatings affect the wettability of soils. *Journal of Geophysical Research* 64: 263-267.
- Wagner, O.R. 1977. The use of tracers in diagnosing interwell reservoir heterogeneities. *Jour. Petroleum. Tech.* p. 1410-1416.
- Wallis, M.G., and D.J. Horne. 1992. Soil water repellency. *Adv. Soil Sci.* 20: 91-146.
- Walter, U., M. Beyer, J. Klein, and H.J. Rehm. 1991. Degradation of pyrene by *Rhodococcus* sp. UW1. *Appl. Microbiol. Biotechnol.* 34: 671-676.

- Wang, B., M. Jin, J.R. Nimmo, L. Yang, and W. Wang. 2008. Estimating groundwater recharge in Hebei Plain, China under varying land use practices using tritium and bromide tracers. *Jour. Hydro.* 356: 209-222.
- Wang, Z., Q.J. Wu, L. Wu, C.J. Ritsema, L.W. Dekker, and J. Feyen. 2000. Effects of soil water repellency on infiltration rate and flow instability. *Journal of Hydrology* 231–232: 265–276.
- Ward, P.R., and J.M. Oades. 1993. Effect of clay mineralogy and exchangeable cations on water-repellency in clay-amended sandy soils. *Aust. J. Soil Res.* 31: 351-364.
- Watson, C.L., and J. Letey. 1970. Indices for characterizing soil-water repellency based upon contact angle-surface tension relationships. *Soil Science Society of America Proceedings* 34: 841–844.
- Watson, C.L., B.L. McNeal, and J. Letey. 1969. The effect of surfactants on the hydraulic conductivity of salt-affected soils. *Soil Science* 108: 58–63.
- Watson, C.L., J. Letey, and M.A. Mustafa. 1971. The influence of liquid surface tension and liquid-solid contact angle on liquid entry into porous media. *Soil Science* 112: 178–183.
- Wessel, A.T. 1998. On using the effective contact angle and the water drop penetration time for classification of water repellency in dune soils. *Earth Surf. Processes Landforms* 13: 555-561.
- Wesseling, J.G., C.R. Stoof, C.J. Ritsema, K. Oostindie, and L.W. Dekker. 2009. The effect of soil texture and organic amendment on the hydrological behaviour of coarse-textured soils. *Soil Use and Management.* 25:274-283.

- Wessolek, G., H. Stoffregen, and K. Täumer. 2009. Persistency of flow patterns in a water repellent sandy soil – conclusions of TDR readings and a time-delayed double tracer experiment. *Jour. Hydro.* 375: 524-535.
- Wiecko, G., and R.N. Carrow. 1992. Wetting agent effects on soil physical properties and turfgrass growth. *Agron. Abs.* pp. 178.
- Williams, S., M.E. Sharpe, and J. Holt. 1989. *Bergey's Manual of Systematic Bacteriology*. Williams and Wilkins, Baltimore, MD.
- Woche, S.K., M.-O. Goebel, M.B. Kirkham, R. Horton, R.R.V. der Ploeg, and J. Bachmann. 2005. Contact angle of soils as affected by depth, texture, and land management. *European Journal of Soil Science* 56(2): 239–251.
- Yamashita, Y., and K. Sakamoto. 2016. Hydrophilic-lipophilic balance (HLB): classical indexation and novel indexation of surfactant. *Encyclopedia of Biocolloid and Biointerface Science*. 570-574.
- Yorl, C.A. 1993. A questionnaire survey of dry patch on golf courses in the United Kingdom. *Journal of Sports Turf Research*. 69: 20-26.
- Zhang, R., and P. Somasundaran. 2006. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Advances in Colloid and Interface Science*. 123; 213-229.
- Zisman, W.A. 1964. Relation of the equilibrium contact angle to liquid and solid constitution. In: Gould, R.F. (Ed.), *American Chemical Society. Advances in Chemistry Series Vol. 43*, pp. 1-51.
- Zontek, S.J., and S.J. Kostka. 2012. Understanding the different wetting agent chemistries. *Green Section Record*. 50: 1-6.

CHAPTER II

Determination of Selected Soil Surfactants Effects on Physical Properties of Water

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Abstract

Soil hydrophobicity, which causes water to bypass hydrophobic rootzones, is a reoccurring problem on United States Golf Association (USGA) sand-based greens. Negative outcomes, such as preferential flow occur leading to reduced water availability and ultimately plant death. Golf course superintendents commonly apply wetting agents to ameliorate these effects. However, limited information on their performance is available when deciding which wetting agent to utilize. Therefore, the objective of this experiment was to assess various wetting agents' influence on water properties, water infiltration and their ability to rewet hydrophobic sands. Laboratory experiments were conducted to assess the influence of various wetting agents on liquid surface tension (γ ; mN m^{-1}) and solid-liquid contact angle (θ ; $^{\circ}$) at 5 rates based on the label rates. Analysis of the 23 different wetting agents available demonstrated a wide range of γ , from 44.8 mN m^{-1} to 22.0 mN m^{-1} , significantly reducing the γ of water by 38.5% to 64.5%, and aiding infiltration into water repellent sand. Based on their γ , the infiltration (i ; mm min^{-1}) and rewettability rates were determined for the six wetting agents through artificial hydrophobic sand (AHS). The addition of any wetting agent treatment resulted in a steady infiltration rate between 24 to 27 mm min^{-1} . All treatments enhanced water infiltration into the water repellent soil, while water alone failed to infiltrate into the

AHS. Following three dry-wet cycles, NIS was able to maintain a steady infiltration rate of water of 27 mm min^{-1} , similar to the initial infiltration rate. However, columns treated with PoP resulted in a gradual decrease in rewettability rate until not infiltrating into the column after 3 dry-wet cycles. These results suggest that there are significant differences in infiltration and rewettability for the wetting agents tested.

Abbreviations and key words: AHS, artificial hydrophobic sand; i , infiltration rate; NIS, nonionic surfactant, Capacity[™]; PoP, poloxanlene, poly, H₂O Maximizer[™]; rewettability; soil hydrophobicity; θ , solid-liquid contact angle; γ , surface tension; USGA, United States Golf Association; wetting agents.

Introduction

Climate change and steady reduction of water availability in the United States and globally has led to an increase of soil hydrophobicity, especially where sandy soil is abundant (Cisar et al., 2000; Dekker et al., 2005a; Doerr et al., 2000). In addition to agricultural land, soil water repellency affects golf courses, coastal land and pastures (Wallis & Horne, 1992; Doerr et al., 2006). Soil water repellency (SWR), which is the inability of water to wet a soil due to hydrophobic organic coatings covering the surface of the soil particle, is known to cause localized dry spot (LDS) (Doerr et al., 2000; Tucker et al., 1999; Wilkinson and Miller, 1978). Despite management intensity, water repellency is prevalent in the USGA sand-based greens, leading to LDS occurrence (Karnok & Beall, 1995; Tucker et al., 1990). Along with water repellency and resulting LDS, irregular infiltration patterns occur and create preferential flow pathways, known as fingering (Wang et al., 2000). This process is where water moves unevenly and more quickly throughout the soil profile, resulting in variations in water retained in the rootzone (Tucker, 1990; Wang et al., 2000). Ultimately, this soil condition results in uneven water distribution, water infiltration, poor playability and visually unappealing putting greens for golfers.

Water repellency develops from a variety of sources, such as root exudates, fungal hyphae and wax degradation from leaf cuticles (Doerr et al., 2000; Hallett, 2007). With sand particles having the smallest specific surface area of all soil particles, this phenomenon occurs more commonly in USGA sand-based greens (Karnok and Tucker, 1989; Larsbo et al., 2008). A water-repellent sand is known to have an initial θ value $>90^\circ$ and under these conditions, the soil will not spontaneously wet (Carrillo et al., 1999:

Emerson and Bond, 1963; Song et al., 2014b). Addition of a wetting agent to water reduces the γ and the θ of the solution, leading to a reduction in the level of hydrophobicity of a water-repellent soil and allowing infiltration (DeBano, 2000; Feng et al., 2002; Pelishek et al., 1962; Song et al., 2014). Approximately 94% of golf course superintendents overcome this by applying wetting agents to alleviate the soil water repellency and to potentially enhance soil water infiltration and retention into water-repellent sand-based greens (Kostka et al., 2005; Karnok et al., 2004; Karnok, 2006).

Wetting agents lower the γ of water by reducing the attraction of water molecules to each other at the liquid-air interface (Bauters et al., 1998; Feng et al., 2002; Esteves et al., 2016). Due to the correlation between θ and γ , lowering the γ , which reduces the θ of water, allows absorption of water into the water-repellent soil (Carrillo et al., 1999; Feng et al., 2002; Letey et al., 1998; Müller and Deurer, 2011; Song et al., 2014b). This is based on the assumption that soil pores are similar to capillary tubes (Feng et al., 2002). Within the capillary equation, the liquid entry pressure head (h_p), or the ponding head pressure needed to allow entry of water into a hydrophobic soil media, is directly related to γ and the θ (Feng et al., 2002). By lowering the γ of the water, and consequently reducing the θ , the h_p is reduced, thus increasing the infiltration into water-repellent soils (Feng et al., 2002).

When present in the soil, wetting agents, being amphiphilic compounds, allow the hydrophobic, non-polar, region of their molecules to adhere onto the hydrophobic sand particles, and consequently position the hydrophilic, polar, region of the compound toward the soil pore to interact and attract water molecules towards the sand particle surface (Karnok et al., 2004; Müller & Deurer, 2011). This process allows wetting agents

to alter water-repellency and transform a non-wettable soil into a wettable media, aiding in water infiltration (Cisar et al., 2000; Dekker et al., 2005b; Karnok et al., 2004).

The wetting agents on the turf market have limited information that quantifies the effect on γ , along with θ angle. Additionally, there is limited information available that documents the effect of wetting agents on water infiltration into water-repellent, sand-based media, and their ability to maintain reduced water repellency and water infiltration over time after application (Feng et al., 2001; Song et al., 2014b; Throssell, 2005). Therefore, the objectives of this study were to quantify the effect of various wetting agents on γ and θ of water when mixed in solution, and the influence of selected wetting agents on water infiltration and rewettability into water-repellent sands.

Materials and Methods

Surface Tension and Contact angle

Selected wetting agents were evaluated for γ at five rates: 0.25x, 0.5x, 1x, 2x, and 4x of the label rate using an Attension Theta Lite tensiometer (Biolin Scientific, Inc., Linthicum Heights, MD). The γ was determined by a pendant drop tensiometer which utilizes a needle, a camera, a light source and computer (Berry et al., 2015). A droplet of solution is dispensed and suspended from a 0.41 mm diameter needle (Img. 2.1). The pendant drop method utilizes small volumes of liquid solution to measure low γ . A balance between gravity and γ forces determines the pendant droplet shape of the suspended solution. Elongation of the droplet is due to the gravity forces, while the spherical shape of the droplet is due to the solutions' γ . The Attension Theta Lite tensiometer utilizes a light source facing the camera, with the solution droplet suspended between. This allows for the droplet to be detected due to a difference in light contrast

passing through the droplet. The pendant drop method utilizes the Young-Laplace equation (Eq. 2.1), which relates pressure differences across a curved interface and the related interfacial γ (Berry et al., 2015).

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P \equiv \Delta P_0 - \Delta \rho g z \quad \text{Eq. 2.1}$$

where ΔP is the pressure difference between inside and outside of the droplet, R_1 and R_2 are the radii of curvature in the suspended droplet, $\Delta \rho$ is the density difference between the droplet phase density and the surrounding continuous phase density, g is the gravitational constant and z representing the hydrostatic column effect (Berry et al., 2015; Hernández-Baltazar and Garcia-Fadrique, 2005). The equation can also be written based on a reference pressure ΔP_0 at $z = 0$ and a hydrostatic pressure $\Delta \rho g z$ (Berry et al., 2015). Since the needle hangs parallel to gravity, droplet axisymmetry can be utilized and equation 2.1 can be expressed in cylindrical coordinates, with x and z being horizontal and vertical coordinates, respectively, and with φ being the tangent angle of the droplet. As such, the Young-Laplace equation can be expressed by equation 2.2a through 2.2c as a coupled set of dimensionless differential equations, based on the arc length s measured from the drop apex (Berry et al., 2015; Hansen and Rødsrud, 1990; Hernández-Baltazar and Garcia-Fadrique, 2005).

$$\frac{d\varphi}{d\bar{s}} = 2 - \beta \bar{z} - \frac{\sin \varphi}{\bar{r}} \quad \text{Eq. 2.2a}$$

$$\frac{d\bar{r}}{d\bar{s}} = \cos \varphi \quad \text{Eq. 2.2b}$$

$$\frac{d\bar{z}}{d\bar{s}} = \sin \varphi \quad \text{Eq. 2.2c}$$

The variables denoted with bars, \bar{s} , \bar{r} , \bar{z} , refer to dimensionless quantities scaled by R_0 , which is the radius of the drop curvature at the droplet apex or drop dimension (Berry et al., 2015; Hansen and Rødsrud, 1990; Hernández-Baltazar and Gracia-Fadrique, 2005). In equation 2.2a, β is the shape factor of the droplet, known as the Bond number (Berry et al., 2015; Hansen and Rødsrud, 1990; Hernández-Baltazar and Gracia-Fadrique, 2005; Thiesen et al., 1995). The Bond number is a dimensionless number that measures the relation of gravitational and capillary forces on surface tension, and characterizes the shape of droplets including the properties of the fluid (Hernández-Baltazar and Gracia-Fadrique, 2005).

By determining the β associated with the hanging pendant drop, coupled with the R_0 at the apex of the drop, the γ of the drop can be determined by equation 2.3.

$$\gamma = \frac{\Delta\rho g R_0^2}{\beta} \quad \text{Eq. 2.3}$$

Based on the series of 300 images captured in a 15 second time period, the OneAttension (Biolin Scientific, Inc., Linthicum Heights, MD) software calculates the liquid surface tension based on these series of equations.

A total of 23 commercialized wetting agents at various concentrations of 0.25x, 0.5x, 1x, 2x and 4x of the label rates, with tap water utilized as a control, were tested and arranged in a factorial combination of wetting agents and their concentrations. Subsamples of three measurements per droplet and three droplets or replications were completed for each wetting agent at a given concentration. Analysis of variance was conducted using the Proc GLM procedure of SAS 9.4 (SAS Institute, Cary, NC). Significant mean separation was performed based on Fisher's Protected LSD at $P = 0.05$.

Based on the γ determined, θ was calculated using the following equation 2.4 (Carrillo et al., 1999; Letey et al., 1998; Song et al., 2014b):

$$\cos\theta = \left[\left(\frac{\gamma_{ND}}{\gamma} \right)^{\frac{1}{2}} - 1 \right] \quad \text{Eq. 2.4}$$

where γ is the liquid surface tension of wetting agent solutions or water, and γ_{ND} is the 90° surface tension of the water-repellent sand. The γ_{ND} was determined from water-repellent sand which was developed by following the procedures described by Bauters et al. (1998) and Bradford and Leij (1996). Hydrophobicity of the water-repellent sand was determined using the molarity of ethanol droplet test (MED) when sand was packed to a bulk density (D_b) of 1.7 g cm⁻³ (Doerr, 1998; King, 1981; Roy and McGill, 2002; Watson and Letey, 1970). A MED value of 5.4 was determined for the water-repellent sand, which is greater than the threshold for severe hydrophobicity with a MED value ≥ 4.0 (Karnok and Tucker, 2001; Watson and Letey, 1970). The γ_{ND} was determined by measuring the γ of the ethanol solution representing the 5.4 MED value, as it was the lowest ethanol solution concentration able to penetrate the water-repellent sand in 5 seconds or less, which was determined to be 36.95 mN m⁻¹. Wetting agent contact angles were determined based on their surface tension values and tested at their different concentrations using equation 2.4.

Infiltration and Rewettability

Washed silica sand meeting the USGA specifications for putting green construction (U.S. Golf Association, 2004) was used for this study to create water repellent sand (Song et al., 2014a). The AHS was created following procedures established by Bauters et al. (1998) and Bradford and Leij (1996) by mixing 120 kg of sand with 70 g octadecylamine (Sigma-Aldrich, St. Louis, MO) and 60 L of tap water in

a concrete mixer. The sand was mixed for 24 h before being dried in an oven at 75°C for 36 h. Once dry, the sand was rinsed three times with tap water to remove excess octadecylamine and dried again at 75°C for 36 h. Sand was thoroughly mixed and then stored in a sealed plastic container for future use. Treated sands were tested for hydrophobicity by the MED test when sands were packed to a bulk density (D_b) of 1.7 g cm⁻³ (Doerr, 1998; King, 1981; Roy and McGill, 2002; Watson and Letey, 1970). The treated sands resulted in a MED value of 5.4, which is considered as severely hydrophobic (Karnok and Tucker, 2001; King, 1981; Watson and Letey, 1970). Tap water droplets were applied to the water-repellant sand, did not penetrate and eventually evaporated from the sand surface. The particle distribution of the sand was 8.3% very coarse sand, 38.6% coarse sand, 47.3% medium sand, 4.8% fine sand, and 1.0% very fine sand. Total porosity was determined to be 38.2% with 23.2% air-filled porosity at a bulk density of 1.7 g cm⁻³ (Nimmo, 2004).

The θ and water entry pressure head (h_w), were determined for the water repellent sand as these factors affect infiltration. The θ of tap water was 107°, which was determined using an Attension Theta Lite tensiometer. The h_w was determined to be 8.5 cm by using the water-ponding method (Wang et al., 1998). For all experiments, the same batch of water-repellent sands was used.

Following a procedure established by Song et al. (2014a) with modifications, Harvel Clear PVC tubes (Georg Fischer Harvel LLC, Easton, PA) with a 5.08 cm inner diameter and 0.48 cm wall thickness, were used to measure infiltration. PVC tubes were cut into two lengths of 20 cm for use as a sand column and 12.5 cm to hold the wetting agent treatment solution. Fine fabric mesh was adhered to the bottom of the 20 cm tubes

to hold the sand but allow for an exchange of water and air. A 5.08-cm diameter no-hub rub coupler with a length of 10 cm (Fernco Inc., Davison, MI) was used to attach the 12.5 cm upper wetting agent treatment column to the 20 cm lower sand column, to form a 30.5-cm continuous infiltration column. The interior walls of the 20 cm sand columns were coated with a Teflon Non-Stick Dry-Film Lubricant (DuPont, Wilmington, DE) to prevent preferential flow pathways along the sides of the infiltration columns.

The AHS were slowly added to the infiltration columns in four separate filling events and tapped multiple times after each filling to create an evenly packed column with a bulk density of 1.7 g cm^{-3} , and depth of 18.42 cm. The infiltration experiment started with application of a constant ponding depth (h_o) by using a Mariotte bottle syphoning system with a 1-L bottle placed on a scale on a raised surface. Based on previous studies, each wetting agent was mixed in tap water at 0.25x rate based on the label information (Song et al., 2014a), to produce a consistent wetting front pattern through the column for the infiltration studies. Wetting agent solutions were delivered to the infiltration columns via the syphon system. Using equation 2.5:

$$i = \frac{\Delta v}{r^2 \pi \Delta t} \quad \text{Eq. 2.5}$$

the change in the solution mass in the bottle (Δv) was recorded every minute (Δt) for 30 minutes and utilized to calculate the infiltration rate (i), where r is the inner radius of the column (Song et al., 2014a). During the infiltration study a constant ponding depth (h_o) of 6.35 cm was maintained throughout all experiments. Saturated hydraulic conductivity (K) was also calculated utilizing equation 2.6:

$$K = \frac{i_c L}{\Delta h} \quad \text{Eq. 2.6}$$

where i_c is the steady infiltration rate, Δh is the change in hydraulic head across the column, and L is the length of the infiltration sand column (Reynolds and Elerick, 2002; Song et al. 2014).

Based on the γ values determined, six wetting agents were selected, to test infiltration and rewettability. Treatments included a poloxanlene, poly (PoP) (H₂O Maximizer[™]; Kalo, Inc., Overland Park, KS) a dihydrooxirane, epihydrin (DE) (TriCure AD[™]; Mitchell Products, Millville, NJ), a nonionic surfactant (NIS) (Capacity[™]; Becker Underwood, Ames, IA), a nonionic polyol (NIPA) (Aqueduct[®]; Aquatrols, Paulsboro, NJ), an alkoxyated polyols (AoP) (Primer Select[®]; Aquatrols, Paulsboro, NJ), and a nonionic polyol (NIPI) (Infiltrix[®]; Aquatrols, Paulsboro, NJ) as well as water as an untreated control. Infiltration of water alone was tested at a h_o of 6.35 cm, but water did not infiltrate into the water-repellent sand as expected; therefore, infiltration data were not collected.

After the initial infiltration of wetting agent solutions, the sand columns were carefully disassembled and dried in an oven at 55°C until reaching a consistent weight (Song et al., 2014a). Rewettability was then determined by reattaching the dry, wetting agent-treated sand columns to the infiltration system and applying tap water alone to the sand columns at the same h_o of 6.35 cm. This process was then repeated twice to establish three dry-wet cycles total for each wetting agent selected.

The infiltration experiment was designed as a completely randomized design with three replications. Through the study, two runs, each with three replications, were completed. Analysis of variance was conducted using the Proc GLM procedure of SAS 9.4 (SAS Institute, Cary, NC). Treatment by run interaction was not significant; thus, data

were pooled over runs and significant means were separated based on Fisher's Protected LSD at $P = 0.05$.

Results and Discussions

Liquid Surface tension and liquid-solid contact angle

Significant differences for γ (mN m^{-1}) and θ ($^{\circ}$) were found among the 23 various wetting agents tested at 0.25x, 0.5x, 1x, 2x and 4x of the label rate. Regardless, all wetting agents tested dramatically reduced the γ of tap water, which was determined to be 72.8 mN m^{-1} . This significant decrease in γ of tap water leads to improved infiltration and water distribution in hydrophobic sands (Fig. 2.1). Generally, wetting agents tested also demonstrated a dosage effect with reduced γ associated with higher concentration (Fig. 2.1). It is widely accepted that an increase of surfactant concentration in solution correlates to a decrease in surface tension (Bernett and Zisman, 1959; Esteves et al., 2016; Funasaki and Hada, 1979; Lin et al., 1999).

Surface tension values of the selected wetting agents dramatically varied at the concentrations tested. At a concentration of 0.25x of the label rate, the lowest γ value determined was Triplo[™] at 26.43 mN m^{-1} and the highest was 46.41 mN m^{-1} for Infiltrix[®] (Fig. 2.2). At the 1x, or label rate concentration, the lowest γ value determined being Pervade with a value of 25.88 mN m^{-1} and the highest value, again, was Infiltrix[®] at 44.75 mN m^{-1} (Fig. 2.3). Lastly, at 4x the label rate, the lowest γ value determined being 24.81 mN m^{-1} for AD-Spray[™] and the highest value was Hydro-Wet[®] Injectable with a value of 42.77 mN m^{-1} and (Sup Fig. 2.3). This demonstrates the effect that different concentrations of the selected wetting agents can have on γ .

Exceptions to the general trend for γ and wetting agent concentration increasing are Tricure AD[®], LescoFlo[™] Ultra, Cascade[™] Plus and Capacity. Except for Capacity, the

other three wetting agents displayed a slight increase in γ from 0.25x to 4x of the labeled rate. TriCure AD[®] had only a 0.46 mN m⁻¹ difference in γ between 0.25x and 4x, while LescFlo[™] Ultra and Cascade[™] Plus had a 1.32 mN m⁻¹ and 1.52 mN m⁻¹ difference in γ , respectively. Capacity demonstrated a different trend than all other wetting agents, with 0.25x exhibiting the highest γ of 31.71 mN m⁻¹, 1x with the lowest γ of 29.94 mN m⁻¹, and 4x having an increase in γ to 30.48 mN m⁻¹. These γ values could be related to the wetting agent's critical micelle concentration (CMC).

Wetting agent or surfactant molecules align on the surface of a liquid and decrease surface tension with increasing concentration, until the concentration of surfactant molecules at the liquid surface becomes overcrowded and monomers aggregate, resulting in molecules called micelles (Esteves et al., 2016; Li and Chen, 2002; Lin et al., 1999). Micelles are self-associating surfactant monomers whose hydrophobic regions become attracted to each other and form ball like structures of surfactant molecules with their hydrophilic regions facing into solution, due to a saturation of surfactant molecules floating in solution (Domínguez et al., 1997; Hait and Moulik, 2001; Leibler et al., 1983; Lin et al., 1999). When a wetting agent's CMC has been reached, the γ will either level out to a steady plateau or a minimum γ value is reached, but as surfactant concentration continually increases, the γ can slightly increase and then reach a constant equilibrium value (Lin et al., 1999). Multiple factors could cause this phenomenon, such as various impurities in the surfactant becoming more concentrated in solution as the surfactant micelles are formed or the presence of a mixture of surfactants within the selected wetting agent solution (Lin et al., 1999). For TriCure AD[®], LescFlo[™] Ultra and Cascade[®] Plus, because the 0.25x concentration has a lower γ

value than the 1x concentration, equivalent to the label rate, a potential case could be made that the label rate of these wetting agents could be reduced to 0.25x of the label rate and still achieve similar results.

However, generally wetting agent solutions had tight γ value clustering. Normally, wetting agents with a γ under 33.0 mN m^{-1} demonstrated a tight distribution throughout the five concentrations (Fig. 2.1). Wetting agents with a γ above 33.0 mN m^{-1} showed a distribution of γ values which ranged from 3.0 mN m^{-1} to 8.0 mN m^{-1} difference between concentrations. The CMC of these wetting agents could aid in explaining why the distribution varies greatly between the various concentrations. Wetting agents with a γ above 33.0 mN m^{-1} demonstrate the general trend seen in surfactants, where the lower concentration of surfactant equates to a higher γ value. Following this trend, these wetting agents' γ distribution could be on the down slope of the surface tension versus surfactant concentration curve, ultimately leading up to the CMC value when higher concentrations are tested. Determining the CMC values of these wetting agents would more accurately predict if this explanation is plausible.

The θ of the selected wetting agents were determined based on their γ values, to directly correlate their ability to spontaneously infiltrate an AHS media. The AHS, with a MED value of 5.4, generated a γ_{ND} value of 36.95 mN m^{-1} . Hence, theoretically, wetting agents with a resulting γ value under 36.95 mN m^{-1} would spontaneously wet and infiltrate the AHS. The θ was determined utilizing Eq. 4, based on the various wetting agent γ values and γ_{ND} of the AHS that was determined.

At a concentration of 0.25x of the label rate, the lowest θ value was Triplo™ at 79.5° and the highest value was Infiltrix® at 96.2° (Fig. 2.4). Fourteen wetting agents at

0.25x of the label rate had a θ less than 90° , indicating they could all spontaneously wet the AHS. When tested at the 1x of the label rate, the lowest θ value was Pervade at 78.8° and the highest value was again Infiltrix[®] at 95.2° (Fig. 2.5). Seventeen wetting agents tested had a θ under 90° , indicating that 74% of the wetting agents tested in this study could spontaneously wet the AHS at their label rate. At 4x the label rate, the number of wetting agents with a θ less than 90° increased to nineteen, leaving only Surfside[®] 37, Primer Select[®], Infiltrix[®] and Hydro-Wet[®] injectable as the only wetting agents that were not able to spontaneously wet the AHS at the increased concentration. AD-Spray[™] had the lowest θ value at 77.3° and Hydro-Wet[®] Injectable demonstrated the highest θ value at 94.0° at 4x of the label rate (Sup Fig. 2.6).

Based on the surface tension values determined (Fig. 2.1), three different categories were established at less than 30 mN m^{-1} , between 30 to 40 mN m^{-1} , and greater than 40 mN m^{-1} . At the label rates, eleven wetting agents are less than 30 mN m^{-1} , eight wetting agents in between 30 to 40 mN m^{-1} , and four wetting agents fall into the greater than 40 mN m^{-1} . To determine if these categories represented a direct effect on infiltration into water-repellent sand, six wetting agents were selected within these categories where infiltration and rewettability were tested.

Infiltration

Six wetting agents' initial infiltration rates into an 18.42 cm hydrophobic sand column under a constant h_o of 6.35 cm were determined and displayed as a function of time (Fig. 2.6), in addition to seepage time (T_s) and hydraulic conductivity (K) (Table 2.1 & Table 2.2). Based on their 0.25x label rate; DE, NIS, PoP, NIPA, AoP, and NIPI were selected based on their range of γ values, being 29.82, 31.71, 33.29, 39.41, 45.07, and

46.41 mN m⁻¹, respectively (Table 2.1). Initial infiltration rates of all wetting agents displayed either immediate wetting or a steady increase of infiltration, until reaching a steady flow rate through the column (Fig. 2.6). The infiltration patterns seen differ from a traditional wettable soil, where infiltration is initially rapid and then decreases over time (Song et al., 2014; Wang et al., 2000). These patterns are consistent with infiltration patterns into water-repellent soils (Feng et al., 2001, 2002; Song et al., 2014a; Wang et al., 2000). As proposed by Feng et al. (2001), these results support the conclusion that when wetting agent solutions infiltrate into water repellent soils, the wetting front depth increases as well as the hydraulic head, resulting in a soil water content increase and ultimately leading to increased infiltration (Carrillo et al., 2000; Song et al., 2014a).

Water repellent columns treated with only water, representing the untreated control, did not infiltrate after 30 minutes, so no infiltration curves were determined. Wetting agent solutions displayed similar steady flow infiltration rates (Fig. 2.6). NIPA, NIS, and AoP immediately reached their steady flow rate after a minute of ponding, with NIPA and NIS reaching a steady flow rate of 27.68- and 27.32-mm min⁻¹, respectively, while AoP displayed a steady flow rate of 25.60 mm min⁻¹. In contrast, other wetting agents reached their steady flow rate over a longer period of time. DE reached its steady flow rate of 25.06 mm min⁻¹ within 7 minutes of ponding. PoP and NIPI reached their steady flow rates of 24.59 and 24.81 mm min⁻¹, respectively, after 10 minutes or longer. Due to a consistent h_o maintained throughout all experiments, infiltration patterns seen are representative of the individual wetting agent solution applied and their subsequent manipulation of water repellency severity within the columns, resulting from the adsorption of each wetting agent to the hydrophobic sand particles (Feng et al., 2002;

Song et al., 2014a). Research has shown that infiltration patterns and the resulting degree of water repellency in soils are correlated to the ratio of h_o to the h_p ; as an increase in the h_o/h_p ratio occurs, it results in an increase in infiltration rate (Feng et al., 2001; Song et al., 2014a).

Over time, under a consistent h_o , the wetting agent solutions began to seep out of the water repellent sand columns. Significant differences were seen in T_s among the various wetting agent solutions tested (Table 2.2). Wetting agents that displayed the quickest T_s also reached their steady flow rates more quickly, such as NIS and NIPA which seeped out within 99 to 105 seconds, respectively. In comparison, NIPI, which had the slowest T_s of 255 seconds, took longer to reach its steady flow rate. The T_s of NIPI is greater than 2-fold higher than that of NIS or NIPA.

The K was determined based on each wetting agent's steady flow rate (Table 2.2), with no statistical differences observed. All wetting agents resulted in a K value at or above 18.2 mm min^{-1} , which meets or exceeds the recommended minimum saturated hydraulic conductivity (K_{sat}) of USGA putting green rootzones of 2.5 mm min^{-1} (USGA, 2004). A Pearson's correlation test found no distinct overall correlation between wetting agent solution surface tension and their resulting infiltration rates.

Rewettability

Following the initial application of wetting agent solutions, each treated column was exposed to three dry-wet cycles of water only, at the same h_o , to measure the rewettability as a function of time after 1, 2, and 3 dry-wet cycles in Fig. 2.7, 2.8, 2.9, respectively (Song et al., 2014a). Rewettability flow patterns after the first dry-wet cycle were similar to the initial infiltration of wetting agent solutions (Fig. 2.6 and 2.7). Water

infiltration after the first dry-wet cycle into treated water repellent sand columns showed two different patterns depending on the wetting agent treated (Fig. 2.7). Four wetting agent treated columns: NIPA, NIS, PoP and AoP, demonstrated a typical water infiltration pattern for wettable soils, as water infiltration decreases over time, until reaching a steady flow rate, which are similar results from Feng et al. (2002) but differs from Song et al. (2014a) results. However, two wetting agent treated columns, NIPI and DE, displayed an initial rapid increase in water infiltration, within six minutes or less, before reaching a steady flow rate. These patterns differ from typical water infiltration for wettable soils, as seen in Feng et al. (2002), but are similar to the results from Song et al. (2014a). Five wetting agent treatments AoP, DE, NIPA, NIPI, and PoP, decreased the water infiltration steady flow rate after the first dry-wet cycle. Treatment of AoP reduced steady flow rate by only 0.1%, from 25.60 to 25.37 mm min⁻¹, which was the lowest reduction of all wetting agent treatments. Similarly, NIPA only slightly decreased steady flow rate only by 1.5% from 27.68 to 27.26 mm min⁻¹, while NIPI showed the largest decrease in steady flow rate from the initial infiltration steady flow rate by 22.2% from 24.81 to 19.29 mm min⁻¹ (Fig. 2.7). Only treatment of NIS, showed an increase in steady flow infiltration rate, after the first dry-wet cycle, of 3.0%, by increasing from 27.32 to 28.17 mm min⁻¹ (Fig. 2.7). These results are comparable to Feng et al. (2002) and Song et al. (2014a), where certain wetting agents treated water repellent sand showed an increase in infiltration rate under rewetting compared to the initial infiltration of the wetting agent solution.

After the second dry-wet cycle, a progressive decline of the steady flow infiltration rate was seen as compared to the first dry-wet cycle, with the exception of

NIS and NIPI (Fig. 2.8). Application of NIS maintained and increased the steady flow infiltration rate by 2.6%, from 28.17 to 28.92 mm min⁻¹, after the first dry-wet cycle and by 5.5%, from 27.32 to 28.92 mm min⁻¹, from the initial steady flow infiltration rate (Fig. 2.8). Also, NIS displayed an infiltration curve consistent with a wettable soil, demonstrating a higher infiltration rate, which then decreased until reaching a steady flow infiltration rate (Feng et al., 2002). All other wetting agent treatments displayed infiltration curves of a typical non-wettable soil, with a rapid increase of infiltration rate until reaching a steady flow infiltration rate, which is similar to results from Song et al. (2014a). Treatment of NIPI maintained its steady flow infiltration rate of 19.29 to 19.54 mm min⁻¹ following the first to second dry-wet cycle; but showed a significant decrease in steady flow infiltration rate of 21.2%, from 24.81 to 19.54 mm min⁻¹, as compared to the initial steady flow infiltration rate (Fig. 2.8). The four other wetting agent treatments: NIPA, PoP, AoP and DE, displayed a significant decrease in steady flow infiltration rate following the second dry-wet cycle. AoP and PoP treated columns displayed the most substantial decrease in steady flow infiltration rate. Following the second dry-wet cycle the steady flow infiltration rate of AoP decreased by 21.2% from 25.37 to 20.00 mm min⁻¹ and by 21.9%, from 25.60 to 20.00 mm min⁻¹, when compared to the initial steady flow infiltration rate (Fig. 2.8). However, the most dramatic decrease in steady flow infiltration rate of all wetting agent treatments after the second dry-wet cycle was PoP, by 50.0%, from 21.01 to 10.50 mm min⁻¹, as compared to the first dry-wet cycle and a 57.3% decrease, from 24.59 to 10.50 mm min⁻¹, as compared the initial steady flow infiltration rate of the wetting agent solution.

Following the third dry-wet cycle, NIS continued to display an infiltration curve similar to a wettable soil, while the other wetting agent treated columns displayed a non-wettable soil pattern, where a rapid increase in infiltration rate occurred until reaching their steady flow rate, with the exception of PoP which did not infiltrate after three dry-wet cycles (Fig. 2.9) (Feng et al., 2002; Song et al., 2014a). However, NIS had a slight decrease in steady flow infiltration rate of 3.0%, from 28.92 to 28.06 mm min⁻¹, between the second to third dry-wet cycle (Fig. 2.9). Additionally, NIPA and AoP demonstrated decreased steady flow infiltration rates from the second to the third dry-wet cycle. In contrast, NIPI and DE demonstrated an increase in steady flow infiltration rate from the second to third dry-wet cycle, by 8.4 or 8.1%, respectively (Fig. 2.9). After the three dry-wet cycles, NIS maintained the highest steady flow infiltration rate, of 28.06 mm min⁻¹, compared to all other wetting agent treatments. Three wetting agent treatments, NIPI, NIPA and DE, all resulted in a similar steady flow infiltration rate of 21.33, 22.50 and 22.72 mm min⁻¹, respectively. AoP resulted in the lowest steady flow infiltration rate, of those that infiltrated, of 15.48 mm min⁻¹, following the third dry-wet cycle.

Over the three dry-wet cycles, the six wetting agent treatments displayed distinct differences in rewettability infiltration into the treated AHS columns. Only one wetting agent treatment, NIS, slightly increased steady flow water infiltration rate after the three dry-wet cycles by maintaining 27.87 mm min⁻¹, which is a 1.5% increase as compared to the initial infiltration of the wetting agent solution. All other wetting agent treated columns showed a progressive decrease in steady flow water infiltration following the three dry-wet cycles.

Additionally, T_s were collected for each dry-wet cycle and significant differences between wetting agent treatments were seen (Table 2.3). Following the first dry-wet cycle, NIS, NIPI, and PoP all exhibited reduced T_s compared to the initial infiltration (Table 2.2 & 2.3). In contrast, the application of AoP, DE, and NIPA all increased T_s when compared to the initial infiltration cycle. Columns treated with PoP displayed the greatest decrease in T_s by 29.2%, from 195 to 138 seconds (Table 2.3). However, all wetting agent treated columns increased T_s by 1.6-fold or greater after the second dry-wet cycle, except for NIS which only increased T_s by 10% from 90 to 100 seconds (Table 2.3). In general, wetting agent treated columns which had the quickest T_s also reached their steady flow infiltration rate faster. Treatment of NIS, which maintained the highest infiltration rate and reached steady flow infiltration rate the quickest, also resulted in the fastest T_s over all three dry-wet cycles when compared to all other wetting agent treated columns. Due to water not infiltrating into PoP treated columns after the third dry-wet cycle, its T_s could not be determined.

The K was also calculated throughout all three dry-wet cycles with significant differences observed (Table 2.3). NIS treated columns maintained a K value of 20.7 mm min⁻¹ or greater throughout each dry-wet cycle and resulted in significantly greater K values compared to all other wetting agent treated columns. NIPI, NIPA, and DE all maintained a K value of 14.5 mm min⁻¹ or higher throughout all three dry-wet cycles. Application of PoP and AoP progressively decreased in K values from the first to third dry-wet cycle, and a K value was not calculated for the third dry-wet cycle of PoP treated columns as water was unable to penetrate. However, all wetting agents, except PoP,

maintained a higher saturated hydraulic conductivity (K_{sat}) after three dry-wet cycles than the recommended USGA K_{sat} of 2.5 mm min⁻¹.

Conclusions

The γ of water was significantly reduced when mixed in solution with all wetting agents tested. When applied at the label rate, the γ of water was decreased by 38.5% to 64.5%, depending on the wetting agent utilized. Additionally, measured γ demonstrated variation among the wetting agents' ability to reduce the γ of water, disproving the idea that all wetting agents are similar. Wetting agent γ groupings from less than 30 mN m⁻¹, between 30 and 40 mN m⁻¹, greater than 40 mN m⁻¹ were created based on the values determined in this study.

All wetting agents tested demonstrated an ability to initially improve water infiltration into a water repellent USGA-grade sand media, as compared with the application of just water alone. However, depending on the wetting agent applied, significant differences were seen in water infiltration curves, water movement and rewettability. Overall, these results suggest that wetting agents perform differently over time through various dry-wet cycles. Certain wetting agents, such as NIS, potentially have a greater longevity in the soil and are able to maintain a higher, continued performance in comparison to other wetting agents, such as PoP, that have reduced longevity and performance after multiple dry-wet cycles. Understanding the different abilities of wetting agents to persist in a sand-based rootzone and maintain infiltration rates over time is vital information to a golf course superintendent, to allow the proper planning of the frequency at which wetting agents should be re-applied.

Treatments, such as NIS and DE, were able to maintain consistent rewettability infiltration rates throughout the three dry-wet cycles. This contrasts with other wetting treatments, such as PoP and AoP, which progressively and significantly declined in rewettability infiltration rates over the three dry-wet cycles, with PoP not allowing water infiltration after the third dry-wet cycle. However, regardless of the wetting agent used, no correlation was seen between the surface tension value of wetting agents and their resulting infiltration and rewettability rate. This potentially indicates that wetting agents influence on water's surface tension alone is unable to determine their function in a water repellent soil. Understanding this, it is important to note that not all wetting agents' functions are to improve infiltration. Certain wetting agents may be directed to improve water retention or a uniform wetting front within the sand-based rootzone. Golf course superintendents should define the goal they wish to achieve before choosing and applying various wetting agents.

References

- Bauters, T.W.J., D.A. DiCarlo, T.S. Steenhuis, and J.Y. Parlange. 1998. Preferential flow in water repellent sands. *Soil Sci. Soc. Am. J.* 62:1185-1190.
- Bernett, M.K., and W.A. Zisman. 1959. Relation of wettability by aqueous solutions to the surface constitution of low-energy solids. *The Journal of Physical Chemistry.* 63: 1241-1246.
- Berry, J.D., M.J. Neezon, R.R. Dagastine, D.Y.C. Chan and R.F. Tabor. 2015. Measurement of surface and interfacial tension using pendant drop tensiometry. *Journal of Colloid and Interface Science.* 454: 226-237.
- Bradford, S.A., and F.J. Leij. 1996. Predicting two- and three-fluid capillary pressure-saturation relationships of porous media with fractional wettability. *Water Resour. Res.* 32:251-259.
- Carrillo, M.L.K, J. Letey, and S.R. Yates. 1999. Measurement of initial soil-water contact angle of water repellent soils. *Soil Sci. Soc. Am. J.* 63:433-436.
- Carrillo, M.L.K., J. Letey, and S.R. Yates. 2000. Unstable water flow in a layered soil: I. Effects of a stable water-repellent layer. *Soil Sci. Soc. Am. J.* 64:450-455.
- Cisar, J.L., K.E. Williams, H.E. Vivas, and J.J. Haydu. 2000. The occurrence and alleviation by surfactants on soil-water repellency on sand-based turfgrass system. *J. Hydrol.* 231:352-358.
- DeBano, L.F. 2000. Water repellency in soils: A historical overview. *J. Hydrol.* 231-232:4-32.
- Dekker, L.W., C.J. Ritsema. 1994. How water moves in a water repellent sandy soil. I. Potential and actual water repellency. *Water Resour. Res.* 30: 2507-2517.

- Dekker, L.W., K. Oostindie, and C.J. Ritsema. 2005a. Exponential Increase of Publications Related to Soil Water Repellency. *Soil Research* 43(3): 403–41.
- Dekker, L.W., K. Oostindie, and C.J. Ritsema. 2005b. Effects of surfactant treatments on the wettability of a water repellent grass-covered dune sand. *Aust. J. Soil. Res.* 43:383-395.
- Doerr S.H. 1998. On standardizing the ‘Water Drop Penetration Time’ and the ‘Molarity of an Ethanol Droplet’ techniques to classify soil hydrophobicity: A case study using medium textured soils. *Earth Surf. Process. Landforms.* 23: 663-668.
- Doerr, S.H., R.A. Shakesby, and R.P.D. Walsh. 2000. Soil water repellency; its causes, characteristics and hydro-geomorphological significance. *Earth-Sci. Reviews.* 51: 33-65.
- Doerr, S.H., R.A. Shakesby, L.W. Dekker, and C.J. Ritsema. 2006. Occurrence, prediction and hydrological effects of water repellency amongst major soil and land-use types in a humid temperate climate - Doerr - 2006 - *European Journal of Soil Science* - Wiley Online Library. *European Journal of Soil Science* 57: 741–754.
- Emerson, W.W., and R.D. Bond. 1963. The rate of water entry into dry sand and calculation of the advancing contact angle. *Aust. J. Soil Res.* 1:9-16.
- Esteves, R., B. Dikici, M. Lehman, Q. Mazumder, and N. Onukwuba. 2016. Determination of aqueous surfactant solution surface tensions with a surface tensiometer. *Beyond: Undergraduate Research Journal.* 1(4).
- Feng, G.L., J. Letey, and L. Wu. 2001. Water ponding depths affect temporal infiltration rates in a water repellent sand. *Soil Sci. Soc. Am. J.* 65:315-320.

- Feng, G.L., J. Letey, and L. Wu. 2002. The influence of two surfactants on infiltration into a water-repellent soil. *Soil Sci. Soc. Am. J.* 66:361-367.
- Funasaki, N., and S. Hada. 1979. Surface tension of aqueous solutions of surfactant mixtures. The composition of mixed micelles. *The Journal of Physical Chemistry.* 83(19): 2471-2475.
- Hansen, F.K., and G. Rødsrud. 1990. Surface tension by pendant drop, I. A fast standard instrument using computer image analysis. *Journal of Colloid and Interface Science.* 141(1):1-9.
- Hernández-Baltazar, E., and J. Garcia-Fadrique. 2005. Elliptic solution to the Young-Laplace differential equation. *Journal of Colloid and Interface Science.* 284(1): 213-216.
- Karnok, K.J. 2006. Which wetting agent is best? *Golf Course Manage.* 74:82-83.
- Karnok, K.J., and K.A. Tucker. 1989. The cause and control of localized dry spots on bentgrass greens. *Golf Course Manage.* 57:28-34.
- Karnok, K.J., and Beall, M., 1995. Localized dry spots caused by hydrophobic soil: what have we learned? *Golf Course Management* 8: 57-59.
- Karnok, K.J., K. Xia, and K.A. Tucker. 2004. Wetting agents: What are they and how do they work? *Golf Course Manage.* 76:109-111.
- King, P.M. 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect measurement. *Aust. J. Soil Res.* 19:275–285.
- Kostka, S.J., J.L. Cisar, C.J. Ritsema, L.W. Dekker, S. Mitra, M.A. Franklin, and S.E., McCann. 2005. Surfactants and soil water repellency in golf course soils – water

- use and environmental implications. Proc. 25th Irrigation Association Conference. p.235-246.
- Larsbo, M., T.S. Aamlid, L. Persson, and N. Jarvis. 2008. Fungicide leaching from golf greens: Effects of root zone composition and surfactant use. *J. Environ. Qual.* 37:1527-1535.
- Letey, J., M.L.K. Carrillo, X.P. Pang. 2000. Approaches to characterize the degree of water repellency. *Jour. of Hydrology.* 231-232: 61-65.
- Li, J.L., and B.H. Chen. 2002. Solubilization of model polycyclic aromatic hydrocarbons by nonionic surfactants. *Chemical Engineering Science* 57(14): 2825–2835.
- Lin S.Y., Y. Lin, E. Chen, C. Hsu, C. Kwan. 1999. A study of the equilibrium surface tension and the critical micelle concentration of mixed surfactant solutions. *Langmuir.* 15:4370-4376.
- Müller. K., and M. Deurer. 2011. Review of the remediation strategies for soil water repellency. *Agriculture, Ecosystems and Environment.* 144:208-221.
- Nimmo, J.R. 2004. Porosity and pore size distribution. In: D. Hillel, editor, *Encyclopedia of soils in the environment.* Elsevier, London. p. 295–303.
- Pelishkek, R.R., J. Osborn, and J. Letey. 1962. The effect of wetting agents on infiltration. *Soil Sci. Soc. Am. Proc.* 26:595-598.
- Reynolds, W.D., and D.E. Elerick. 2002. Constant head soil core (tank) method. In: J.H. Dane and G.C. Topp, editors, *Methods of soil analysis. Part 4. Physical methods.* SSSA Book Ser. 5. SSSA, Madison, WI. P. 804-808.

- Roberts, F.J., and B.A. Carbon. 1972. Water repellence in sandy soils of Southwestern Australia: II. Some chemical characteristics of hydrophobic skins. *Aust. J. Soil Res.* 10:35-42.
- Roy, J.L., and W.B. McGill. 2002. Assessing soil water repellency using the Molarity of Ethanol Droplet (MED) test. *Soil. Sci.* 167(2): 83-97.
- Song, E., J.G. Schneider, S.H. Anderson, K.W. Goyne, and X. Xiong. 2014a. Wetting agent influence on water infiltration into hydrophobic sand: I. Rewettability. *Agron. Jour.* 106:1873-1878.
- Song, E., J.G. Schneider, S.H. Anderson, K.W. Goyne, and X. Xiong. 2014b. Wetting agent influence on water infiltration into hydrophobic sand: II. Physical Properties. *Agron. Jour.* 106:1879-1885.
- Thiessen, D.B., D.J. Chione, C.B. McCreary, W.B. Krantz. 1996. Robust digital image analysis of pendant drop shapes. *Journal of Colloid and Interface Science.* 177(2): 686-665.
- Throssell, C. 2005. GCSAA-USGA wetting agent evaluation: Update. *Golf Course Manage.* 77:71-83.
- Tucker, K.A., K.J. Karnok, D.E. Radcliffe, G. Landry, R.W. Roncadori, and K.H. Tan. 1990. Localized dry spots as caused by hydrophobic sands on bentgrass greens. *Agron. J.* 82:549-555.
- U.S. Golf Association. 2004. USGA recommendation for a method of putting green construction. [www.usga.org/course_care/articles/construction/greens/USGA-Recommendations-For-A-Method-Of-Putting-GreenConstruction\(2\)/](http://www.usga.org/course_care/articles/construction/greens/USGA-Recommendations-For-A-Method-Of-Putting-GreenConstruction(2)/) (accessed 3 August 2017).

- Wallis, M.G., Horne, D.J., 1992. Soil water repellency. *Adv. Soil Sci.* 20: 91-146
- Wang, Z., Q.J. Wu, L. Wu, C.J. Ritsema, L.W. Dekker, and J. Feyen. 2000. Effects of soil water repellency on infiltration rate and flow instability. *J. Hydrol.* 231-232:265-276.
- Watson, C.L., and J. Letey. 1970. Indices for characterizing soil water repellence based upon contact angle-surface tension relationships. *Soil Sci. Soc. Am. Proc.* 34:841–844.
- Wilkinson, J.F., and R.H. Miller. 1978. Investigation and treatment of localized dry spots on sand golf greens. *Agron. J.* 70:299-304.

Table 2.1. Treatments, abbreviations, active ingredients and their 0.25x surface tension (γ ; mN m⁻¹) values applied to a hydrophobic sand infiltration column.

Abbreviation	Treatment	Active Ingredient	Surface Tension (mN m ⁻¹)
AoP	Primer Select	100% - Alkoxylated polyols	45.07
DE	TriCure AD	100% - Dihydrooxirane, epihydrin	29.82
NIPA	Aqueduct	50% - Nonionic polyols : 5% - 1,2-Propanediol	39.41
NIPI	Infiltrix	20% - Nonionic polyols	46.41
NIS	Capacity	100% - Nonionic surfactant	31.71
PoP	H ₂ O Maximizer	28% - Carbohydrate surfactant, poloxanlene, poly (2-propenamide)	33.29

Table 2.2. Seepage time (T_s ; sec) and saturated hydraulic conductivity (K ; mm min⁻¹) influenced by various wetting agents at the 6.35 cm ponding depth infiltrated into 20 cm artificial hydrophobic sand columns[‡].

Wetting agent	Concentration§	T_s [†]	K
	g L ⁻¹	s	mm min ⁻¹
AoP*	1.95	119 b [¶]	19.0
DE	3.91	201 c	18.6
NIPA	7.81	105 a	20.6
NIPi	1.95	255 d	18.5
NIS	7.81	99 a	20.4
PoP	9.77	195 c	18.3

*NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPi, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

[¶]Means followed by different letters for each parameter indicate significant differences based on Fisher's Protected LSD at $P = 0.05$.

[†] Seepage time = required time for the initial water to exit the bottom of the sand column.

[‡] Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at the 6.35-cm ponding depth, thus no data were collected.

§ The wetting agent concentrations are equivalent to one-fourth of label rates for each product.

Table 2.3. Seepage time (T_s ; sec) and saturated hydraulic conductivity (K ; mm min⁻¹) of water at the 6.35-cm ponding depth infiltrated into 20 cm artificial hydrophobic sand columns previously treated with wetting agents and dried at 55°C for 1, 2, and 3 dry–wet cycles[‡].

Wetting Agent	Concentration [§]	T_s [†]			K		
		First cycle	Second cycle	Third cycle	First cycle	Second cycle	Third cycle
	g L ⁻¹		s			mm min ⁻¹	
AoP*	1.95	123 c [°]	389 d	383 c	18.9 b	14.9 c	11.5 c
DE	3.91	205 e	338 c	285 b	16.2 c	15.5 bc	16.9 b
NIPA	7.81	108 b	280 b	262 b	20.3 ab	17.7 b	16.7 b
NIPI	1.95	199 e	429 e	378 c	14.3 d	14.5 c	15.9 b
NIS	7.81	90 a	100 a	137 a	20.9 a	21.5 a	20.9 a
PoP	9.77	138 d	371 d	----¶	15.6 cd	7.8 d	----

*NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

[°] Means followed by different letters in each column indicate significant differences based on Fisher's Protected LSD at $P = 0.05$.

[†] Seepage time = required time for the initial water to exit the bottom of the sand column.

[‡] Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at the 4.4-cm ponding depth, thus no data were collected.

[§] The wetting agent concentrations are equivalent to one-fourth of label rates for each product.

[¶] Sand columns did not seep out from the bottom of the sand columns and/or reach steady flow, and therefore no T_s and/or K were calculated.

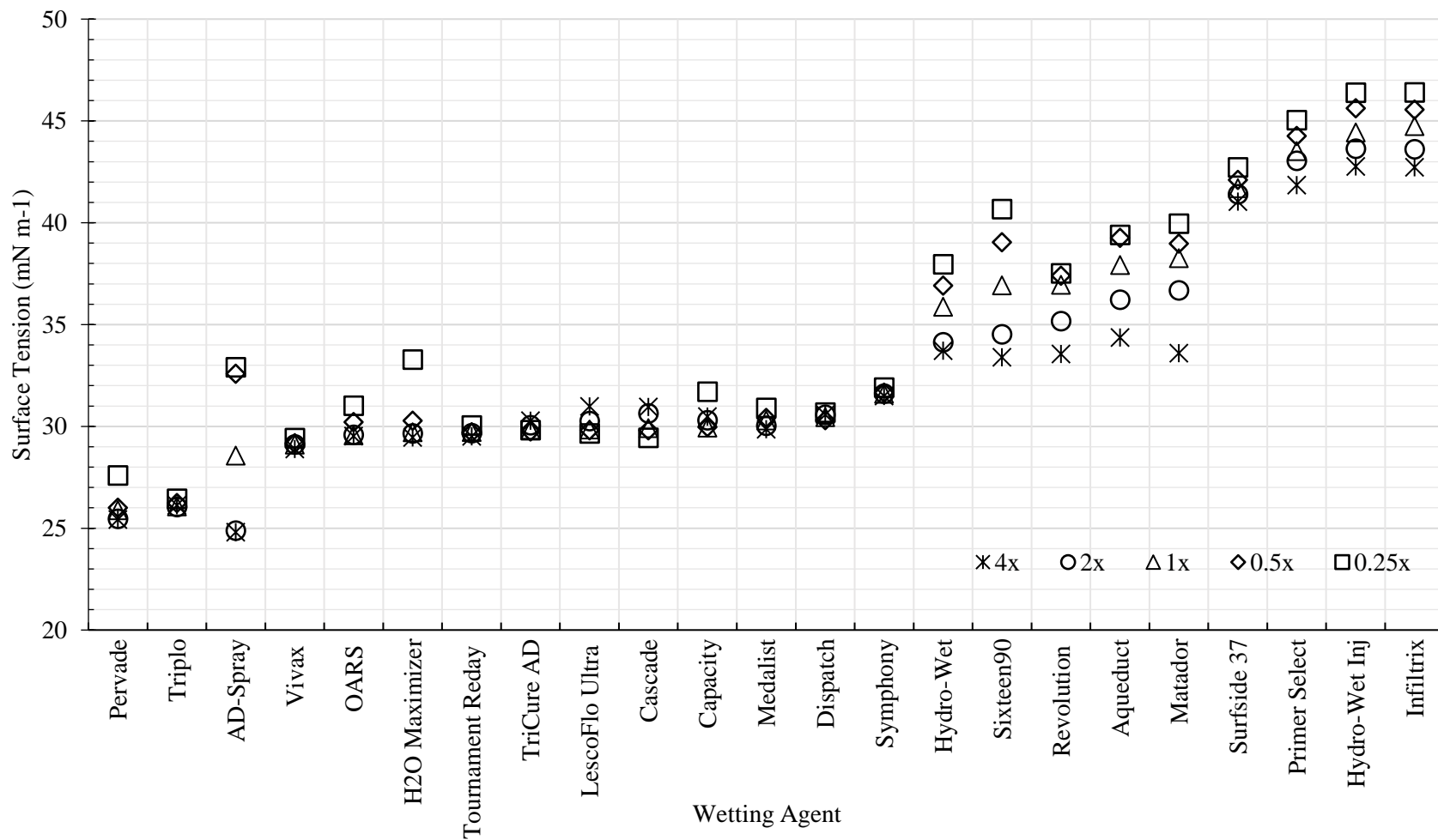


Figure 2.1. Distribution of surface tensions (mN m⁻¹) of various wetting agents at five different rates (0.25x, 0.5x, 1x, 2x, 4x) based on the monthly label rate.

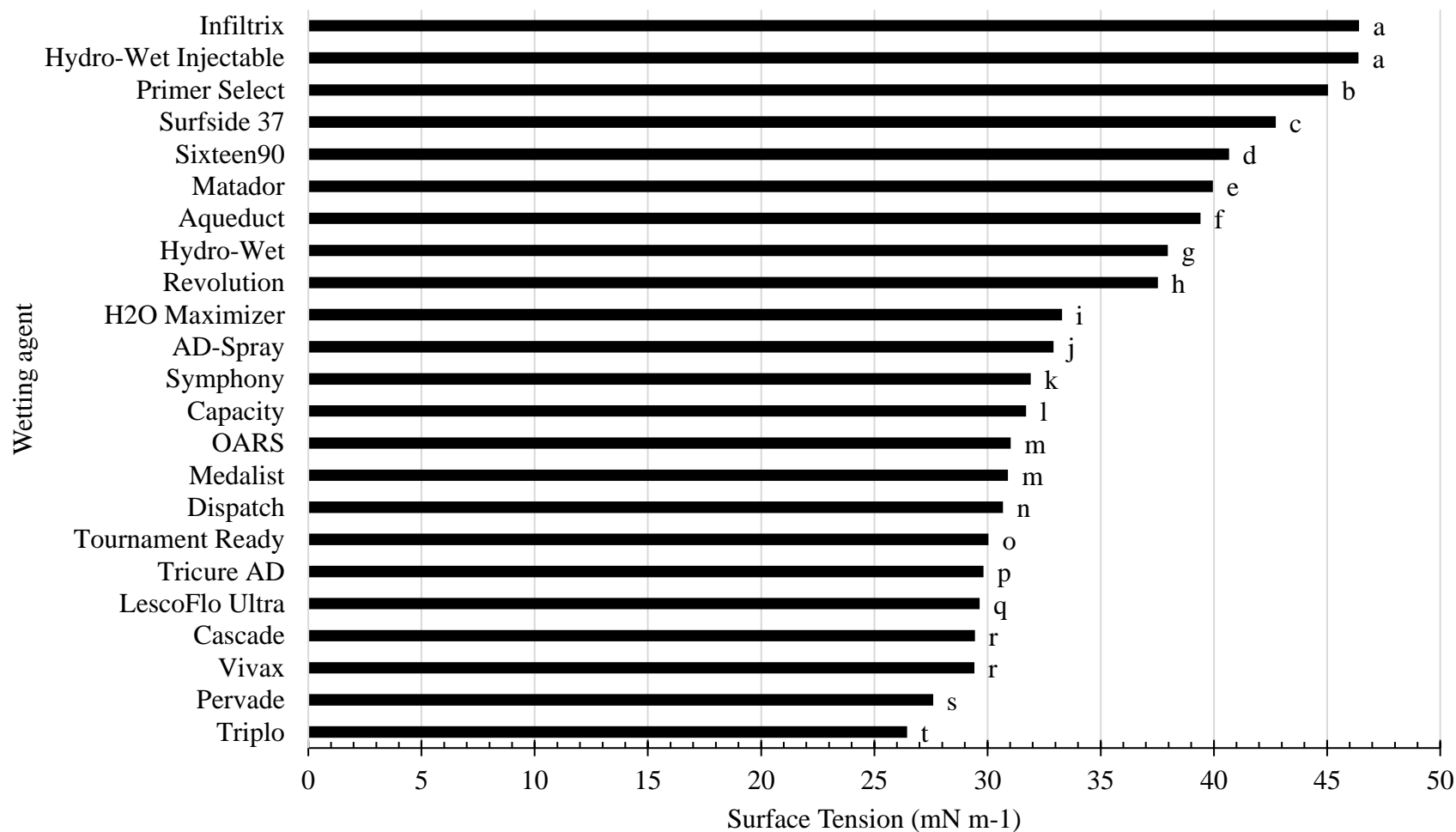


Figure 2.2. Surface tension (mN m⁻¹) of various wetting agents at 0.25x of their suggested label rates. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.

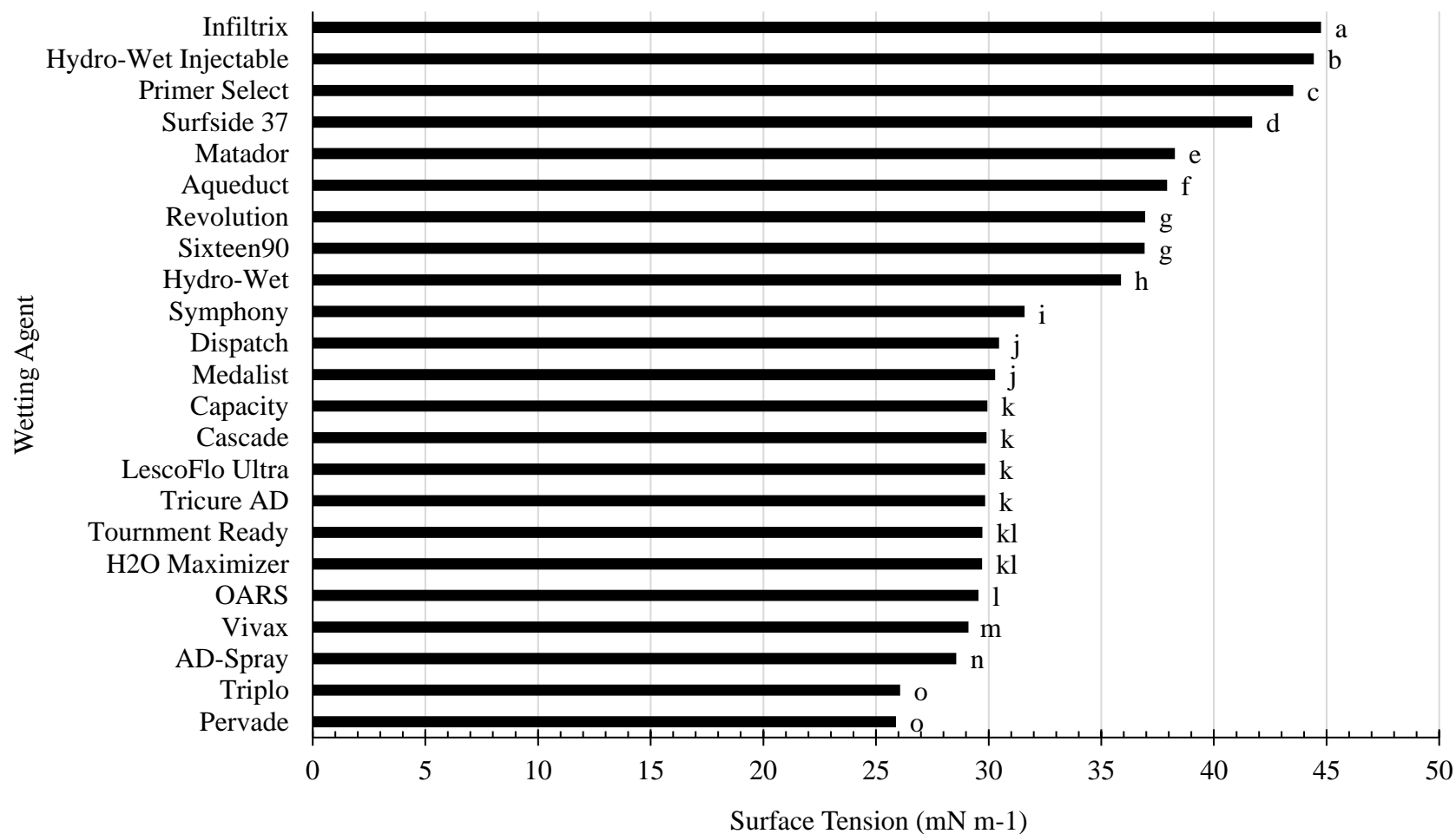


Figure 2.3. Surface tension (mN m⁻¹) of various wetting agents at 1x of their suggested label rates. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.

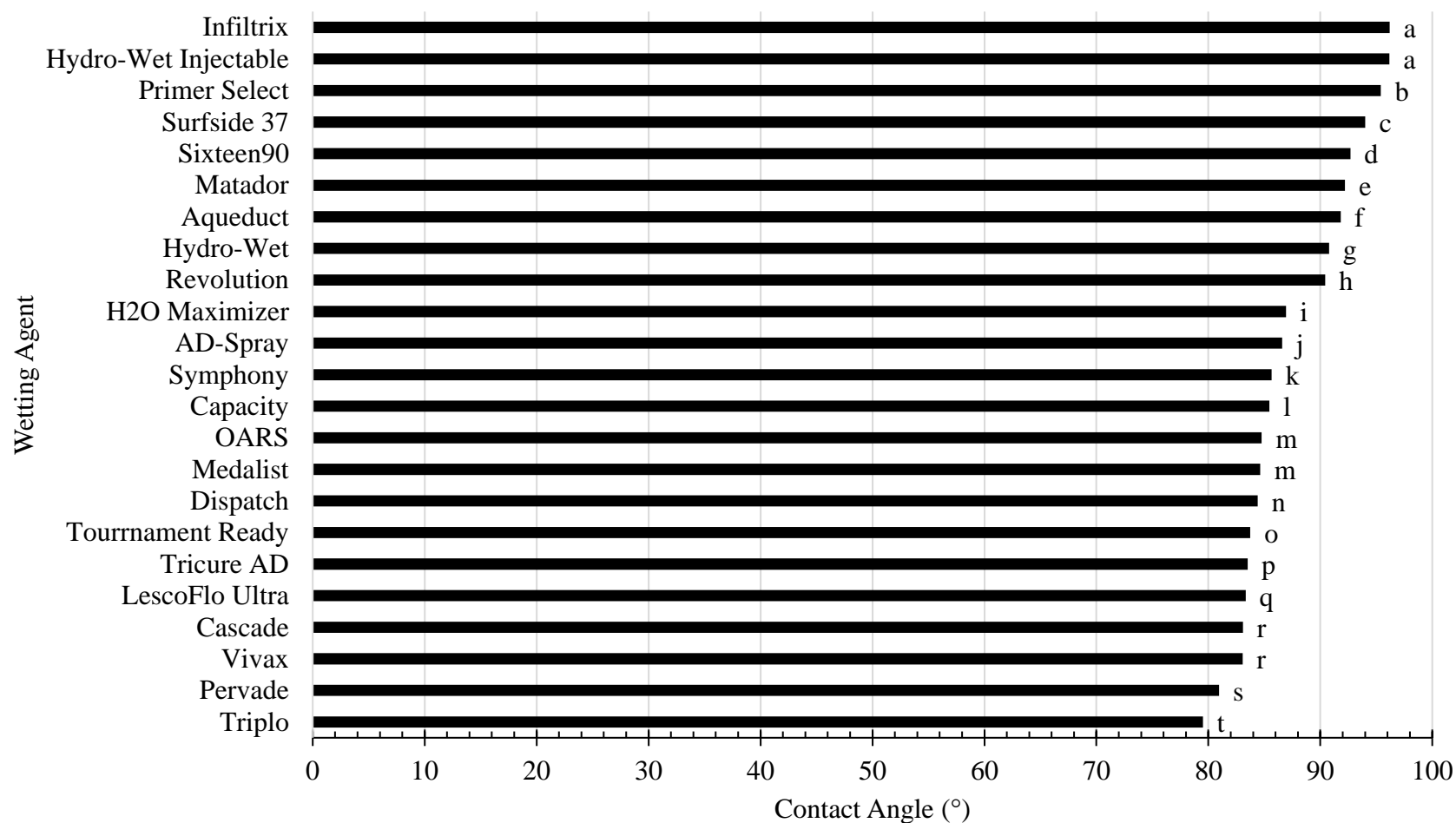


Figure 2.4. Contact angle (°) of various wetting agents at 0.25x of their suggested label rates. Values were determined based off 5.4 molarity of ethanol droplet test (MED) on artificial hydrophobic sand, which had a 90° surface tension of 36.95 mN m^{-1} . Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.

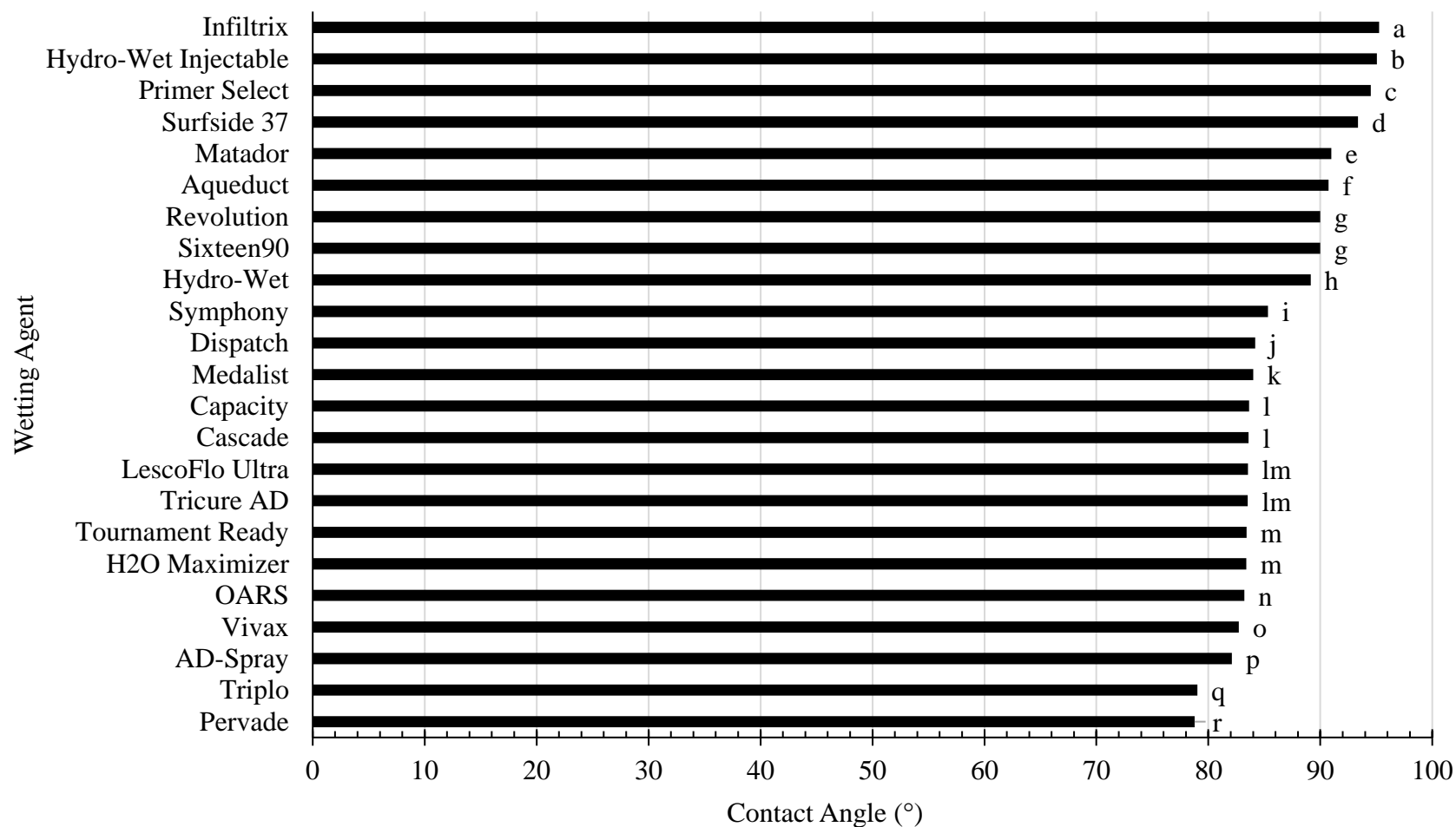


Figure 2.5. Contact angle (°) of various wetting agents at 1x of their suggested label rates. Values were determined based off 5.4 molarity of ethanol droplet test (MED) on artificial hydrophobic sand, which had a 90° surface tension of 36.95 mN m^{-1} . Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.

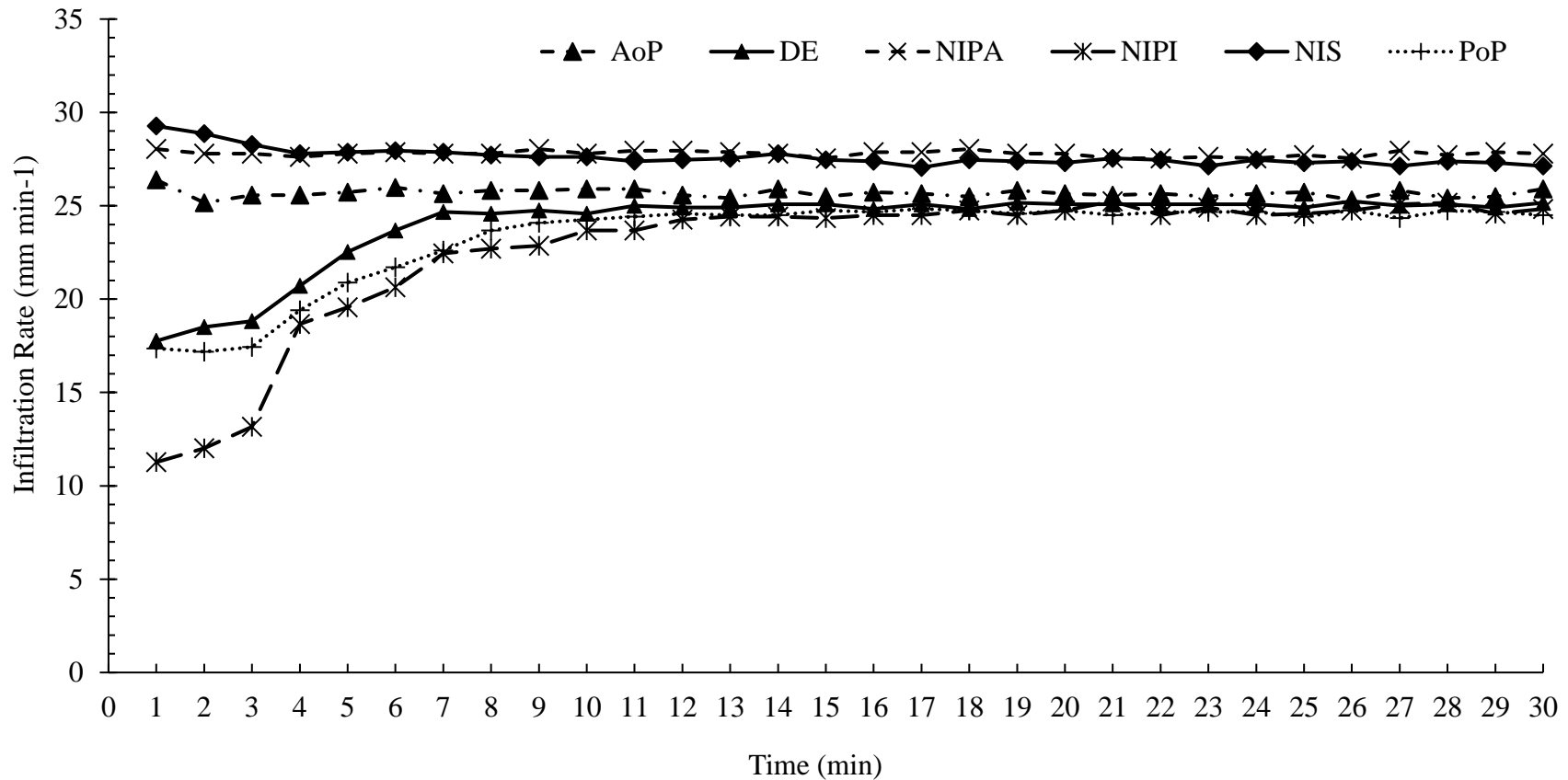


Figure 2.6. Infiltration (mm min^{-1}) as a function of time influenced by six wetting agents, NIPA, NIS, PoP, NIPI, AoP, and DE, into measured under a constant ponding depth of 6.35 cm. Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at the 6.35 cm ponding depth, thus no data were collected.

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epichlorohydrin, TriCure AD; UC, untreated control.

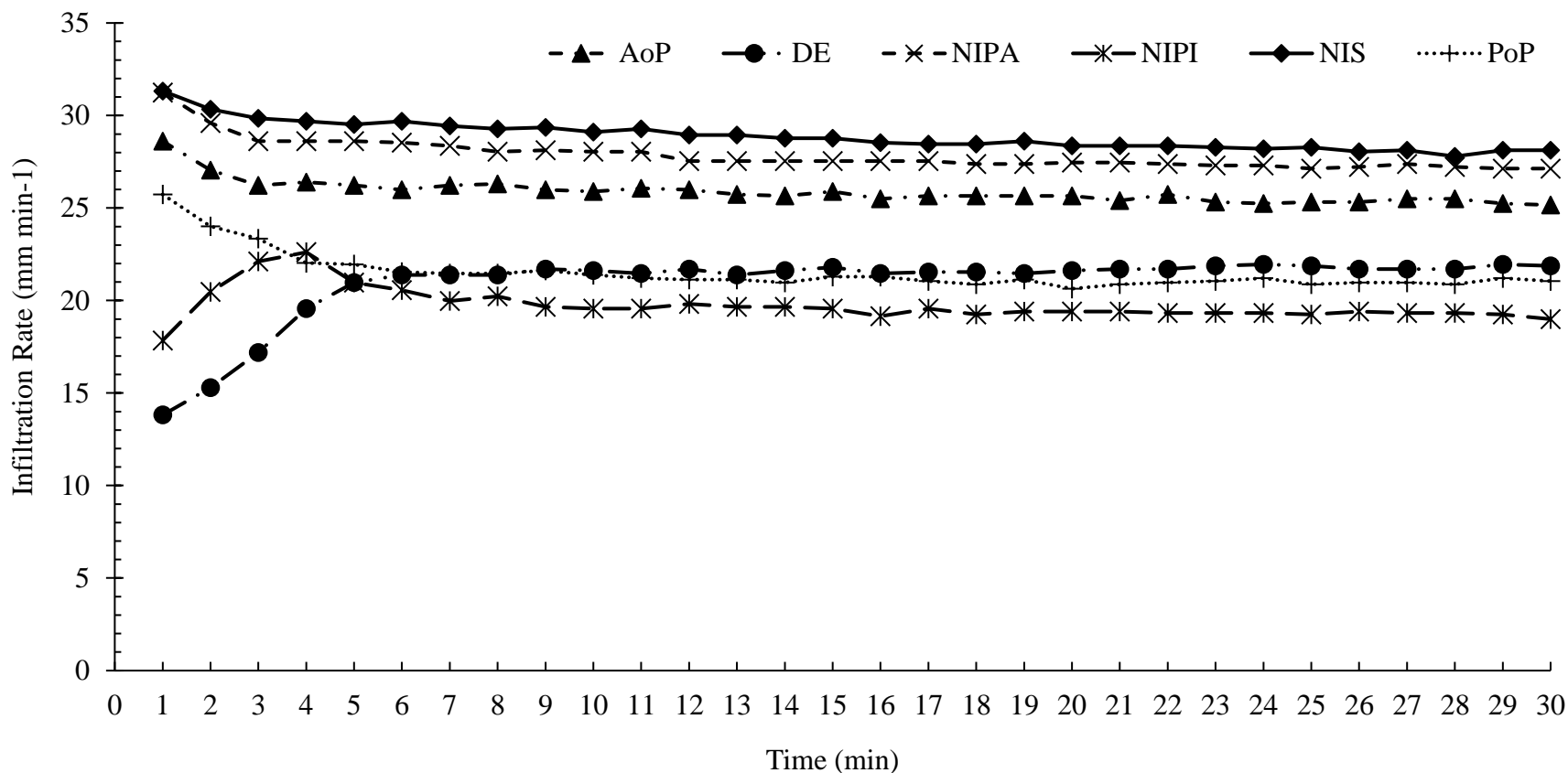


Figure 2.7. Water infiltration (mm min^{-1}) as a function of time into 20 cm artificial hydrophobic sand columns previously treated with various wetting agents under a constant ponding depth of 6.35 cm after the first dry-wet cycle. Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at 6.35 cm ponding depth, thus no data were collected.

†NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

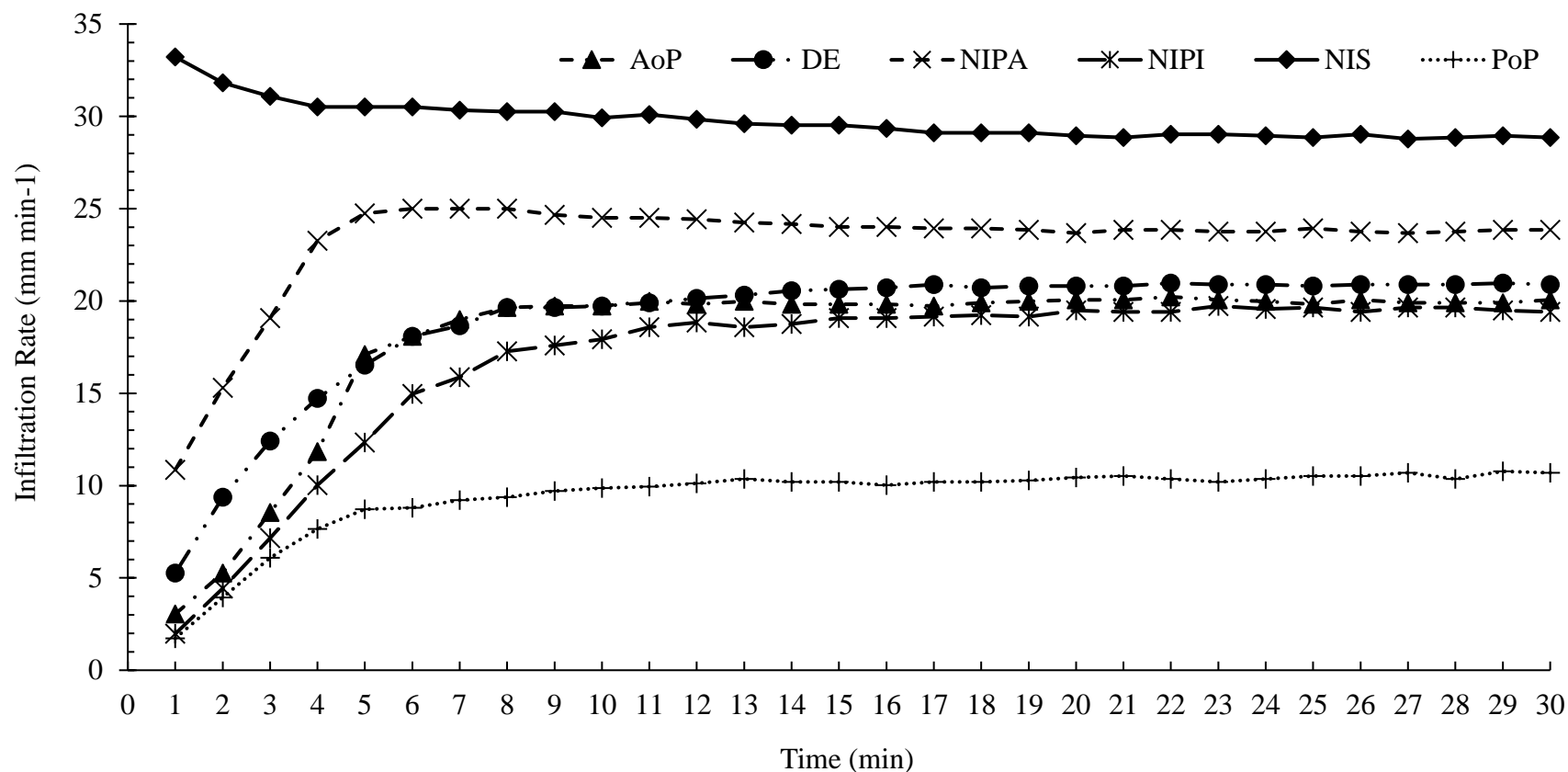


Figure 2.8. Water infiltration (mm min^{-1}) as a function of time into 20 cm artificial hydrophobic sand columns previously treated with various wetting agents under a constant ponding depth of 6.35 cm after the second dry-wet cycle. Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at 6.35 cm ponding depth, thus no data were collected.

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

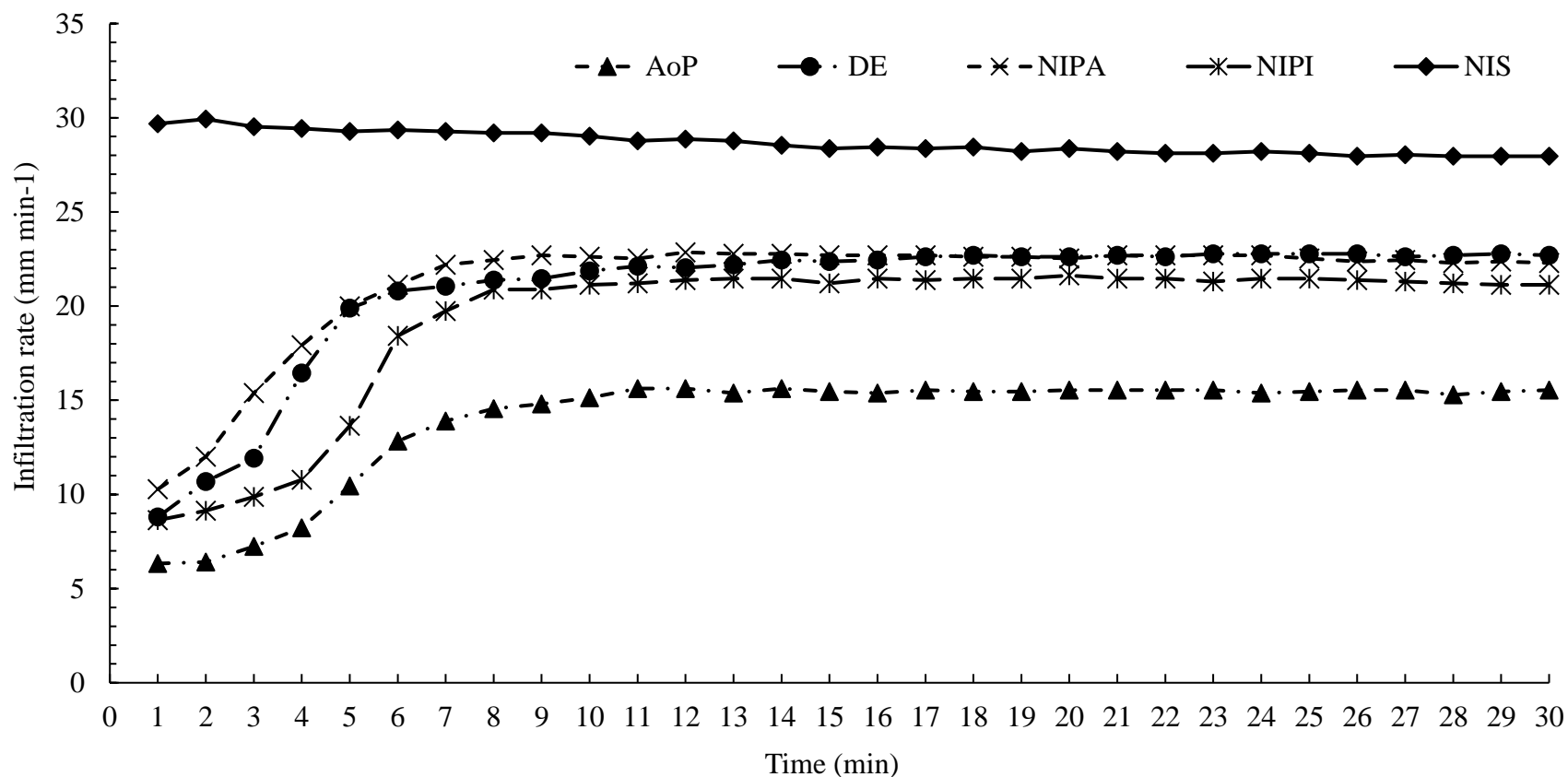


Figure 2.9. Water infiltration (mm min^{-1}) as a function of time into 20 cm artificial hydrophobic sand columns previously treated with various wetting agents under a constant ponding depth of 6.35 cm after the third dry-wet cycle. PoP and untreated control with water-only treatment did not infiltrate into the hydrophobic sand at 6.35 cm ponding depth, thus no data were collected.

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

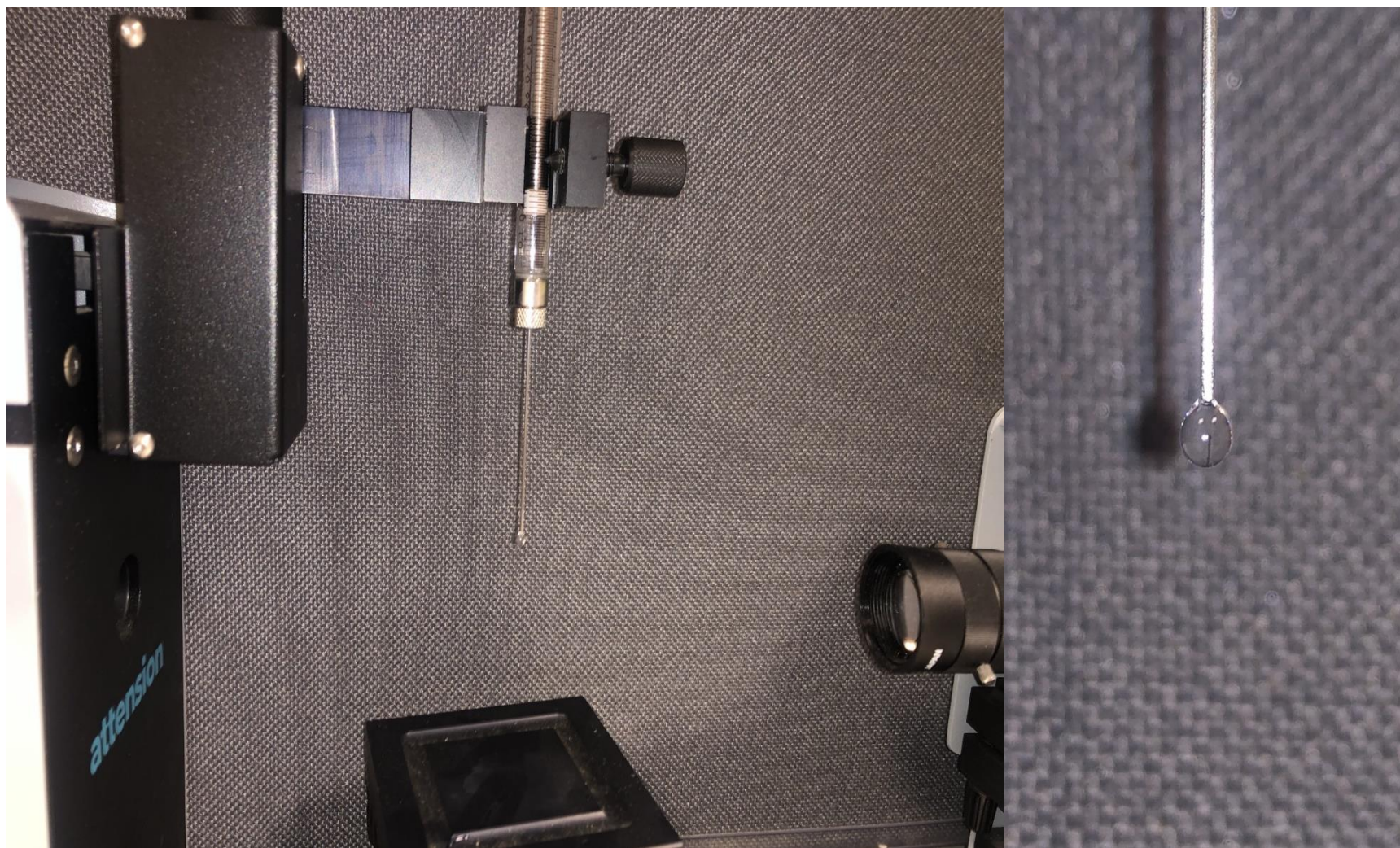
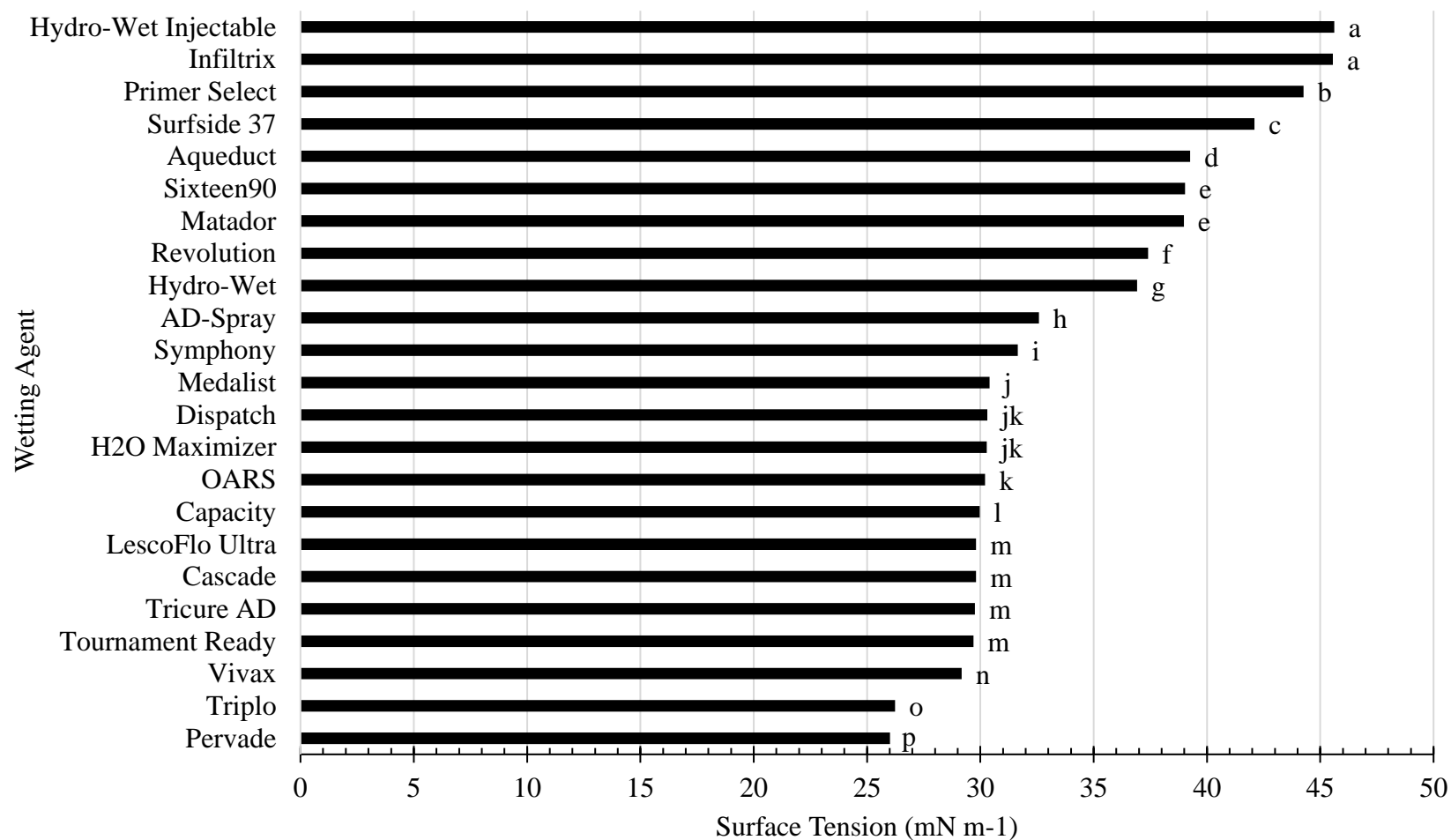
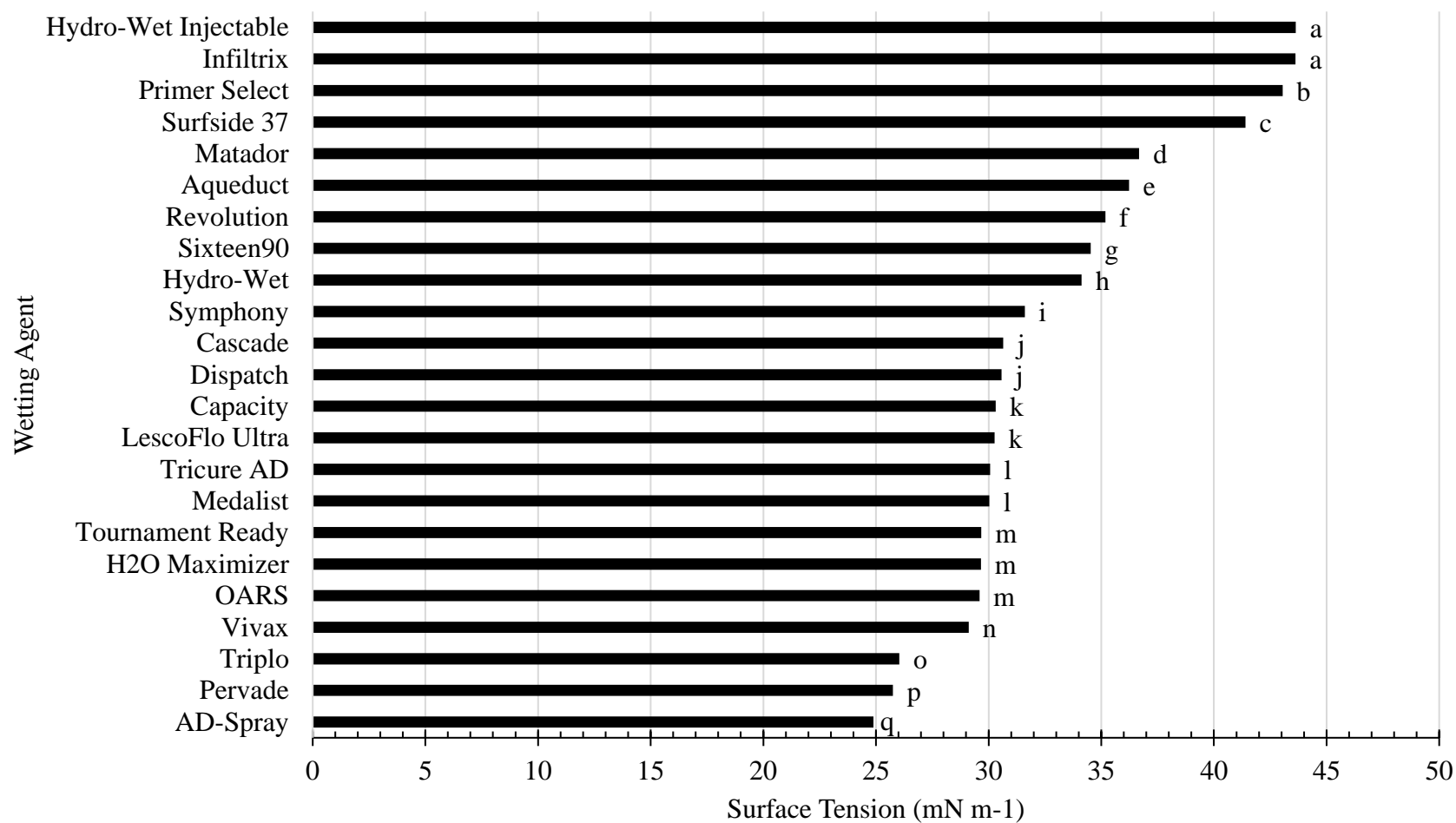


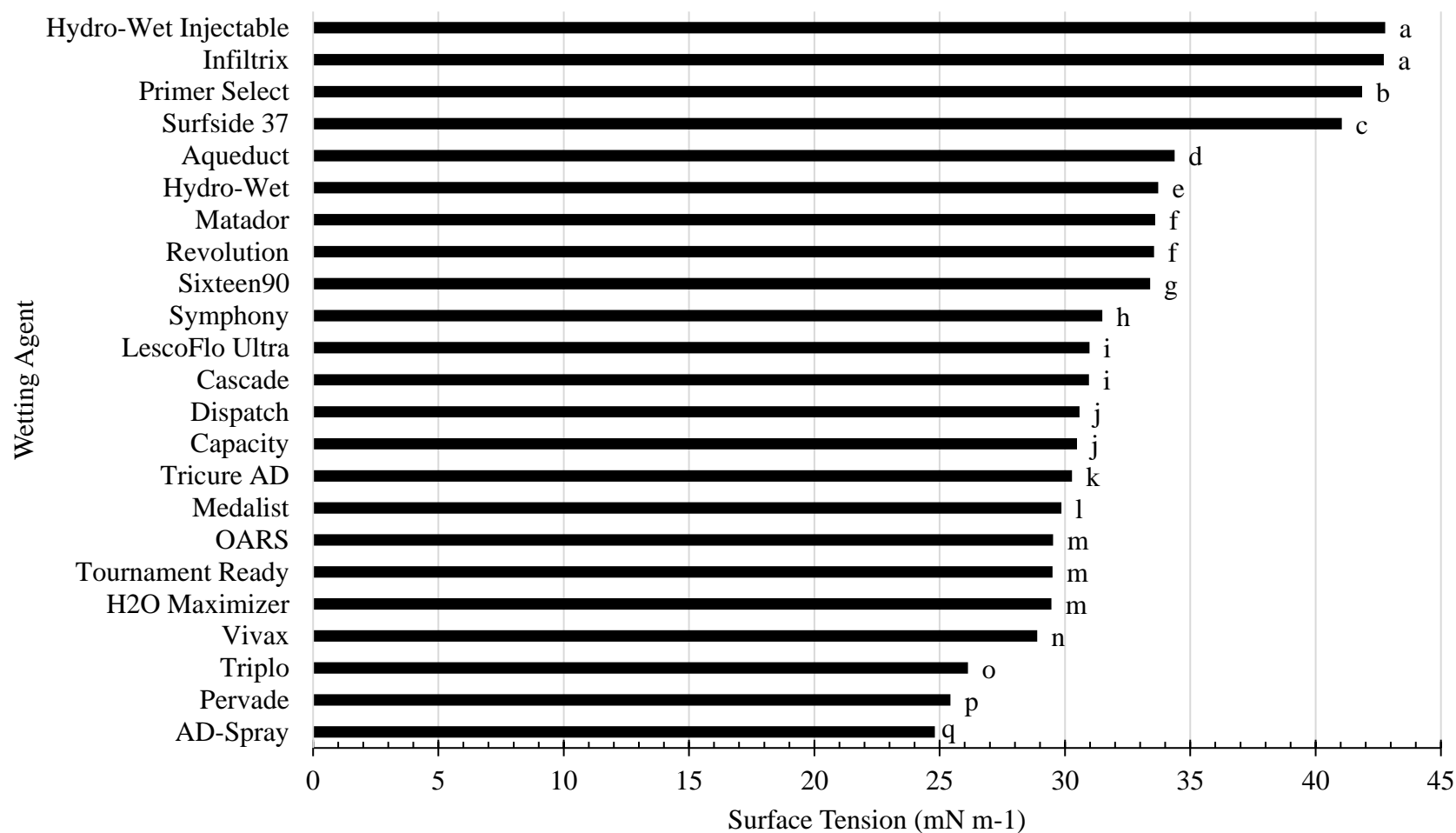
Image 2.1. Water droplet suspended from needle to measure surface tension (γ) utilizing the Attention Theta Lite tensiometer.



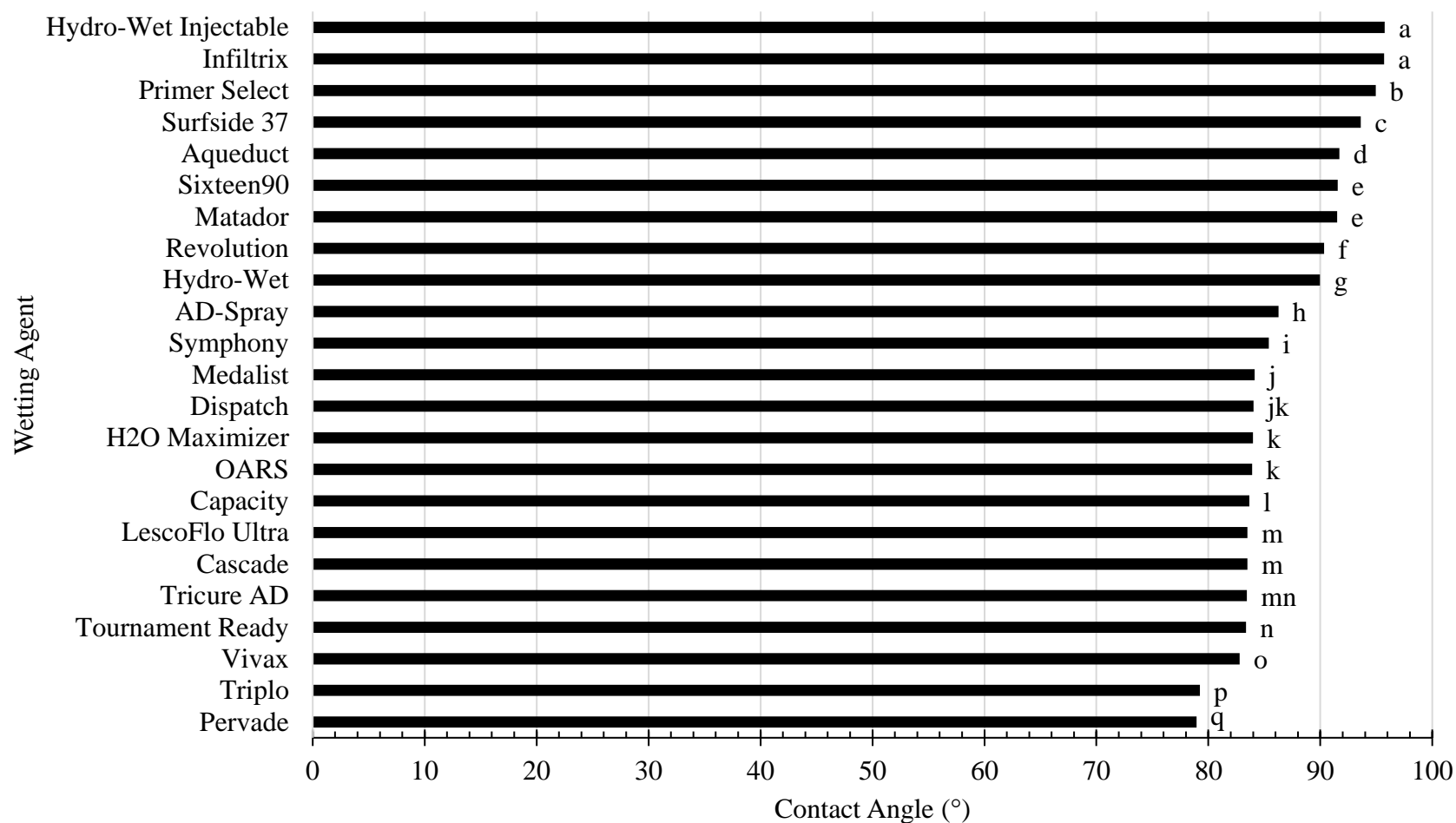
Supplementary figure 2.1. Surface tension (mN m⁻¹) of various wetting agents at 0.5x of their suggested label rates. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.



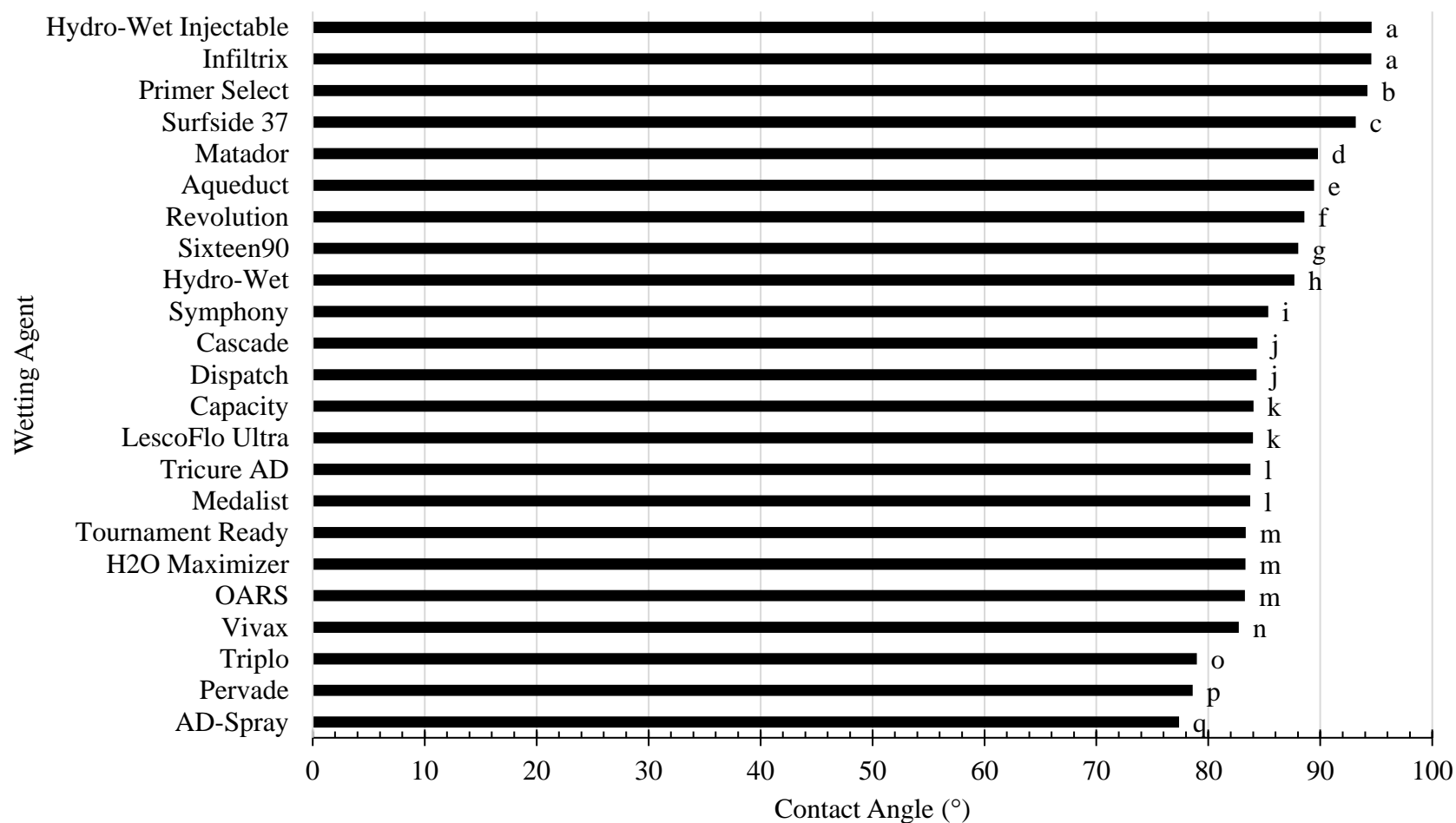
Supplementary figure 2.2. Surface tension (mN m⁻¹) of various wetting agents at 2x of their suggested label rates. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.



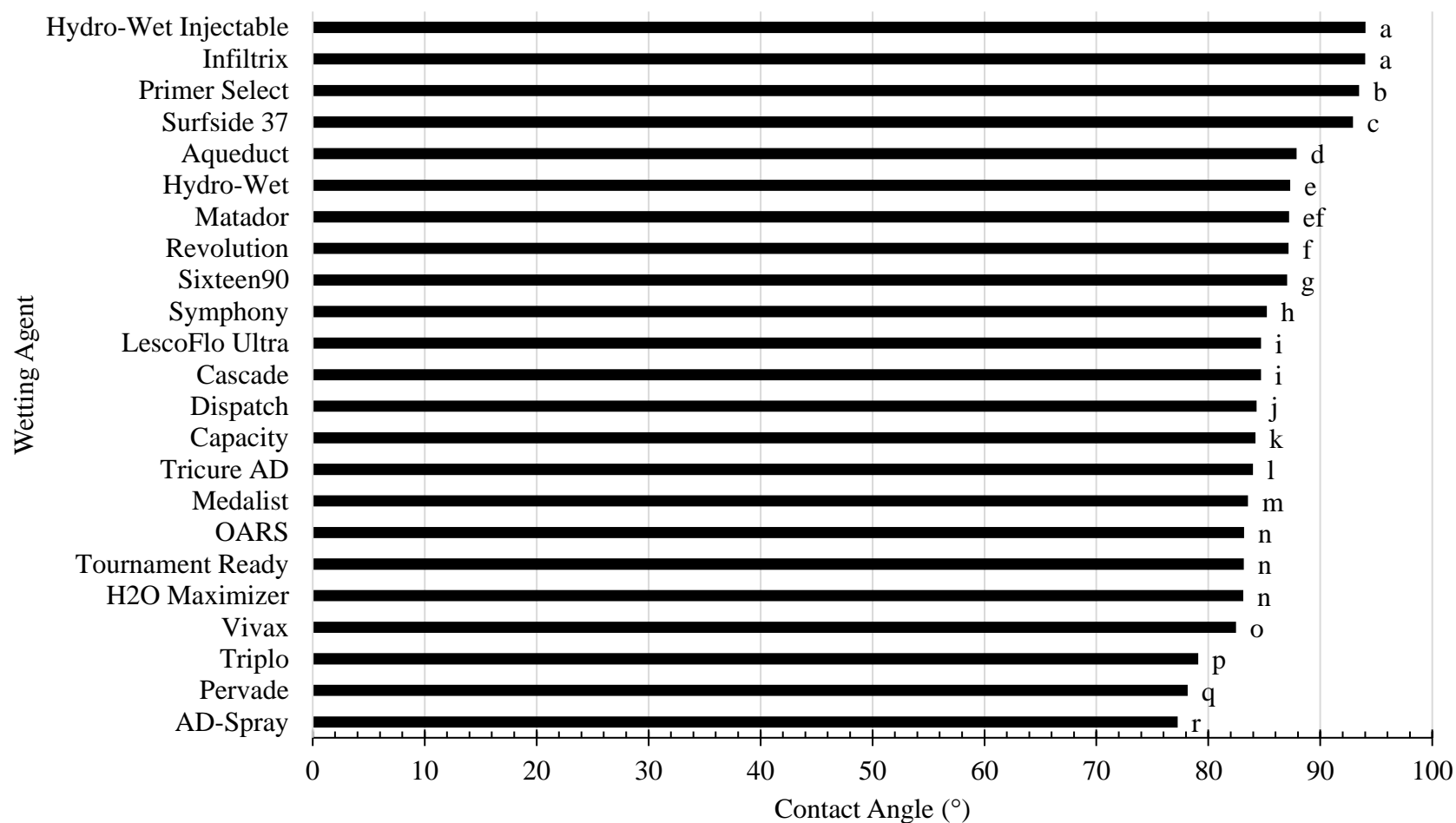
Supplementary figure 2.3. Surface tension (mN m⁻¹) of various wetting agents at 4x of their suggested label rates. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.



Supplementary figure 2.4. Contact angle (°) of various wetting agents at 0.5x of their suggested label rates. Values were determined based off 5.4 molarity of ethanol droplet test (MED) on artificial hydrophobic sand, which had a 90° surface tension of 36.95 mN m^{-1} . Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.



Supplementary figure 2.5. Contact angle (°) of various wetting agents at 2x of their suggested label rates. Values were determined based off 5.4 molarity of ethanol droplet test (MED) on artificial hydrophobic sand, which had a 90° surface tension of 36.95 mN m^{-1} . Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.



Supplementary figure 2.6. Contact angle (°) of various wetting agents at 4x of their suggested label rates. Values were determined based off 5.4 molarity of ethanol droplet test (MED) on artificial hydrophobic sand, which had a 90° surface tension of 36.95 mN m^{-1} . Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P < 0.05$.

CHAPTER III

Improving Infiltration and Rewettability on Water-Repellent Sand Greens based on Wetting Agent Application

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Abstract

Wetting agents are widely applied by golf course superintendents across the world to ameliorate localized dry spot (LDS) on putting greens caused by soil water repellency (SWR). It is known that wetting agents provide an ability to influence water infiltration by altering the surface tension (γ) of water, however, there are limited studies testing wetting agents that influence γ differently to understand its effect on infiltration in field conditions. The objective of this study was to evaluate the influence of six wetting agents on water infiltration, volumetric water content (VWC), LDS and turf quality (TQ) based on their γ . Two field experiments were conducted in 2018 on ‘Penn A-4’ and ‘007’ creeping bentgrass (*Agrostis stolonifera* L.) putting greens built based on United States Golf Association (USGA) recommendations at the University of Missouri Turfgrass Research Facility, Columbia, MO, where SWR had previously been identified. The wetting agents were applied monthly from May to October. Wetting agents were able to enhance or maintain water infiltration one month after the initial application, however, infiltration rates then varied among the wetting agents throughout the year, such as NIPA resulting in 58.3% or greater variation in infiltration rate. Overall, wetting agent application reduced the average LDS by 24.0% and significantly improved or maintained

average TQ as compared with the untreated control. Nevertheless, significant differences in among the wetting agent's performance were seen between the two locations, potentially due to underlying soil property variations. Golf course superintendents should be aware of their putting green soil properties, as it could alter the desired purpose of the wetting agent application.

Abbreviations and key words: infiltration; LDS, localized dry spot; MED, molarity of ethanol droplet test; NIPA, non-ionic polyols, Aqueduct; SWR, soil water repellency; γ , surface tension; TQ, turf quality; USGA, United States Golf Association; VWC, volumetric water content; WDPT, water droplet penetration test; wetting agent

Introduction

Soil water repellency (SWR), the inability of water to adhere to soil due to the presence of hydrophobic coatings, is a growing concern with sand-based rootzones, which not only affects golf course putting greens, but also impacts agricultural land globally (DeBano, 2000; Dekker et al., 2005; Roper et al., 2015). With the increased limitation of water globally this issue is going to continue to increase and reduce available land for agriculture (Hallett, 2007). Soil water repellency is generally thought to occur from an increase in organic coatings surrounding a soil particle (Doerr et al., 2006; Hallett, 2007; Roper et al., 2015). Since sandy soils have the lowest specific surface area, but the largest particle size of all soil types, hydrophobic materials that induce SWR have a much greater impact on sands than other soil types (Woche et al., 2005). Sand particles covered by soil organic matter (SOM) reduce the overall surface tension (γ) of a solid and increase soil hydrophobicity (Doerr et al., 2000; Kern et al., 1986; Tucker et al. 1990). The direct origin of SWR has not yet been confirmed, but it has been attributed to a multitude of factors such as; plant root exudates, fungal species, degradation of plant leaf waxes and decomposing organic matter (Mainwaring et al., 2004; Hallett et al., 2006). When these substances are wet, they are strongly hydrophilic, but when the volumetric water content (VWC) drops below a critical level, the hydrophilic portions of these molecules will bind strongly to other hydrophilic soil surfaces and leave the hydrophobic portion exposed toward the soil pore, causing SWR (Dekker et al., 1998; Dekker et al., 2001). This causes water to move into the soil by preferential flow patterns with non-uniform wetting fronts, resulting in pockets of dry soil, which in turn leads to localized

dry spot (LDS) and irregular infiltration patterns (Bauters et al., 1998; Oostindie et al., 2008).

Different management methods have been utilized to ameliorate SWR across the world. The addition of wax-degrading bacteria to consume hydrophobic coatings has been studied, which selected four out of 37 different wax-degrading bacteria species in Australian soils and inoculating those cultures into bags containing grey sand with a 3.9 molarity of ethanol droplet test (MED) water repellency (Roper, 2004). These were monitored over a period of 250 days and the MED measured throughout to assess the effectiveness of the wax-degrading bacteria treatments. Three of the treatments resulted in a reduction in MED value, with a *Rhodococcus* sp. isolate reducing water repellency to an MED value of 1 over 150 days, while the other two isolates, another *Rhodococcus* sp. and a *Mycobacterium* sp., resulted in a reduction in MED to <1.5 after the 250 days (Roper, 2004). The other isolate, a *Nocardia* sp., did not significantly reduce the water repellency of the grey sand when compared to the control, which only had deionized water added (Roper, 2004). Another amelioration method tested the use of adding clay during the construction of the sand-based rootzone to increase the overall surface area of the soil (Dlapa et al., 2004; Wallis & Horne, 1992). Dlapa et al. (2004), described adding different percentages of kaolinite or Ca-montmorillonite clays to water repellent sand and assessing them for their ability to reduce water repellency. Clays were added at 1, 2, and 3% of the water repellent silica sand mass and mixed on a shaker table before performing the water droplet penetration test (WDPT) to measure the level of water repellency. Results showed the addition of kaolinite clay, at all percentages, reduced the WDPT by 7-fold or greater as compared to the control, whereas the addition of Ca-montmorillonite

increased the WDPT by up to 24.5% (Dlapa, 2004). This research established that utilizing the correct clay amendments, such as kaolinite, can be effective in reducing water repellency in a sand-based soil, while other clay amendments, such as Ca-montmorillonite, can increase water repellency.

Still, the main amelioration technique utilized by golf course superintendents is the application of wetting agents or soil surfactants. A surfactant is a surface-active substance that can reduce the γ when mixed with a liquid. By lowering the γ of water or a solution, the contact angle between water and the soil particle is effectively decreased, allowing the water to adsorb to the hydrophobic sand particles (Müller & Deurer, 2011). These surfactants are amphiphilic molecules, containing a strong polar, hydrophilic head group and a strong non-polar, hydrophobic tail group. The hydrophobic tail portion is repelled by the water and orients toward the hydrophobic sand particles, allowing the hydrophilic portion to protrude into the soil pore, attracting water (Müller & Deurer, 2011). There are a multitude of different soil surfactant, or wetting agent, chemistries available that perform differently (Kostka & Zontek, 2012).

Golf course superintendents and turf managers ultimately use wetting agents for different purposes, such as enhancing water infiltration, improving water retention or maintain a balance between the two. Given the lack of information provided by the manufacturers regarding the chemical makeup of these wetting agents, applicators are left to rely on previous experiences or product technical sheets. Previous studies have been performed to identify the function of each specific wetting agent chemical class to better determine which product best addresses a particular management issue (Zontek & Kostka, 2012).

Currently, the wetting agents on the turf market fall into three main chemical groups: anionic, cationic and nonionic surfactants (Zontek & Kostka, 2012). Anionic surfactants or blends are negatively charged and offer quick wetting but can be phytotoxic depending on the application rate (Gardner, 2016; Zontek & Kostka, 2012). Anionic wetting agents were the original surfactant chemistry introduced into the turf market in 1950 and are now utilized less by golf course superintendents. The most common wetting agent chemistry is nonionic surfactants, which are broken into six different subgroups: polyoxyethylene (POE), block co-polymers, modified methyl capped block co-polymer, alkyl polyglucoside (APG), humic substance redistribution molecules and multibranch regenerating wetting agents (Gardner, 2016; Zontek & Kostka, 2012). A majority of the current wetting agents on the turf market fall into one of the nonionic chemistry classes. The POE group were the original nonionic surfactants on the market and offered enhanced soil-water movement and alleviated LDS (Zontek & Kostka, 2012). Block co-polymer wetting agents have multiple variations, such as straight, reverse, straight and reverse blends or modified. Straight block co-polymers have been shown to enhance water movement, while reverse block co-polymers have shown enhanced water retention within a sand-based rootzone (Zontek & Kostka, 2012). Blends of both straight and reverse block co-polymers aim to bring the benefits of both chemistries, and have displayed the ability to more effectively improve turf quality and LDS amelioration (Zontek & Kostka, 2012). A modified methyl capped block co-polymer wetting agent, due to its chemical configuration, has resulted in greater air-to-water balance leading to increased soil water availability, turf performance and longevity in the soil (Zontek & Kostka, 2012). The APG wetting agents are commonly found in blends with block co-

polymers to enhance the performance of the block co-polymer. Depending on the blend, the APG wetting agents have demonstrated increased infiltration and penetration rates or the improvement of water availability and reduction of evapotranspiration (Zontek & Kostka, 2012). Finally, the humic substance redistribution wetting agents claim to increase water penetration and decrease SWR by redistributing hydrophobic molecules coating the sand particles. However, recent studies have shown that some wetting agents in this class can actually increase SWR in a soil after repeated application (Song et al., 2018).

Due to the broad functionality of these wetting agent chemical classes, further research needs to be conducted to determine precisely how these wetting agents will perform, prior to application. Therefore, this study was conducted to investigate the impact of repeated applications of selected wetting agents on infiltration rates, water retention, and turf performance based on their γ value to better understand the influence different wetting agent chemical classes may have. Wetting agents were selected based on different surface tension values, chemical properties and effects on water movement previously evaluated in a laboratory study.

Materials and Methods

Field plots were established in two separate locations in the spring of 2018 at the University of Missouri Turfgrass Research Facility in Columbia, Missouri. One location was established on a ‘Penn A-4’ creeping bentgrass (*Agrostis stolonifera* L.) putting green, while the other was established on a ‘007’ creeping bentgrass putting green. Both locations consist of washed silica sand that meet the United States Golf Association (USGA) recommendations for green construction. (USGA, 2018). Soil properties

measured included: particle size distribution, porosity, bulk density, particle density, nutrient composition, organic matter (O.M.), cation exchange capacity (CEC) and molarity of ethanol droplet (MED) water repellency (Table 3.1). Both locations sand-based rootzones met the USGA recommendation for particle size distribution (USGA, 2018). Water repellency, as determined by the MED droplet test, for both locations were considered moderately water repellent (Doerr, 1998; King, 1981).

Individual plots measuring 1.5 by 1.5 m with a 0.3 m border between plots were established at both locations where LDS was previously documented. Treatments applied included six wetting agents, poloxanlene, poly (PoP) (H₂O Maximizer; Kalo, Inc., Overland Park, KS) dihydrooxirane, epihydrin (DE) (TriCure AD; Mitchell Products, Millville, NJ), nonionic surfactant (NIS) (Capacity; Becker Underwood, Ames, IA), nonionic polyols (NIPA) (Aqueduct; Aquatrols, Paulsboro, NJ), alkoxylated polyols (AoP) (Primer Select; Aquatrols, Paulsboro, NJ), and nonionic polyols (NIPI) (Infiltrix; Aquatrols, Paulsboro, NJ), as well as water as an untreated control. All wetting agents were applied at the label suggested rates (Table 3.2).

Wetting agents were applied utilizing a CO₂ pressurized backpack sprayer with XR8004 TeeJet (TeeJet® Spraying Systems, Wheaton, IL) flat fan nozzle tips calibrated to deliver 374 L ha⁻¹ at a pressure of 275.8 kPa with a speed of 4.8 km h⁻¹. Treatments at both sites were initially applied on May 19, and then reapplied every month thereafter on June 20, July 20, August 22 and September 19. Following the label suggestions, irrigation was applied following wetting agent applications of NIS, DE, AoP and PoP. Following application of NIPI and NIPA, plots were irrigated the following morning before the next mowing event.

During the experiment, plots were maintained at a 0.125 cm mowing height using a Toro Greensmaster 3150 (The Toro Company, Bloomington, MN). Irrigation of 1.27 cm water was provided in the morning for six days a week throughout the entirety of the study, except when precipitation occurred. Fertilization was applied at 16.14 kg N ha⁻¹ to the plot areas every three weeks. Fungicides, with a rotation of different active ingredients, were applied approximately every three weeks to prevent fungal diseases. Application dates, active ingredient rates and fungicide brand names applied are listed in Supplementary Table 3.1.

Data collected included visual assessment of turf quality based on a 1 to 9 scale, with 9 being a perfect stand of turf, 6 being minimally acceptable and 1 being extremely poor or dead turf (Morris, 1998). Other data collected included visual percent of LDS coverage (%), and overall turf performance that was assessed by using a handheld sensor (GreenSeeker; NTech Industries, Inc., Ukiah, CA) to generate normalized difference vegetation index (NDVI) (Bell et al., 2004). Volumetric water content (VWC, v/v %) was determined by averaging five random subsample measurements in each plot using a time domain reflectometer (TDR) soil moisture sensor (Campbell Scientific, Logan, UT) with rod length measuring 11 cm. All of the measurements described above were performed every week throughout this experiment. On a monthly schedule, water infiltration rate (m hr⁻¹) was assessed using a double ring infiltrometer (Tur-Tec International, Tallahassee, FL) (Bouwer, 1986; ASTM, 2003). Additionally, a forward looking infrared (FLIR) thermal camera (FLIR Systems, Inc., Wilsonville, OR) was utilized each week starting in July to determine canopy temperature for each location. A summarization of daily

precipitation and average air temperature (°C) was compiled through the South Farm Weather Station, Columbia, MO (Fig. 3.1).

In both locations, all treatments were arranged in a randomized complete block design with four replications. Data were subjected to ANOVA using PROC GLM in SAS 9.4 (SAS Institute Incorporated, Cary, NC). Significant differences among means were separated using Fisher's Protected LSD at $P \leq 0.05$. In addition, a correlation test was applied to LDS, VWC and infiltration rate data.

Results and Discussions

Localized dry spot

Prior to treatment application on the 'Penn A-4' creeping bentgrass putting green, LDS coverage ranged from 16.3 to 21.3% (Table 3.3), demonstrating the presence of SWR prior to the application of treatments. Consistently, the untreated control displayed the highest LDS coverage throughout the season, with the greatest percent of LDS found in June at 17.5%, during the high temperature summer months, and lowest percent of LDS found in September at 7.5% (Fig. 3.1). The untreated control maintained a LDS coverage of 15.7% from 0 to 70 DAIT. Fourteen days after the initial treatment application, all wetting agent treatments significantly reduced LDS by at least 31% or greater, except for NIPi which did not significantly reduce LDS coverage in plots. However, 28 days following the initial application, all wetting agents reduced initial LDS coverage by 60.1% or greater compared to the initial LDS coverage. Application of NIPA and NIS significantly reduced LDS at 28 DAIT, with coverage of 1.3% LDS, more quickly than any other wetting agent application. Following the second treatment application, on June 20, temperatures averaged at 25.7°C from 42 to 70 DAIT (Fig. 3.1).

Even after the second treatment application, a significant increase in LDS coverage was seen among all treatments, except PoP and AoP, which maintained similar LDS coverage, from 42 to 70 DAIT (Table 3.3). This is also represented by significantly higher putting green canopy temperatures seen at 49 and 56 DAIT than throughout the rest of the season (Fig. 3.2). This trend is consistent with other studies, where Cisar et al. (2000) saw four out of five wetting agent treatments increase LDS coverage by 52.6% or greater from July to August. At 70 DAIT, only the application of NIPA and PoP resulted in significantly different LDS coverage than the untreated control. Following the third application, on July 20, a significant decrease in LDS coverage was seen from 70 to 84 DAIT in all treatments, except in PoP and NIPI treated plots where greater than 7.5% LDS was seen (Table 3.3). Even when significantly higher canopy temperatures were seen at 84 DAIT compared to 70 DAIT (Fig. 3.3). After the fourth application, on August 22, all treatment applications either maintained or reduced LDS coverage from 98 WAIT until the conclusion of the experiment at 139 DAIT.

Overall, all wetting agent treatment applications on ‘Penn A-4’ significantly reduced the initial LDS coverage by at least 84.7% or greater when compared to the end of the experiment. Application of NIPA, was the only treatment that maintained significantly lower LDS coverage as compared to the untreated control, throughout the whole experiment. Application of NIS, PoP, AoP and DE, had one date where the LDS coverage was not significantly different than the untreated control, being 70 DAIT for NIS, AoP and DE, and 98 DAIT for PoP. In contrast, NIPI had four dates where LDS coverage was not significantly different than the untreated control, being 56, 70, 84 and 124 DAIT. From 14 DAIT to 124 DAIT, NIPA maintained the smallest variation in LDS

coverage from 0.0 to 8.8 %, while, NIPI had the largest range in LDS coverage at 2.5 to 12.5. Reduction in LDS has been found in various studies related to wetting agent application and SWR. Kostka (2000) found that monthly application of wetting agents initially reduced LDS coverage by 100% two months after initial application. After two months, the study showed that the untreated plots increased initial LDS coverage by 3-fold.

For the '007' creeping bentgrass putting green location, prior to treatment application, LDS coverage ranged from 13.8 to 18.8% (Table 3.4). Throughout the growing season, LDS coverage varied within the untreated control, ranging from 26.3% in June to 6.3% in October. The untreated control maintained an average LDS coverage of 21.9% from 0 to 70 DAIT. Throughout the growing season, all treated plots showed consistently less LDS coverage, compared to the untreated control. At 14 DAIT, all wetting agent treatments significantly reduced LDS coverage compared to the untreated control by 25% or greater (Table 3.4). Coverage of LDS continued to decline at 28 DAIT, resulting in all treated plots reducing LDS by 54% or greater. Throughout the high air and canopy temperatures, from 42 to 84 WAIT (Fig. 3.1; Fig. 3.3), all wetting agent treatments were able to maintain significantly lower LDS compared to the control by at least 42.6% or greater. This is consistent with Cisar et al., (2000), where all wetting agent applications resulted in a 30.8% or greater reduction in LDS reduction compared to control from July to August. From 84 to 98 DAIT, all wetting agent treatments either maintained or significantly decreased LDS coverage, along with a significant decrease in creeping bentgrass canopy temperature from 84 to 98 DAIT (Fig. 3.3). Following the fourth treatment application on August 22, from 110 DAIT until the end of the

experiment, all wetting agent treatments, except PoP and NIPI, significantly reduced LDS compared to 84 and 98 DAIT. The LDS coverage was significantly reduced at 124 DAIT for all treatments compared to the untreated control by reducing LDS coverage by 60% or greater, except for NIPI.

Overall, all wetting agent treatments, except NIPI, maintained significantly lower LDS coverage than the untreated control throughout the entirety of the experiment at the ‘007’ location. Treatment of NIPI maintained significantly lower LDS coverage than the untreated control throughout the season, until reaching 98 DAIT, where LDS coverage was statistically the same as the control, throughout the remainder of the experiment (Table 3.4). Plots treated with NIPI resulted in the highest LDS coverage at 13.0%, which is at least 17.0% greater than any other wetting agent treatment. Application of NIPA resulted in the lowest LDS coverage throughout the experiment at 7.1%, which is at least 14.1% lower than the LDS coverage of all other treatments. This is consistent with Cisar et al (2000), where NIPA was utilized as well and resulted in an LDS coverage that was 14.2% lower than all other wetting agent treatments except one. Regardless of location, application of NIPA resulted in the lowest LDS coverage and application NIPI resulted in the greatest LDS coverage among all treatments.

Volumetric water content

Application of wetting agent treatments on ‘Penn A-4’ creeping bentgrass resulted in no interaction between treatment and evaluation timing, hence the data were pooled over time (Fig. 3.4). All treatments maintained a VWC above 14%, which is acceptable to maintain adequate growth of turf, as the USGA Green Section recommendation for sand-based putting greens’ VWC is between 12 to 18% (Bengeyfield, 1989). Repeated

application of NIPI, NIPA and NIS resulted in significantly higher VWC than all other treatments. Plots treated with NIPI maintained a higher VWC higher than the untreated control by 7.0% or greater. Application of NIPI, NIPA and NIS resulted in a range of season-long VWC from 15.2% to 15.4%. In contrast, AoP, PoP and DE applications resulted in a VWC equivalent to the untreated control, with DE numerically maintaining a slightly lower VWC of 14.2%, than the untreated control. This is consistent with Leinauer et al. (2001) who found that application of Primer 604 consistently improved the water retention of a USGA sand-based rootzone, while application of Midorich did not significantly increase water retention when compared to the untreated control.

In general, wetting agent applications on ‘007’ creeping bentgrass resulted in lower VWC ranging from 11.9% to 13.7%, with the untreated control maintaining the lowest VWC of all treatments (Fig. 3.5). Application of PoP resulted in the highest VWC at 13.7%, which was an increase of 14.3% as compared to the untreated control. Applications of AoP, DE, NIPA, and NIS also maintained a significantly higher VWC than the untreated control, resulting in an increase of 5.6% or greater. Application of NIPI alone resulted in a non-significantly different VWC than the untreated control. All wetting agent treatments maintained an VWC of 12.4% or above and resulted in a higher VWC than the untreated control.

Variations in VWC maintained by different wetting agent treatments were seen between locations in 2018. In general, treatments, including the untreated control, resulted in a VWC on the ‘007’ creeping bentgrass green that were numerically lower than those on the ‘Penn A-4’ green, signifying a drier rootzone at the ‘007’ location. Applications of wetting agents have been shown to result in an increase and a negligent

effect on VWC (Alvarez et al., 2016; Barton & Colmer, 2011; Karnok & Tucker, 2001; Soldat, 2010). Wetting agents can help to increase water content in a dry sand-based soil and increase uniformity (Alvarez et al., 2016; Karnok & Tucker, 2001). Differences between the particle size distribution of ‘Penn A-4’ and ‘007’ sand-based rootzone were found (Table 3.1). Very coarse and coarse sand particles of the ‘Penn A-4’ rootzone were 20.0% higher than ‘007’. However, the medium and fine sand particles of the ‘007’ rootzone were 10.4% higher than that of ‘Penn A-4’. Both gravel and very fine sand particles were not significantly different in the two rootzones. There was only a 2.4% difference in air-filled porosity between ‘Penn A-4’ and ‘007’; however, the capillary porosity of the ‘Penn A-4’ sand-based rootzone was 25.9% greater than that of ‘007’ (Table 3.1), leading to ‘Penn A-4’ having a 10.8% greater total porosity than ‘007’ (Table 3.1). Capillary pores are known to contribute to the ability of soil to hold and retain water within the soil profile (Amer, 2002). Additionally, Penn A-4’ had a 30% higher O.M. amount at 1.38%, as compared to ‘007’ at 0.98%, potentially attribute to the higher VWC seen overall among the treatments (Table 3.1). Previous studies have shown that an addition of organic matter resulted in between 144% to 434% greater total available water, in a USGA sand-based putting green, compared to no addition of O.M. (Wesseling et al., 2009). In general, at both locations, the application of all wetting agent treatments resulted in a VWC greater than or equal to that of the untreated control. Differences in O.M. percent and porosity between the two locations could also play a role in differences seen between the same wetting agent application.

Infiltration rate

Infiltration rates were assessed on a monthly basis at both locations throughout the growing season. On 'Penn A-4', there was no interaction or significant main effect between treatment and evaluation time seen, due to variations between treated plots (Table 3.5). However, analysis of variance (ANOVA) detected significant treatment differences for infiltration rate and evaluation date (Fig. 3.6). Infiltration rates into the sand-based putting green were significantly faster at zero and one month, with rates being at least 20.7% or greater than throughout the rest of the experiment (Fig. 3.6).

Application of NIPA resulted in an infiltration rate of 1.08 m hr^{-1} one month after the first application, which was the highest for plots treated by NIPA throughout this study (Table 3.5). By the end of the study, the repeated monthly application of NIPA declined to 0.45 m hr^{-1} , which was the lowest infiltration rate for NIPA treated plots (Table 3.5). Throughout the study, NIPA treated plots resulted in the greatest range difference, at 58.3% between the lowest and highest infiltration rate. Plots treated with NIPi resulted in the lowest range in infiltration rates at 19.2%, with the highest being 0.78 m hr^{-1} , prior to wetting agent application, and the lowest being 0.63 m hr^{-1} , being 3 months after the initial treatment application (Table 3.5). Untreated control plots demonstrated the highest infiltration rate, of 0.83 m hr^{-1} , prior to the study initiation and the lowest two months into the study at 0.54 m hr^{-1} (Table 3.5). The results from our study are similar to Gross et al. (2011), when utilizing a double ring infiltrometer. Ten days after wetting agent application, the infiltration rates were either not statistically different or were lower than the control, being just water alone. Gross et al (2011) only saw application of one wetting agent significantly increase infiltration rate compared to all other treatments, 10 days after application. Similarly, infiltration rates measured were

higher prior to wetting agent application and decreased by 10% or greater 10 days following treatment application (Gross et al., 2011). Variations among plots treated with the same wetting agent could be due to the effective low amount of plot area tested by the double-ring infiltrometer. The Turf-Tec double-ring infiltrometer only measures 28.6 cm² of the plot area, relative to the total plot area of 22,500 cm². Testing such a small area of each plot, does not allow for an accurate representation of the infiltration rate throughout the whole plot, potentially leading to variation between plots treated with the same wetting agent. However, regardless of treatment, infiltration rates met the USGA recommended infiltration rate of 150 mm hr⁻¹ (USGA, 2018).

Wetting agent application on the '007' creeping bentgrass putting green however, did result in an interaction between treatment and evaluation time (Table 3.6). Prior to wetting agent treatment, infiltration rates ranged from 0.9 m hr⁻¹ to 1.43 m hr⁻¹ (Table 3.6). One month after initial treatment, all wetting agent treatments-maintained pre-treatment infiltration rates except for the application of NIPA, which significantly increased the infiltration rate by 34.8% (Table 3.6). However, only application of NIS and PoP resulted in significantly lower infiltration rates than the untreated control by 28.6% (Table 3.6). Following two monthly applications of wetting agent treatments, only DE, NIPA, NIS, and PoP were able to maintain infiltration rates similar to one month after the initial treatment application. Two applications of AoP and NIPI resulted in significant decreases in infiltration rate, by 29.6% or greater from month one to month two (Table 3.6). Similarly, infiltration rates into the untreated control plots also declined by 32.3% from month one to month two (Table 3.6). Following three monthly wetting agent applications, only DE, NIS and PoP were able to maintain infiltration rates

comparable to one month after the initial application. Regardless of treatment, no significant difference in infiltration rates were seen between treatments after two- or three-monthly application of wetting agent treatments. In addition, all treatments were able to maintain similar infiltration rates from two to three months after the initial treatment application. Following four monthly wetting agent applications, all treatments, except the untreated control, maintained infiltration rates from three to four months after the initial treatment application. Four months after the initiation of the study, the untreated control had significantly higher infiltration rates when compared to all other wetting agent treatments by 29.5% or greater (Table 3.6).

Application of NIS was the only treatment that resulted in a steady infiltration rate throughout the entire study. A month after the initial application of NIS, the resulting infiltration rate was 0.95 m hr^{-1} (Table 3.6). This steady infiltration rate was maintained through the end of the study, at which time, the infiltration rate was 0.93 m hr^{-1} (Table 3.6). Similarly, one month following the initial treatment of PoP until the end of the study, plots were able to maintain infiltration rates ranging from 0.95 m hr^{-1} at one month and 0.71 m hr^{-1} at four months after the initial wetting agent treatment (Table 3.6). All other wetting agent treatments resulted in a gradual decline of infiltration rates from one month to four months after the initial wetting agent application (Table 3.6). The widest range of infiltration rates following the first treatment application was seen in plots treated with NIPA, where after one month, the infiltration rate was 1.38 m hr^{-1} and after four months the infiltration rate significantly declined by 58.7% to 0.57 m hr^{-1} (Table 3.6). Regardless of treatment, infiltration rates met the USGA recommended infiltration rate of 150 mm hr^{-1} (USGA, 2018).

There are limited field studies which demonstrate the influence of a wetting agent's effect on water infiltration into a water-repellent sand-based rootzone throughout a growing season (Throssell, 2005; Song et al., 2014). However, similar results were reported by Gross et al., (2011) when measuring the influence of a wetting agent on infiltration by utilizing a double ring infiltrometer. In general, Gross et al, (2011) saw a variety of influences on saturated infiltration rates from five wetting agents and water as a control tested. The application of four wetting agents did not significantly increase infiltration rates as compared to control 10 days after wetting agent application (Gross et al., 2011). However, one wetting agent, a propylene oxide-ethylene oxide block polymer, resulted in significantly faster infiltration rates compared to the other wetting agent treatments and control (Gross et al., 2011). This is similar to the results in our study, as application of NIPA increased infiltration rate by 34.8% one month after initial treatment application (Table 3.6). In addition, all wetting agents, except for NIS and PoP, resulted in infiltration rates that were not significantly different than the untreated control. In the case of NIS and PoP, a significant reduction in infiltration rate was seen (Table 3.6). Gross et al. (2011) also saw the infiltration rate of water alone decrease by 14% compared with measuring ten days prior. This was similar to the untreated control in our study one month after trial initiation, which saw a 7% decrease in infiltration rate (Table 3.6). Our results also differed from Mitra et al (2006) where the application of Dispatch[®] showed a significant increase in infiltration rate as compared to the untreated control by 27%. However, only one wetting agent was tested against the control in this study and infiltration rate was not measured multiple times over the growing season (Mitra et al., 2006).

To understand the potential influence of wetting agent application on infiltration rate, a correlation test on LDS, VWC and infiltration rate was conducted on the combined ‘Penn A-4’ and ‘007’ data. A negative correlation was seen between LDS and VWC, indicating that when LDS was reduced when the VWC was higher in plots. Understandably, if the creeping bentgrass had sufficient VWC to utilize, LDS stress was decreased. It was interesting that, LDS and infiltration rates were positively correlated. Potentially, if there was increased LDS in a plot and depending where the double ring infiltrometer was placed the water movement vertically through the center ring could have interacted with a preferential flow pathway, due to the LDS, and increased the infiltration rates seen, even when the outer ring of the double ring infiltrometer was filled twice to prevent lateral movement of water. In contrast, when LDS coverage was low this resulted in lower infiltration rates, which may be related to VWC in plots. Finally, VWC and infiltration rate were negatively correlated, meaning that when higher a VWC was present in plots, the infiltration rate was reduced. Conversely, when lower VWC was present in plots, the results showed an increased infiltration rate. This could potentially be due to increased VWC remaining in the sand-based rootzone during measurement of infiltration rate, which would lead to a reduction in the hydraulic gradient and hence, a reduction of infiltration rate (Miyamoto, 1985). Regardless, observations from this study demonstrated that the simplistic models introduced by Karnok & Tucker (2004) on wetting agents’ influence on the increase of infiltration rates into water repellent soils, are considerably more complex than initially thought (Gross et al., 2011).

Turf quality

Application of all wetting agent treatments significantly increased the turf quality on the 'Penn A-4' creeping bentgrass putting green compared to the untreated control (Fig. 3.7). No interaction between treatment and evaluation timing were found; therefore, data were pooled over time. According to the National Turfgrass Evaluation Program (NTEP), a minimally acceptable turf quality, on a 1 to 9 scale, is represented as 6, which was maintained throughout the season, regardless of treatment. Overall, wetting agent treatments increased turf quality by 4.7 to 13.8% compared to control, suggesting elevated turf quality following wetting agent application. Monthly application of NIPA achieved a turf quality of 8.2 throughout the season, resulting in the highest turf quality amongst all treatments. Applications of NIS and DE significantly increased turf quality by greater than or equal to 9% as compared to control. No significant difference in turf quality was seen as the result of AoP, NIPI and PoP application, but those treatments all resulted in significantly lower turf quality than the other three wetting agent treatments. The turf quality values are representative of the LDS values seen at the 'Penn A-4' location. Application of NIPA resulted in an LDS of 4.4% and also resulted in the highest turf quality value. Higher LDS percentages were seen in plots treated with AoP, NIPI and PoP, which also resulted in significantly lower turf quality values than the other wetting agent treatments. With all wetting agent treatments resulting in higher average turf quality than the untreated control, these results are consistent with Kostka's (2000), where application of Primer 604, at two rates, resulted in a 49.3% increase in turf quality as compared to the control.

Similar treatment effects on turf quality were demonstrated on the '007' creeping bentgrass putting green, where a majority of wetting agent treatments significantly

increased turf quality compared to the untreated control (Table 3.7). Throughout the season, NIPA, NIS and AoP consistently showed significantly greater turf quality, by 9% or greater, compared to the untreated control. With a turf quality of 6.8, the untreated control maintained the lowest turf quality among all treatments. Application of NIPI consistently produced the lowest turf quality, among all wetting agent treatments, and was not statistically different than the untreated control from 28 DAIT till the end of the experiment. Regardless of treatment the minimum acceptable NTEP turf quality value of 6 was maintained throughout the season for all treatments, including the untreated control.

Over the course of the experiment, the untreated control displayed a turf quality of 6.5 from the beginning of the study till 98 DAIT. After 98 DAIT, all treatments, including control, resulted in a turf quality value of 7.3 or greater until the end of the experiment. When the summer temperature stress was reduced (Fig. 3.1), application of AoP, NIPA, NIPI, and NIS resulted in an average turf quality rating of 7.5 or greater from 14 WAIT through the end of the experiment (Table 3.7). Turf quality was significantly increased 28 DAIT after the first wetting agent application, on May 19, as compared to prior treatment of all wetting agents, except for NIPI (Table 3.7). These results are consistent with Aamlid et al. (2009) and Cisar et al. (2000) who reported an increase of turf quality a month after the application of NIPA and other wetting agents, and also observed that wetting agent application consistently improved turf quality compared to the untreated control. In general, all wetting agent treatments, except NIPI, significantly improved and increased turf quality as compared to the untreated control during the experiment.

Normalized Difference Vegetation Index

The NDVI data showed no interaction between evaluation time and treatment on the ‘Penn A-4’ creeping bentgrass putting green, therefore, data were pooled over time (Fig. 3.8). Application of NIPA achieved a significantly higher NDVI compared to all other treatments, except for NIS. Numerically, the NDVI value following application of NIPA and NIS was higher than all other treatments. However, all other wetting agent treatments applied, except for NIPA, maintained an NDVI value that was not significantly different than the untreated control. Regardless of treatment, NDVI values varied between 0.785 (PoP) to 0.795 (NIPA), and are considered acceptable turfgrass NDVI values throughout the experiment (Xiong et al., 2007). Furthermore, the NDVI values for all treatments reflected similar results to turf quality and LDS data collected for the ‘Penn A-4’ location. The highest turf quality and lowest LDS values were obtained following the treatment of NIPA, which resulted in the highest NDVI value. Additionally, AoP, DE, NIPI, PoP and the untreated control resulted in an LDS of 7.0% or greater and also resulted in numerically lower NDVI values.

No interaction between evaluation timing and treatments for NDVI values on the ‘007’ creeping bentgrass putting green were found, so data were pooled over evaluation timing (Fig. 3.9). Application of NIS produced significantly higher NDVI among all treatments over the growing season, except for NIPA. Similar to ‘Penn A-4’, monthly application of NIS and NIPA on ‘007’ achieved numerically greater NDVI values compared to all other treatments. However, NDVI ranged from 0.760 (NIPI) to 0.777 (NIS), indicating acceptable turf performance for all treatments (Xiong et al., 2007). Furthermore, the results of the NDVI values for both locations showed similar results to

visual turf quality and LDS. Application of NIS and NIPA resulted in a turf quality of 7.8 or greater, also resulted in significantly higher NDVI in the case of NIS. In contrast, application of NIPI resulted in the highest LDS coverage, except for the untreated control, and resulted in significantly lower NDVI values compared to all other treatments. In general, wetting agent application did not show a significant increase in NDVI compared to the untreated control, except for the application of NIS.

Canopy temperatures

Canopy temperatures measurements started at 49 DAIT till the end of the study, due to the forward looking infrared (FLIR) thermal camera being acquired in the middle of the study. No interaction was seen between wetting agent treatments and DAIT, however, differences in canopy temperatures was seen among DAIT (Fig. 3.2 & 3.3). Similar canopy temperature, between 30°C to 40°C, can be seen between the two locations. In the ‘Penn A-4’ location, the highest canopy temperature dates were 49, 56, and 84 DAIT, which are all at least 14 days or longer than when the previous wetting agent application was made, as well as when higher air temperatures were seen (Fig. 3.1 & 3.2). Significant reduction in canopy temperatures is seen either on the day of the wetting application, at 98 DAIT, or two days after at 70 DAIT (Fig. 3.2). The lowest canopy temperature was seen at 132 DAIT by $\geq 23.8\%$, which coincides with declining air temperatures (Fig. 3.1 & 3.2).

At the ‘007’ location the highest canopy temperature was seen at 56 DAIT, which is when higher air temperature was seen (Fig. 3.1 & 3.3). Significantly higher canopy temperatures were seen at 49, 56, 84, and 124 DAIT, compared to all other DAIT, which is at least 14 days or longer than when the previous wetting agent application occurred

(Fig. 3.3). Similarly, to the ‘Penn A-4’ location, reduced canopy temperatures were seen either on the date or two days after the monthly application of wetting agents, being at 70 and 98 DAIT (Fig. 3.3). Additionally, the significantly lowest canopy temperature was recorded at 132 DAIT by $\geq 19.3\%$, coinciding with declining air temperatures (Fig. 3.1 & 3.3). At both locations on 98 DAIT, when a wetting agent application was made, a reduction in canopy temperatures by $\geq 6.3\%$ or 8.6% was seen at the ‘Penn A-4’ and ‘007’ locations, respectively.

Conclusions

Differences in wetting agent performance, potentially due to varying soil properties between locations were observed. Nevertheless, this field study demonstrates the ability of wetting agents to improve VWC, reduce LDS, influence infiltration rate and ultimately increase the overall creeping bentgrass turf quality. Applications of wetting agents, such as NIPA and NIS, demonstrated an overall reduction in LDS coverage by maintaining a consistent VWC throughout the growing season, particularly during the peak temperature months in the summer. Even though infiltration rates varied for these two compounds between locations, it demonstrated various wetting agents’ abilities, such as NIS and PoP to maintain a consistent infiltration rate throughout the study and result in an overall higher turf quality.

However, wetting agents are a heterogenous group and their individually unique chemistries allow them each to perform differently from one another in different locations with different soil properties. Some wetting agents may help to maintain infiltration rates, while others may increase the overall VWC and water retention within the soil. Overall, in this study, application of all wetting agents led to a decrease in LDS

and an overall increase in turf quality, highlighting the ability of wetting agents to reduce overall SWR. However, similarly to the previous laboratory study, no correlation was seen between the selected wetting agents influence on water's surface tension and their water infiltration or retention under field conditions. Potentially indicating that a wetting agent's performance is based on the underlying soil properties and conditions, in addition to their effect of the physical characteristics of water. It is important to know the soil properties prior to application of wetting agents, as they could influence the functionality of wetting agents in addressing the water infiltration or retention in a water repellent soil.

References

- Aamlid, T. S., T. Espevig, A. Kvalbein. 2009. The potential of a surfactant to restore turfgrass quality on a severely water-repellent golf green. *Biologia*, Bratislava. 64:620-623.
- Alvarez, G. E. Sevostianova, M. Serena, R. Sallenave, and B. Leinauer. 2016. Surfactant and polymer-coated sand effects on deficit irrigated bermudagrass turf. *Agronomy Journal*. 108:2245-2255.
- Amer, A.M. 2002. Drainable and water-filled pores as related to water storage and conductivity in agricultural soils of the Nile Delta. *Verh. Internat. Verein. Limnology*, Vol.28, part 4, p.1912-1919 Stuttgart-Germany, 28th SIL Congress.
- ASTM. 2003. Standard test method for infiltration rate of soils in field using double-ring infiltrometer. *Annual Book of ASTM Standards* 04.08.
- Barton, L., T. Colmer. 2011. Granular wetting agents ameliorate water repellency in turfgrass of contrasting soil organic matter content. *Plant Soil*, doi:10.1007/s11104-011-0765-3.
- Bauters, T. W. J., D. A. DiCarlo, T. S. Steenhuis, and J. Y. Parlange. 1998. Preferential flow in water-repellent sands. *Soil Science Society of America Journal*. 62:1185-1190.
- Bell, G.E., B.M. Howell, G.V. Johnson, W.R. Raun, J.B. Solie, M.L. Stone. 2004. Optical Sensing of Turfgrass Chlorophyll Content and Tissue Nitrogen. *HortScience* 39(5): 1130–1132.
- Bengeyfield, W.H. 1989. Specifications for a method of putting green construction. W.H. Bengeyfield (ed.) United States Golf Association. Golf House, P.O. Box 708, Far Hills, New Jersey 07931-0708.

- Bouwer, H. 1986. Intake rate: Cylinder infiltrometer. *Methods of Soil Analysis*. Monograph 9. pp. 825-843.
- Cisar J.L., K.E. Williams, H.E. Vivas, J.J. Haydu. 2000. The occurrence and alleviation by surfactants of soil-water repellency on sand-based turfgrass systems. *Jour. Hydro.* 231-232:352-358.
- Cisar J.L. 2001. Evaluation of Aquatrols Aqueduct_ for recovery from localized dry spot. Research summary. <http://www.aquatrols.com/Research/Aqueduct/Aqueduct-Cisar2000-21Dec06.pdf>. Accessed 23 Nov. 2008.
- Dlapa, P., S.H. Doerr, L'. Lichner, M. Šir, M. Tesař. 2004. Effect of kaolinite and Ca-montmorillonite on the alleviation of soil water repellency. *Plant Soil Environ.* 50(8):358-363.
- DeBano, L. F. 2000. Water repellency in soils: a historical overview. *Journal of Hydrology.* 231:4-32.
- Dekker, L. W., C. J. Ritsema, K. Oostindie, and O. H. Boersma. 1998. Effect of drying temperature on the severity of soil water repellency. *Soil Science.* 163(10):780-796.
- Dekker, L. W., K. Oostindie, S. J. Kostka, and C. J. Ritsema. 2005. Effects of surfactant treatments on the wettability of water repellent grass-covered dune sand. *Australian Journal of Soil Research.* 43:383-395.
- Dekker, L. W., S. H. Doerr, K. Oostindie, A. K. Ziogas, C. J. Ritsema. 2001. Water repellency of critical soil water content in a dune sand. *Soil Sci. Soc. J.* 65:1667-1674.

- Doerr, S.H., R. A. Shakesby, and R. P. D. Walsh. 2000. Soil water repellency: its causes, characteristics and hydro-geomorphological significance. *Earth-Science Reviews*. 51:33-65.
- Doerr, S.H., R. A. Shakesby, L. W. Dekker, and C. J. Ritsema. 2006. Occurrence, prediction and hydrological effects of water repellency amongst major soil and land-use types in a humid temperate climate. *European Journal of Soil Science*. 57:741-754.
- Gross, A., R. Mohamed, M. Anda, and G. Ho. 2011. Effectiveness of wetting agent for irrigating sandy soils. *Water*. 38(2).
- Hallett, P. D. 2007. An introduction to soil water repellency. In *Proceedings of the 8th International Symposium on Adjuvants for Agrochemicals*. 6:9.
- Hallett, P. D., N. A. White, and K. Ritz. 2006. Impact of basidiomycete fungi on the wettability of soil contaminated with a hydrophobic polycyclic aromatic hydrocarbon. *Biologia*. 61(19):334-S338.
- Karnok, K. J., and K. A. Tucker. 2001. Wetting agent treated hydrophobic soil and its effect on color, quality and root growth of creeping bentgrass. *International Turfgrass Society Research Journal*. 9:537-541.
- Kern, K., R. David, R. L. Palmer, and G. Cosma. 1986. Complete wetting on ‘strong’ substrates: Xe/Pt (111). *Physical review letters*. 56:2823.
- King, P.M. 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect measurement. *Australian Journal of Soil Research*. 19: 275-285.

- Kostka, S. J. 2000. Amelioration of water repellency in highly managed soils and the enhancement of turfgrass performance through the systematic application of surfactants. *Journal of Hydrology*. 231:359-368.
- Kostka, S.J., J.L. Cisar, S. Mitra, D.M. Park, C.J. Ritsema, L.W. Dekker, and M.A. Franklin. 2007. Irrigation efficiency— Surfactants can save water and help maintain turfgrass quality. *Golf Course Industry* 19:91–95.
- Leinauer, B., P.E. Rieke, D. VanLeeuwen, R. Sallenave, J. Makk, and E. Johnson. 2001. Effects of soil surfactants on water retention in turfgrass rootzones. *International Turfgrass Society Research Journal*. 9:542-547.
- Leinauer, B., and D. Devitt. 2013. Irrigation science and technology. In: B. Horgan, J. Stier, and S. Bonos, editors, *Turfgrass: Biology, use, and management*. Agron. Monogr. 56. ASA, CSSA, and SSSA, Madison, WI. p. 1075–1133.
- Mainwaring, K. A., C. P. Morley, S. H. Doerr, P. Douglas, C. T. Llewellyn, G. Llewellyn, I. Matthews, and B. K. Stein. 2004. Role of heavy polar organic compounds for water repellency of sandy soils. *Environmental Chemistry Letters*. 2:35-39.
- Mitra, S., E. Vis, R. Jumar, R. Plumb, and M. Fam. 2006. Wetting agent and cultural practices increase infiltration and reduce runoff losses of irrigation water. *Biologia*. 61(19):353-357.
- Miyamoto, S. 1985. Effects of wetting agents on water infiltration into poorly wettable sand, dry sod and wettable soils. *Irrig. Sci.* 6:271-279.
- Morris, K. N. 1998. A Guide to NTEP Turfgrass Ratings. National Turfgrass Evaluation Program. <https://www.ntep.org/ntep/reports/ratings.htm> (access 20 February 2019).

- Müller, K., M. Deurer. 2001. Review of the remediation strategies for soil water repellency. *Agriculture, Ecosystems and Environment*. 144:208-221.
- Oostindie, K., L. W. Dekker, J. G. Wesseling, and C. J. Ritsema. 2008. Soil surfactant stops water repellency and preferential flow paths. *Soil Use and Management*. 24:409-415.
- Roper, M. M. 2004. The isolation and characterization of bacteria with the potential to degrade waxes that cause water repellency in sandy soils. *Australia Journal of Soil Research*. 42:427-434.
- Roper, M. M., S. L. Davies, P. S. Blackwell, D. J. M. Hall, D. M. Bakker, R. Jongepier, and P. R. Ward. 2015. Management options for water-repellent soils in Australian dryland agriculture. *Soil Research*. 53:786-806.
- Soldat, D. 2010. Wetting agent research update: Wetting agents in wet conditions. *The Grass Roots*. September/October. 39(5):18-19, 21.
- Song, E., J.G. Schneider, S. H. Anderson, K.W. Goyne, and X. Xiong. 2014. Wetting agent influence on water infiltration into hydrophobic sand: I. Rewettability. *Agronomy Journal*. 106(5):1873-1878.
- Song, E., K.W. Goyne, R.J. Kremer, S.H. Anderson, and X. Xiong. 2018. Surfactant chemistry effects on organic matter removal from water repellent sand. *Soil Sci. Soc. Am. Jour*. 82:1252-1258.
- Throssell C. 2005. GCSAA-USGA wetting agent evaluation. *USGA Turfgrass and Environ. Res. Online* 4 (15). 36 pp.

- Tucker, K. A., K. J. Karnok, D. E. Radcliffe, G. Landry, R. W. Roncadori, and K. H. Tan. 1990. Localized dry spots as a caused by hydrophobic sands on bentgrass greens. *Agronomy Journal*. 82:549-555.
- U.S. Golf Association. 2018. USGA recommendations for a method of putting green construction.
<https://archive.lib.msu.edu/tic/usgamisc/monos/2018recommendationsmethodputtinggreen.pdf> (accessed 12 October 2021).
- Wallis, M. G., and D. J. Horne. 1992. Soil water repellency. In: Stewart, B.A. Ed., *Advances in Soil Science Vol. 20* Springer, New York, pp. 91-146.
- Watson, C.L., and J. Letey. 1970. Indices for characterizing soil-water repellency based upon contact angle-surface tension relationships. *Soil Sci. Soc. Am. Proc.* 34:841-844.
- Wesseling, J.G., C.R. Stoof, C.J. Ritsema, K. Oostindie, L.W. Dekker. 2009. The effect of soil texture and organic amendment on the hydrological behaviour of coarse-textured soils. *Soil Use and Management*. 25:274-283.
- Woche, S. K., M. O. Goebel, M. B. Kirkham, R. Horton, R. R. Van der Ploeg, J. Bachmann. 2005. Contact angle of soils as affected by depth texture and land management. *Eur. J. Soil Sci.* 56:239-251.
- Xiong, X., G. E. Bell, J. B. Solie, M. W. Smith, and B. Martin. 2007. Bermudagrass seasonal responses to nitrogen fertilization and irrigation detected using optical sensing. *Crop Science*. 47(4):1603-1610.
- Zontek, S. J., and S. J. Kostka. 2012. Understanding the different wetting agent chemistries. *USGA Green Section Records*. 50(15):1-6.

Table 3.1. Particle size distribution, porosity, bulk density, particle density, Nutrient composition, organic matter (O.M.), cation exchange capacity (CEC), and level of water repellency (MED) based on King (1981) and Watson and Letey (1970) of 'Penn A-4' and '007' for United States Golf Association (USGA) sand-based putting green specifications.

	Gravel	VCS	CS	MS	FS	VFS	Silt + Clay
	----- mm -----						
	>2.0	2.0-1.0	1.0-0.5	0.5-0.25	0.25-0.10	0.10-0.05	<0.05
	----- % -----						
Penn A-4	1.0	4.7	31.4	54.9	6.8	1.2	0
007	1.1	3.9	25	60.5	8.4	1.1	0

Location	Air-filled porosity [‡]	Capillary porosity	Total porosity	Bulk density	Particle density
	----- v/v, % -----			----- g cm -----	
Penn A-4	24.8	21.6	46.4	1.50	2.60
007	25.4	16.0	41.4	1.57	2.55

Location	Ca [§]	Bray I P	TC	TN	O.M.	CEC	MED
	----- lb/A -----		----- % -----		%	meq 100g	M
Penn A-4	935.3	45.5	0.971	0.097	1.40	2.90	2.0
007	718.0	20.5	0.511	0.057	0.98	2.27	1.7

[†]VCS, CS, MS, FS, and VFS indicate very coarse, coarse, medium, fine, and very fine sand fraction determined by ASTM C 136-96a.

[‡]Air-filled porosity and capillary porosity were determined in the laboratory at -3 kPa soil water pressure.

[§]Ca, Bray I P, TC, and TN correlates to calcium, phosphorus, total carbon, and total nitrogen, respectively.

Table 3.2. Treatments, abbreviations, active ingredients their rates and surface tension (mN m⁻¹) at 1x of the label rate applied to a creeping bentgrass (*Agrostis stolonifera* L.) putting green.

Abbreviation	Treatment	Active Ingredient	Rate (L ha ⁻¹)	Surface Tension (mN m ⁻¹)
AoP	Primer Select	100% - Alkoxylated polyols	19.1	43.5
DE	TriCure AD	100% - Dihydrooxirane, epihydrin	19.1	29.8
NIPA	Aqueduct	50% - Nonionic polyols: 5% - 1,2-Propanediol	25.5	37.9
NIPI	Infiltrix	20% - Nonionic polyols	3.2	44.8
NIS	Capacity	100% - Nonionic surfactant	25.5	29.9
PoP	H ₂ O Maximizer	28% - Carbohydrate surfactant, poloxanlene, poly (2-propenamide)	31.9	29.7
UC	Untreated Control	-----	---	72.8

Table 3.3. Localized dry spot (LDS; %) of an ‘Penn A-4’ creeping bentgrass (*Agrostis stolonifera* L.) putting green as influenced by an interaction between wetting agents applied and days after initial treatment (DAIT).

Trt	----- DAIT -----										
	0 [†]	14	28	42	56	70	84	98	110	124	139
	----- Localized Dry Spot (%) -----										
AoP [‡]	18.8 ab1 [‡]	11.3 bc23	7.5 b2345	6.3 bc3456	8.8 b234	10.0 abc23	5.0 cd456	8.8 bc234	3.8 bc567	2.5 bc67	0.0 b7
DE	16.3 b1	11.3 bc23	6.3 b45	3.8 bcd56	8.8 b34	12.5 ab12	6.3 bc45	6.3 bc45	1.3 c6	2.5 bc56	1.3 b6
NIPA	18.8 ab1	8.8 bc2	1.3 c45	1.3 d45	3.8 c345	6.3 c23	1.3 d45	5.0 c234	1.3 c45	0.0 c5	0.0 b5
NIPI	16.3 b1	12.5 b12	6.3 b345	5.0 bcd45	10.0 ab23	12.5 ab12	10.0 ab23	8.8 bc234	2.5 bc5	5.0 ab45	2.5 b5
NIS	17.5 ab1	7.5 c23	1.3 c5	2.5 cd45	6.3 bc34	11.3 ab2	6.3 bc34	6.3 bc34	3.8 bc345	3.8 bc345	0.0 b5
PoP	21.3 a1	12.5 b2	6.3 b34	7.5 b3	7.5 bc3	8.8 bc23	7.5 bc3	10.0 ab23	6.3 b34	2.5 bc45	0.0 b5
UC	17.5 ab1	17.5 a1	17.5 a1	13.8 a12	13.8 a12	13.8 a12	12.5 a2	13.8 a12	11.3 a2	7.5 a3	10.0 a2

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

[‡]Means in each column labeled by different letters are significantly different based on Fisher’s Protected LSD ($P \leq 0.05$); means in each row labeled by different numbers are significantly different based on Fisher’s Protected LSD ($P \leq 0.05$).

[†]0, 14, 28, 42, 56, 70, 84, 98, 110, 124, 139 DAIT corresponds to May 16, May 30, June 14, June 27, July 11, July 25, August 8, August 22, September 4, September 18, and October 3, 2018.

Table 3.4. Localized dry spot (LDS; %) of a '007' creeping bentgrass (*Agrostis stolonifera* L.) putting green as influenced by an interaction between wetting agents applied and days after initial treatment (DAIT).

Trt	----- DAIT -----										
	0 [¶]	14	28	42	56	70	84	98	110	124	139
	----- Localized Dry Spot (%) -----										
AoP [†]	13.8 b1 [‡]	11.3 b12	6.3 b34	10.0 bc123	12.5 bc12	8.8 d234	12.5 bc12	12.5 bc23	5.0 bc45	1.3 b5	1.3 b5
DE	18.8 a1	13.8 b2	8.8 b34	11.3 bc23	13.8 b2	15.0 bc12	13.8 b2	11.3 bc23	6.3 b4	5.0 b45	1.3 b5
NIPA	17.5 ab1	15.0 b1	5.0 b23	8.8 c2	6.3 d2	8.8 d2	6.3 d2	6.3 c2	1.3 c3	1.3 b3	1.3 b3
NIPI	16.3 ab1	15 b12	7.5 b34	13.8 b12	13.8 b12	16.3 b1	13.8 b12	15.0 ab12	13.8 a12	11.3 a23	6.3 a4
NIS	18.8 a1	13.8 b2	5.0 b456	10.0 bc23	8.8 c34	11.3 cd23	8.8 cd34	7.5 c345	2.5 bc67	3.8 b567	0.0 b7
PoP	16.3 ab1	11.3 b2	6.3 b34	10.0 bc23	11.3 bc2	11.3 cd2	11.3 bc2	6.3 c34	2.5 bc45	2.5 b45	0.0 b5
UC	16.3 ab34	20.0 a23	20.0 a23	23.8 a12	26.3 a1	25.0 a1	18.8 a3	17.5 a3	11.3 a5	12.5 a45	6.3 a6

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

[‡]Means in each column labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

[¶]0, 14, 28, 42, 56, 70, 84, 98, 110, 124, 139 DAIT corresponds to May 16, May 30, June 14, June 27, July 11, July 25, August 8, August 22, September 4, September 18, and October 3, 2018.

Table 3.5. Infiltration rate (m hr^{-1}) into a ‘Penn A-4’ creeping bentgrass (*Agrostis stolonifera* L.) putting green as influenced by wetting agents applied at 0, 1, 2, 3, and 4 months after the initial application. No interaction between treatment and evaluation timing were found.

Treatment	----- Time (month) -----				
	0	1	2	3	4
	----- Infiltration rate (m hr^{-1}) -----				
AoP [†]	0.81	0.96	0.66	0.69	0.58
DE	0.86	0.83	0.50	0.39	0.72
NIPA	0.85	1.08	0.54	0.65	0.45
NIPI	0.78	0.76	0.67	0.63	0.77
NIS	0.82	1.01	0.59	0.49	0.50
PoP	0.85	0.96	0.55	0.68	0.82
UC	0.83	0.72	0.54	0.63	0.77

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

Table 3.6. Infiltration rate (m hr^{-1}) into a '007' creeping bentgrass (*Agrostis stolonifera* L.) putting green as influenced by wetting agents applied at 0, 1, 2, 3, and 4 months after the initial application.

Treatment	----- Time (month) -----				
	0	1	2	3	4
	----- Infiltration rate (m hr^{-1}) -----				
AoP [†]	1.23 a1 [‡]	1.31 a1	0.87 a2	0.90 a2	0.84 bc2
DE	1.4 a1	1.17 ab12	1.06 a23	0.99 a23	0.78 bc3
NIPA	0.90 b2	1.38 a1	1.09 a12	0.85 a23	0.57 c3
NIPI	1.25 a1	1.15 ab1	0.81 a2	0.82 a2	0.76 bc2
NIS	1.16 ab1	0.95 b1	0.91 a1	0.94 a1	0.93 b1
PoP	1.14 ab1	0.95 b12	0.91 a12	0.72 a2	0.71 bc2
UC	1.43 a1	1.33 a1	0.90 a2	0.71 a2	1.32 a1

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

[‡]Means in each column labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 3.7. Turfgrass quality (1-9 scale) of a ‘007’ creeping bentgrass (*Agrostis stolonifera* L.) putting green as influenced by an interaction between wetting agents applied and days after initial treatment (DAIT).

Trt	----- DAIT -----										
	0 [†]	14	28	42	56	70	84	98	110	124	139
	----- Turfgrass quality (1-9 scale) -----										
AoP [‡]	6.5 a4 [‡]	6.8 a4	7.8 a12	7.5 a23	7.0 a34	7.5 a23	7.5 bc23	7.5 ab23	8.3 a1	8.3 a1	8.3 b1
DE	6.3 a4	6.5 a34	7.0 bc3	7.0 ab3	7.0 a3	6.8 bc34	7.0 c3	7.8 ab2	8.0 ab12	8.0 ab12	8.5 b1
NIPA	6.5 a4	7.0 a34	7.5 ab23	7.5 a23	7.3 a3	7.5 a23	8.5 a1	8.0 a12	8.3 a1	8.5 a1	8.5 ab1
NIPI	6.3 a5	6.5 a45	6.8 c345	6.8 bc345	6.3 b5	6.3 c5	7.5 bc12	7.3 bc23	7.0 c234	7.3 c23	8.0 b1
NIS	6.3 a8	7.0 a67	7.5 ab456	7.3 ab567	6.8 ab78	7.3 ab567	8.3 a23	7.8 ab345	8.5 a12	8.0 ab234	9.0 a1
PoP	6.3 a4	6.5 a34	7.0 bc23	7.3 ab2	7.0 a23	7.0 ab23	8.0 ab1	8.0 a1	8.0 ab1	8.0 ab1	8.3 b1
UC	6.3 a4	6.5 a34	6.8 c34	6.3 c4	6.3 b4	6.3 c4	7.0 c23	6.8 c34	7.5 bc12	7.5 bc12	8.0 b1

[†]NIPA, Nonionic polyols, Aqueduct; NIS, Nonionic surfactant, Capacity; PoP, Carbohydrate surfactant, poloxanlene, poly, H₂O Maximizer; NIPI, Nonionic polyols, Infiltrix; AoP, Alkoxylated polyols, Primer Select; DE, Dihydrooxirane, epihydrin, TriCure AD; UC, untreated control.

[‡]Means in each column labeled by different letters are significantly different based on Fisher’s Protected LSD ($P \leq 0.05$); means in each row labeled by different numbers are significantly different based on Fisher’s Protected LSD ($P \leq 0.05$).

[†]0, 14, 28, 42, 56, 70, 84, 98, 110, 124, 139 DAIT corresponds to May 16, May 30, June 14, June 27, July 11, July 25, August 8, August 22, September 4, September 18, and October 3, 2018.

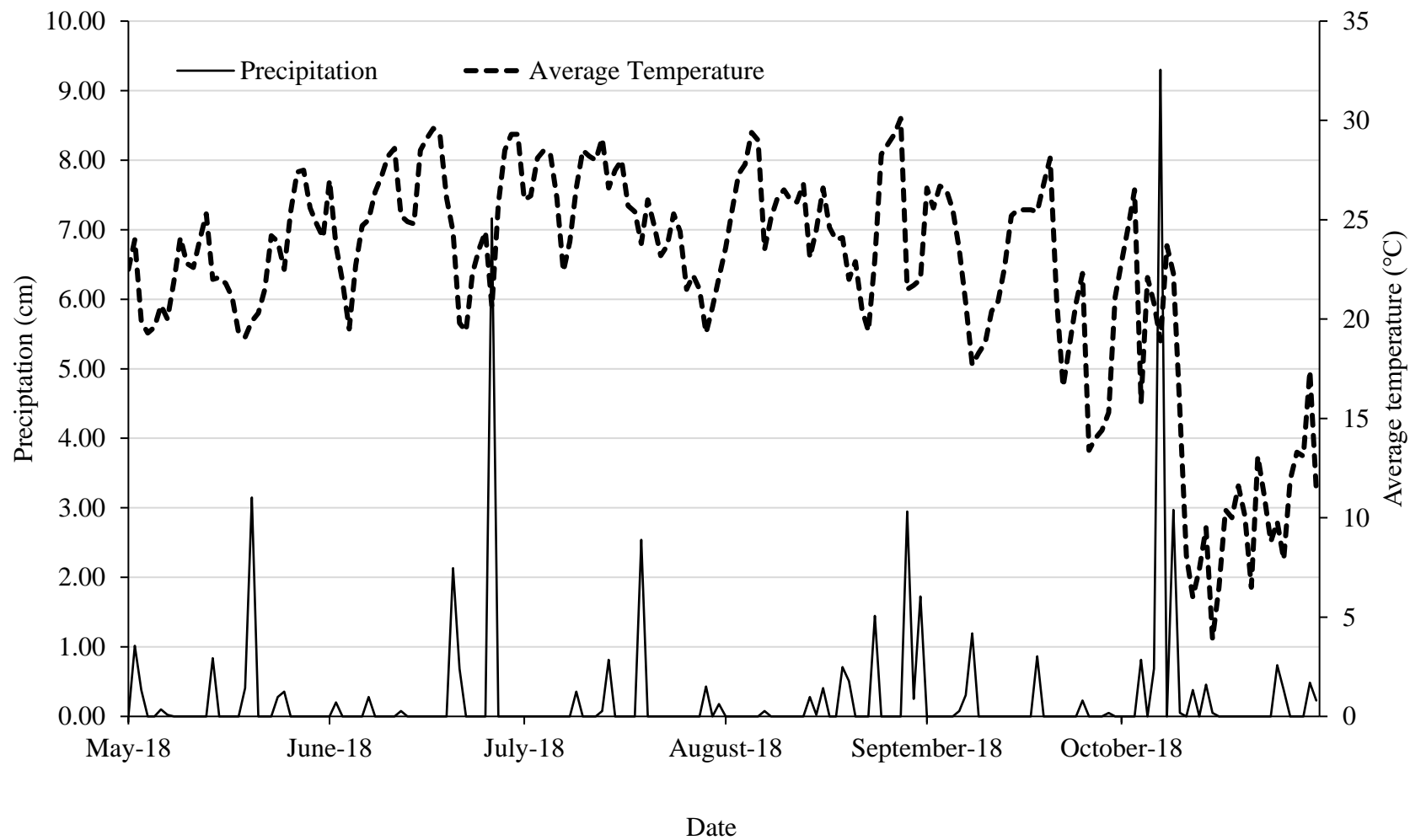


Figure 3.1. Daily precipitation (cm) and average air temperature (°C) during the experimental period from May 2018 to October 2018.

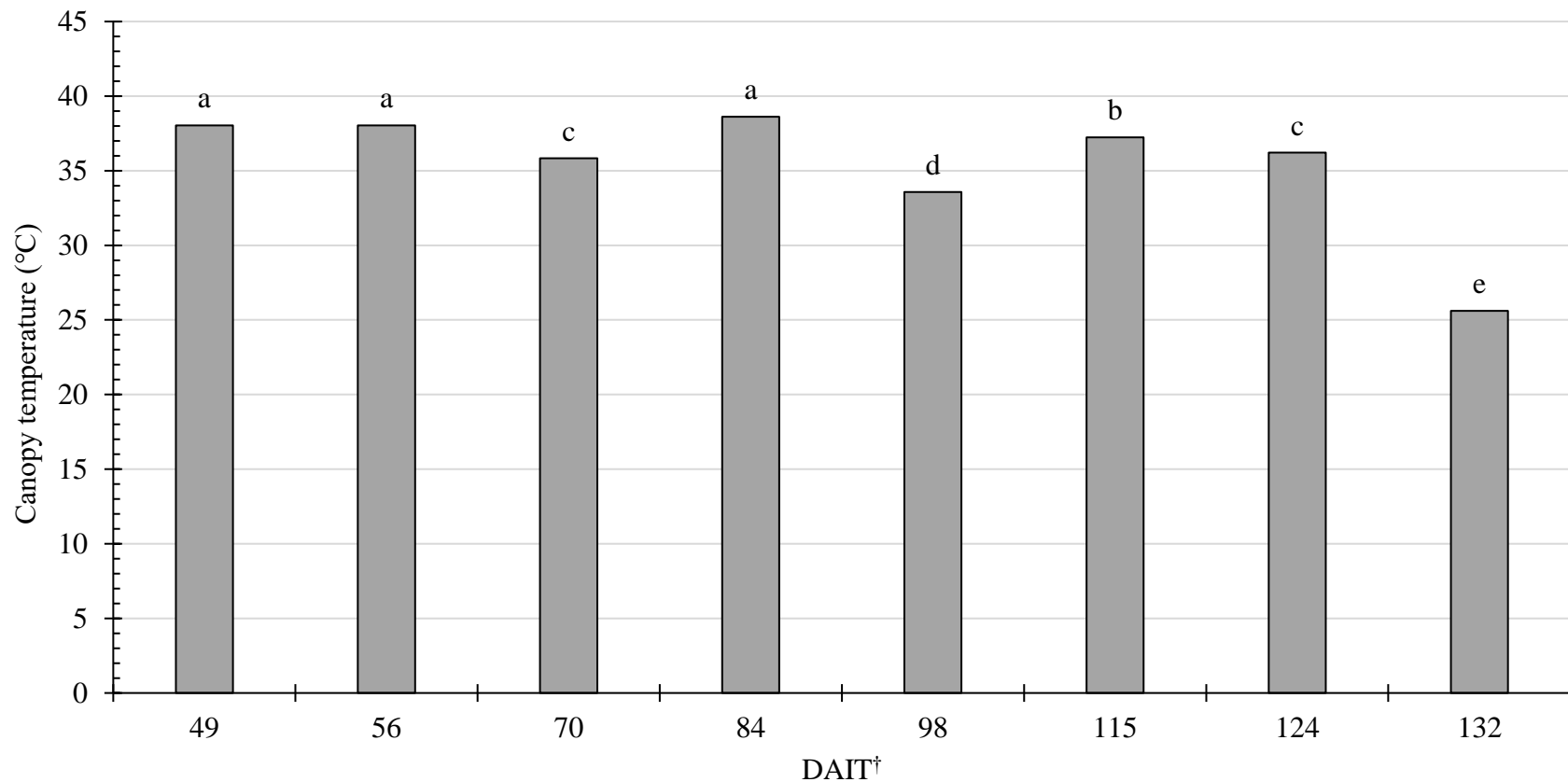


Figure 3.2. Canopy temperature (°C) of ‘Penn A-4’ creeping bentgrass (*Agrostis stolonifera* L.) putting green at 49, 56, 70, 84, 98, 115, 124, and 132 days after initial treatment (DAIT) determined by a forward looking infrared (FLIR) thermal camera (FLIR Systems, Inc., Wilsonville, OR). Bars labeled with different letters are significantly different based on Fisher’s Protected LSD at $P \leq 0.05$.

[†]49, 56, 70, 84, 98, 115, 124, 132 DAIT corresponds to July 4, July 11, July 25, August 8, August 22, September 9, September 18, September 29, 2018.

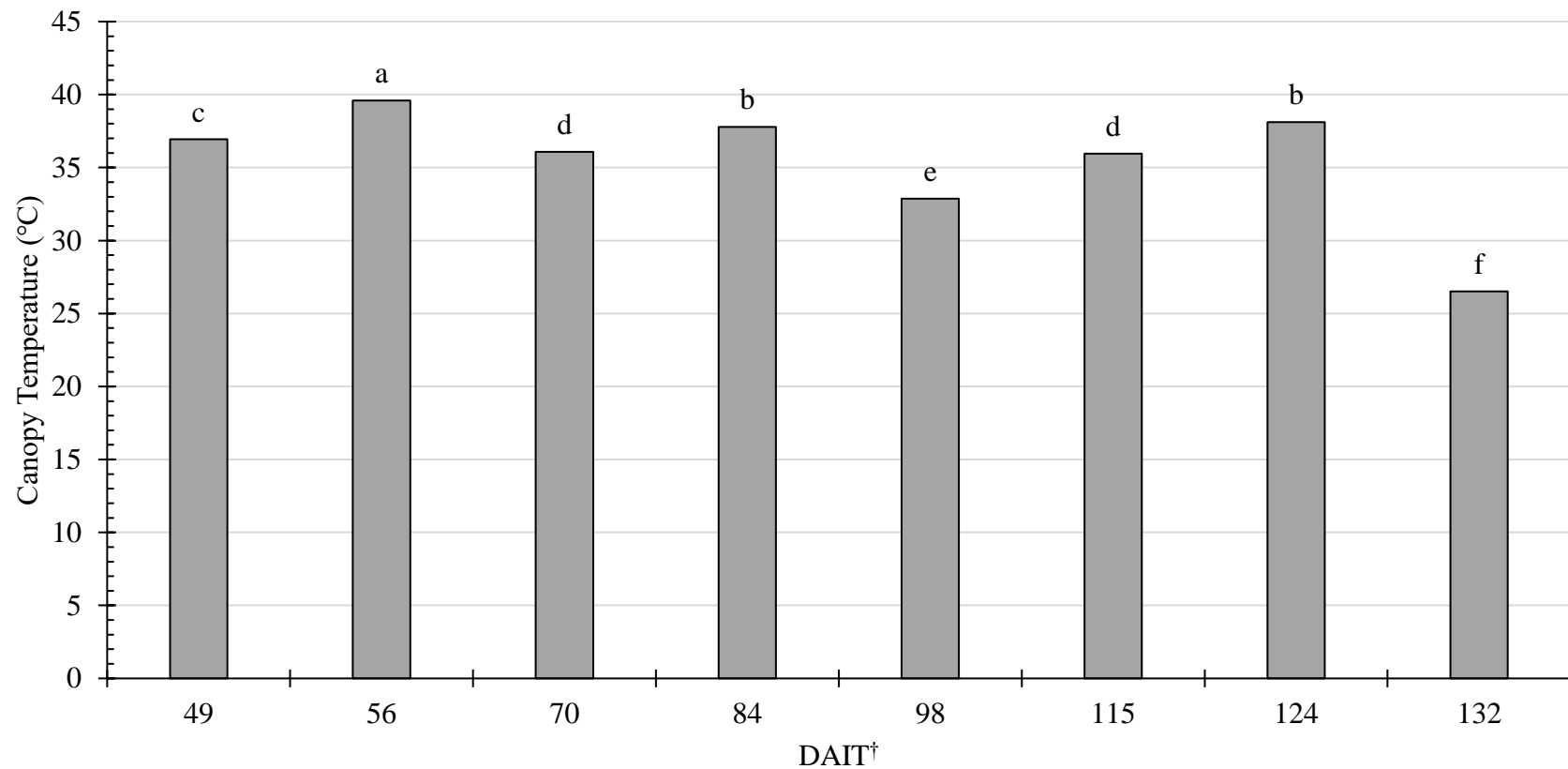


Figure 3.3. Canopy temperature (°C) of '007' creeping bentgrass (*Agrostis stolonifera* L.) putting green at 49, 56, 70, 84, 98, 115, 124, and 132 days after initial treatment (DAIT) determined by a forward looking infrared (FLIR) thermal camera (FLIR Systems, Inc., Wilsonville, OR). Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P \leq 0.05$.

[†]49, 56, 70, 84, 98, 115, 124, 132 DAIT corresponds to July 4, July 11, July 25, August 8, August 22, September 9, September 18, September 29, 2018.

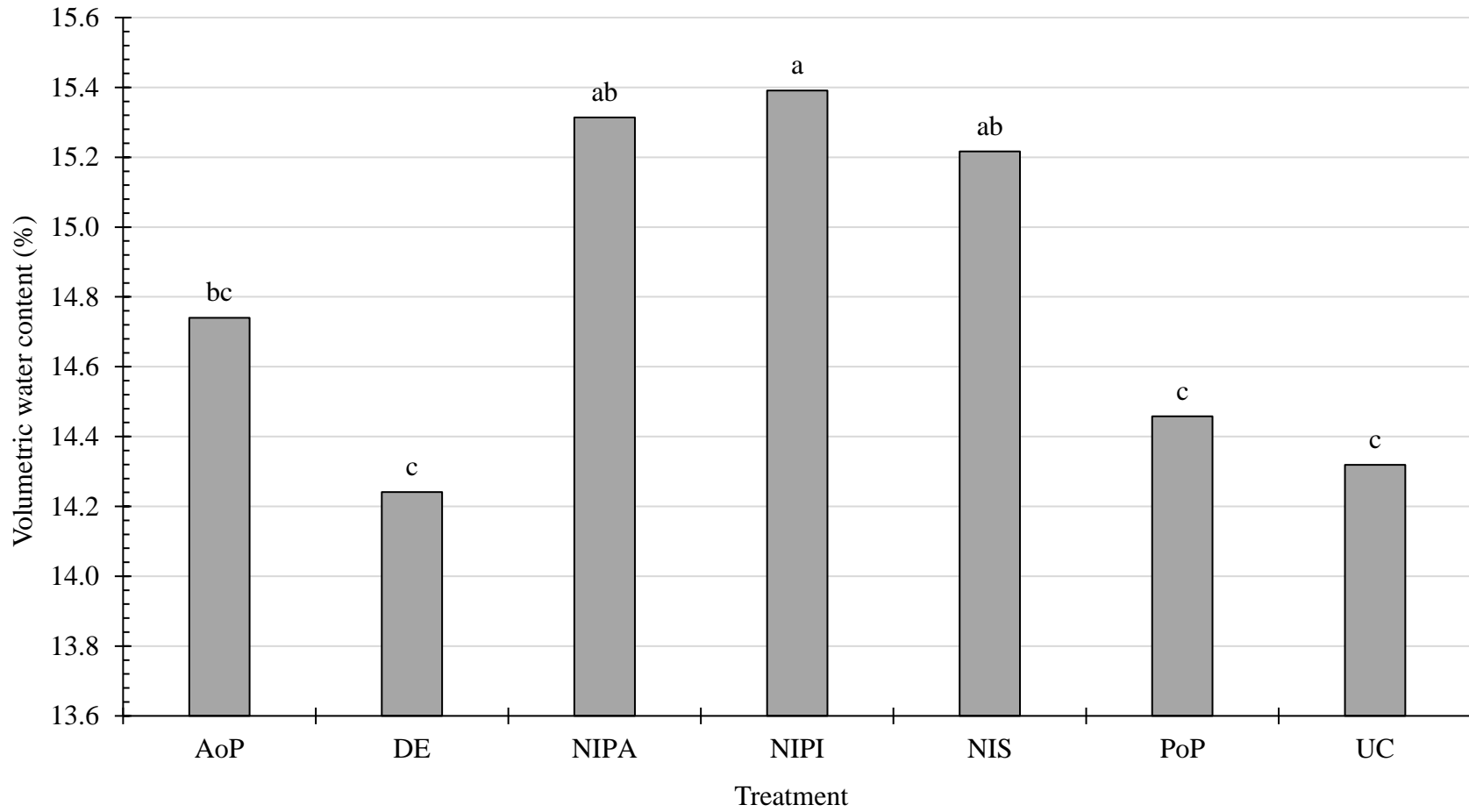


Figure 3.4. Volumetric water content (VWC; %) of a 'Penn A-4' creeping bentgrass (*Agrostis stolonifera* L.) as influenced by wetting agents applied. No interaction between treatment and evaluation timing were found; hence, data were pooled over time. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P \leq 0.05$.

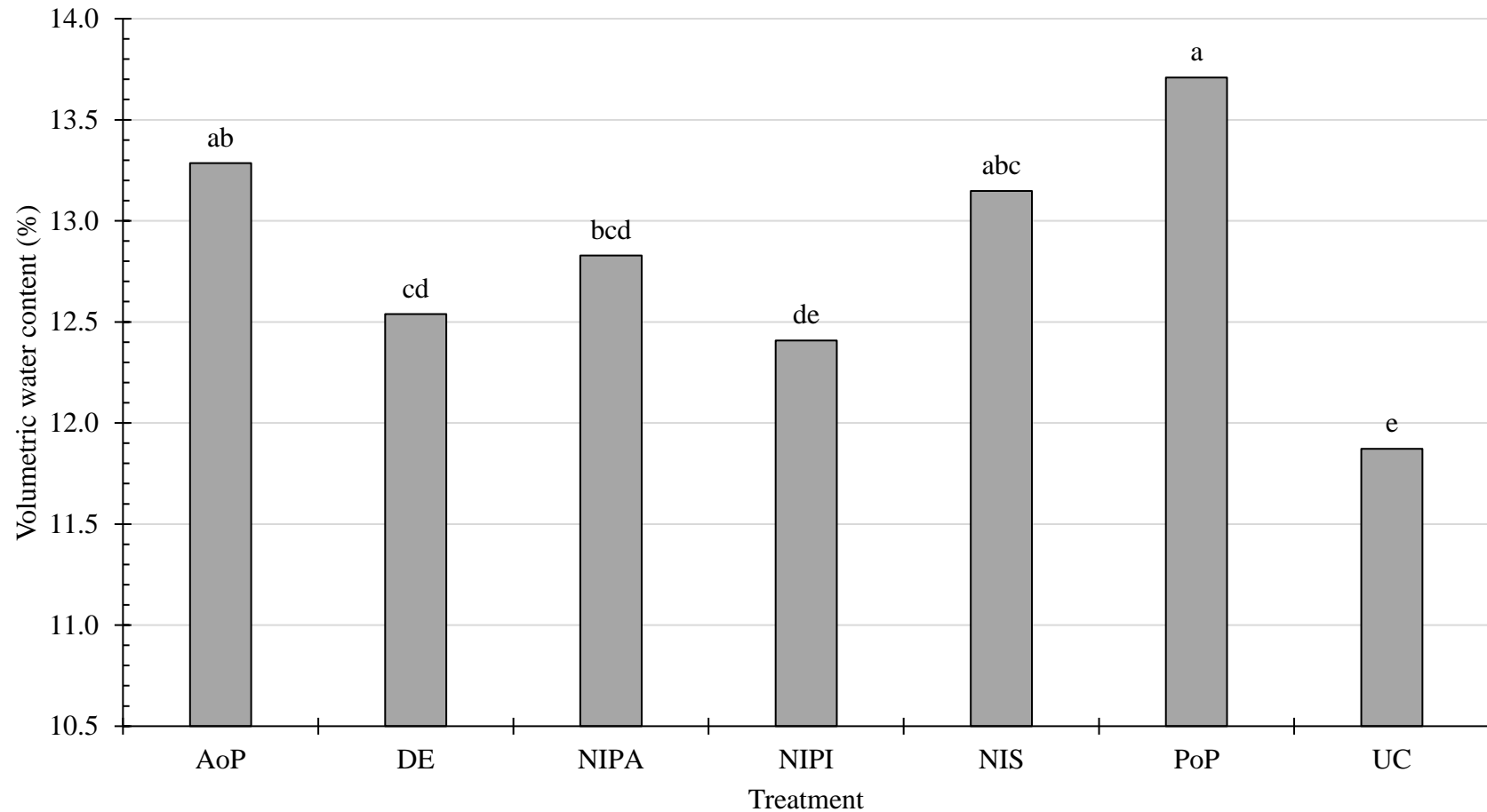


Figure 3.5. Volumetric water content (VWC; %) of a '007' creeping bentgrass (*Agrostis stolonifera* L.) as influenced by wetting agents applied. No interaction between treatment and evaluation timing were found; hence, data were pooled over time. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P \leq 0.05$.

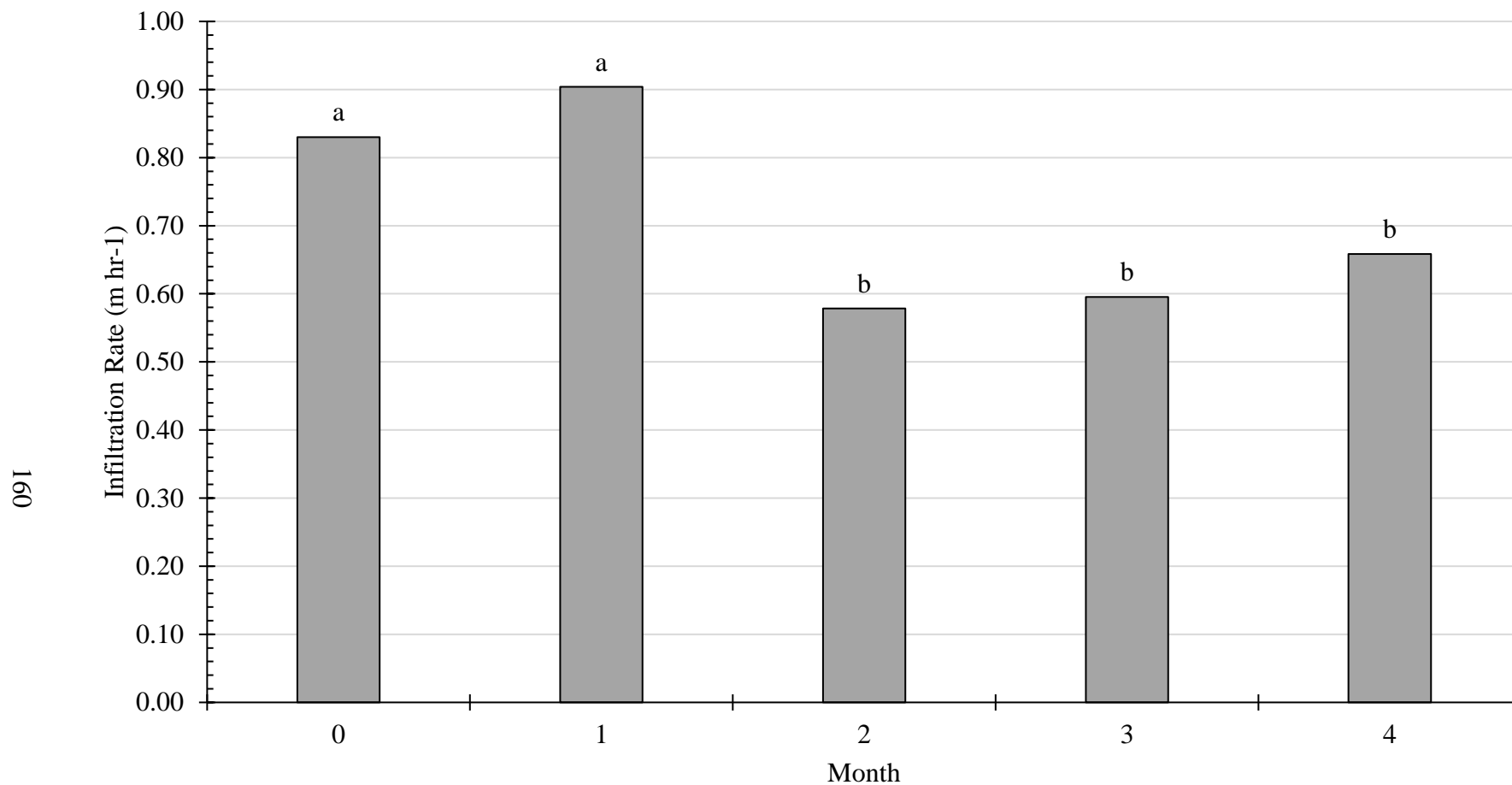


Figure 3.6. Infiltration rate (m hr⁻¹) into an 'Penn A-4' creeping bentgrass (*Agrostis stolonifera* L.) putting green at 0, 1, 2, 3, and 4 months. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P \leq 0.05$.

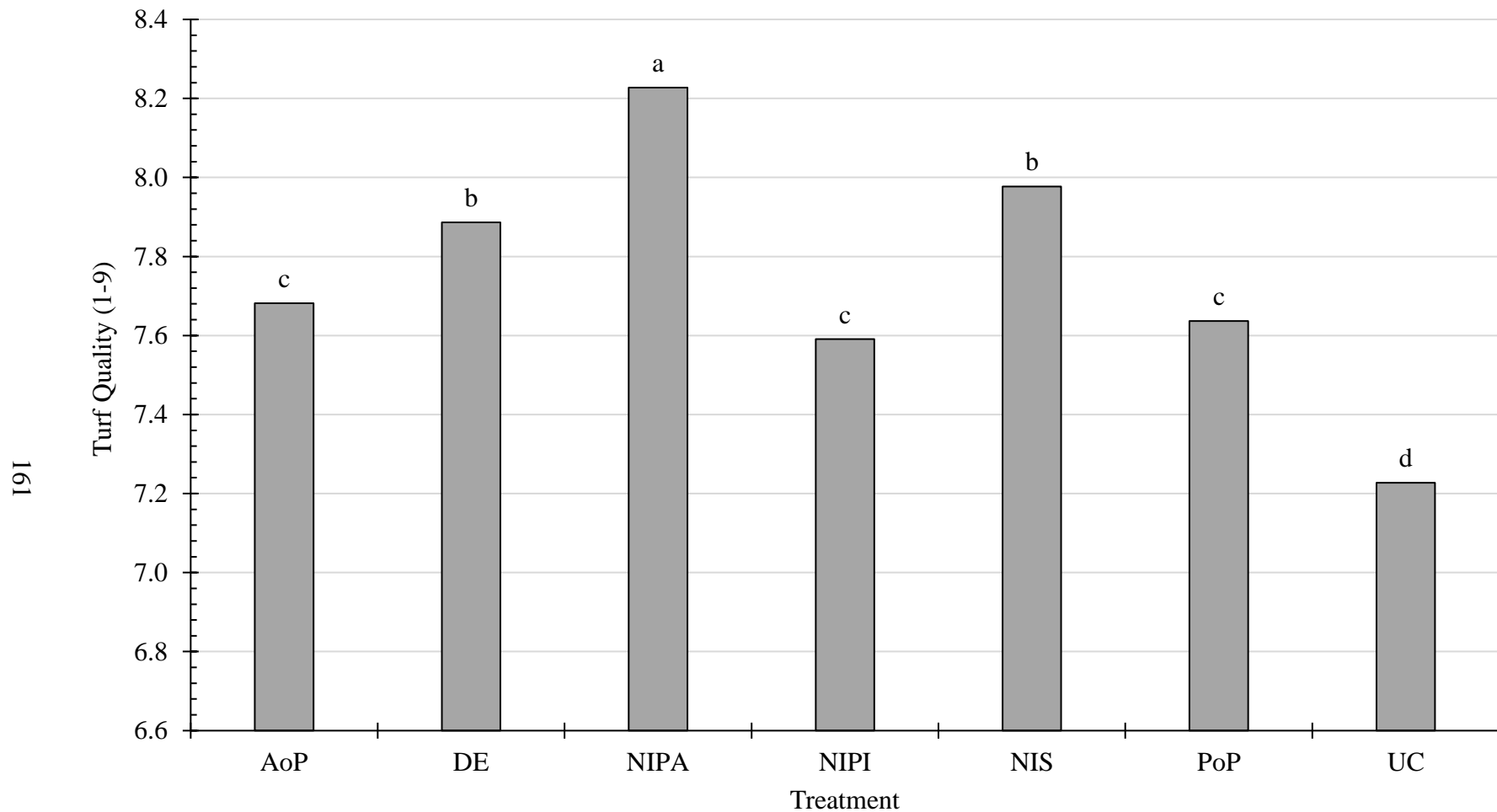


Figure 3.7. Visual assessment of turf quality (1-9) on a ‘Penn A-4’ creeping bentgrass (*Agrostis stolonifera* L.) putting green as influenced by wetting agents applied. No interaction between treatment and evaluation timing were found; hence, data were pooled over time. Bars labeled with a different letter are significantly different based on Fisher’s Protected LSD at $P \leq 0.05$.

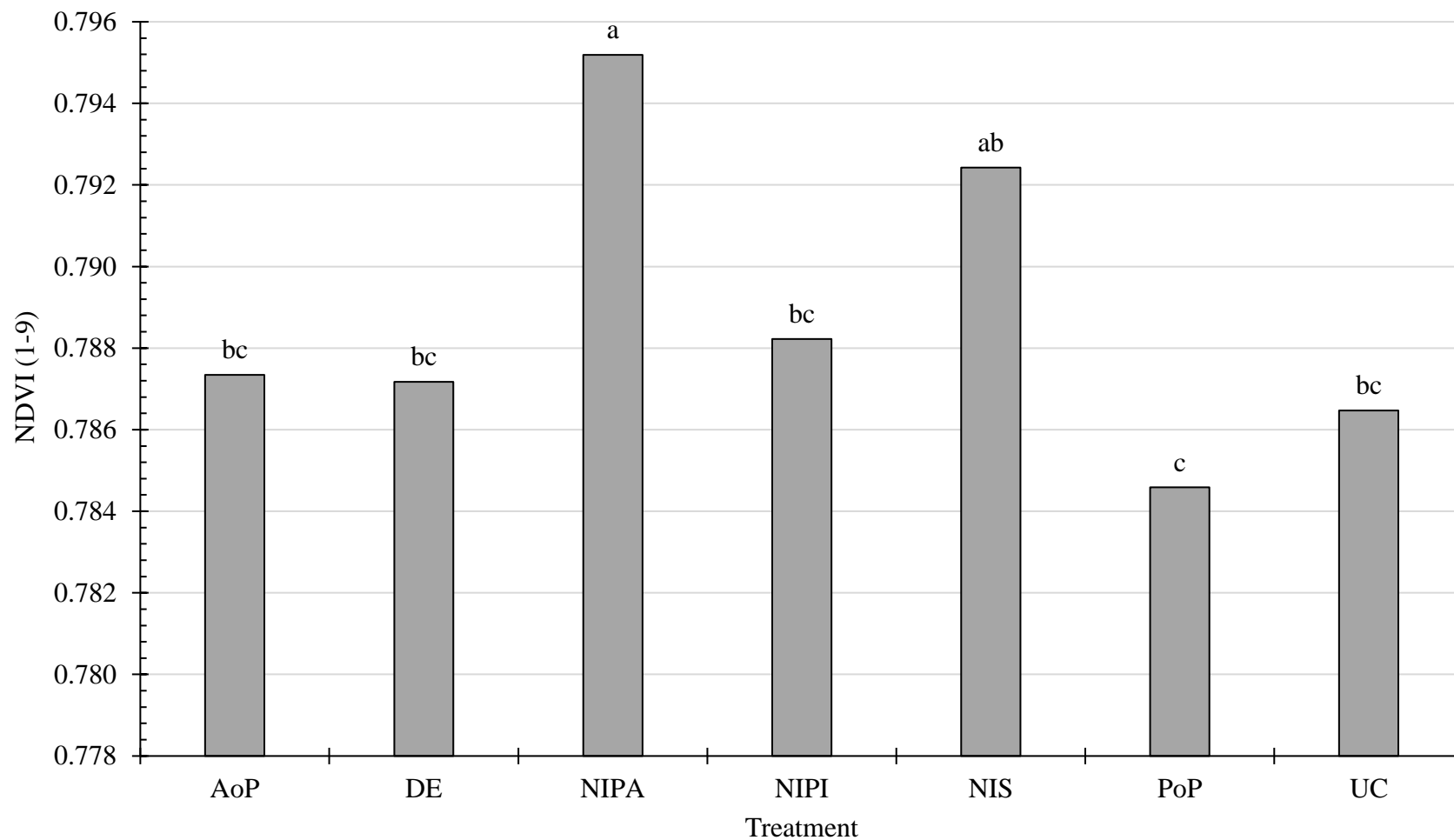


Figure 3.8. Normalized difference vegetation index (NDVI) of a ‘Penn A-4’ creeping bentgrass (*Agrostis stolonifera* L.) as influenced by wetting agents applied. No interaction between treatment and evaluation timing were found; hence, data were pooled over time. Bars labeled with different letters are significantly different based on Fisher’s Protected LSD at $P \leq 0.05$.

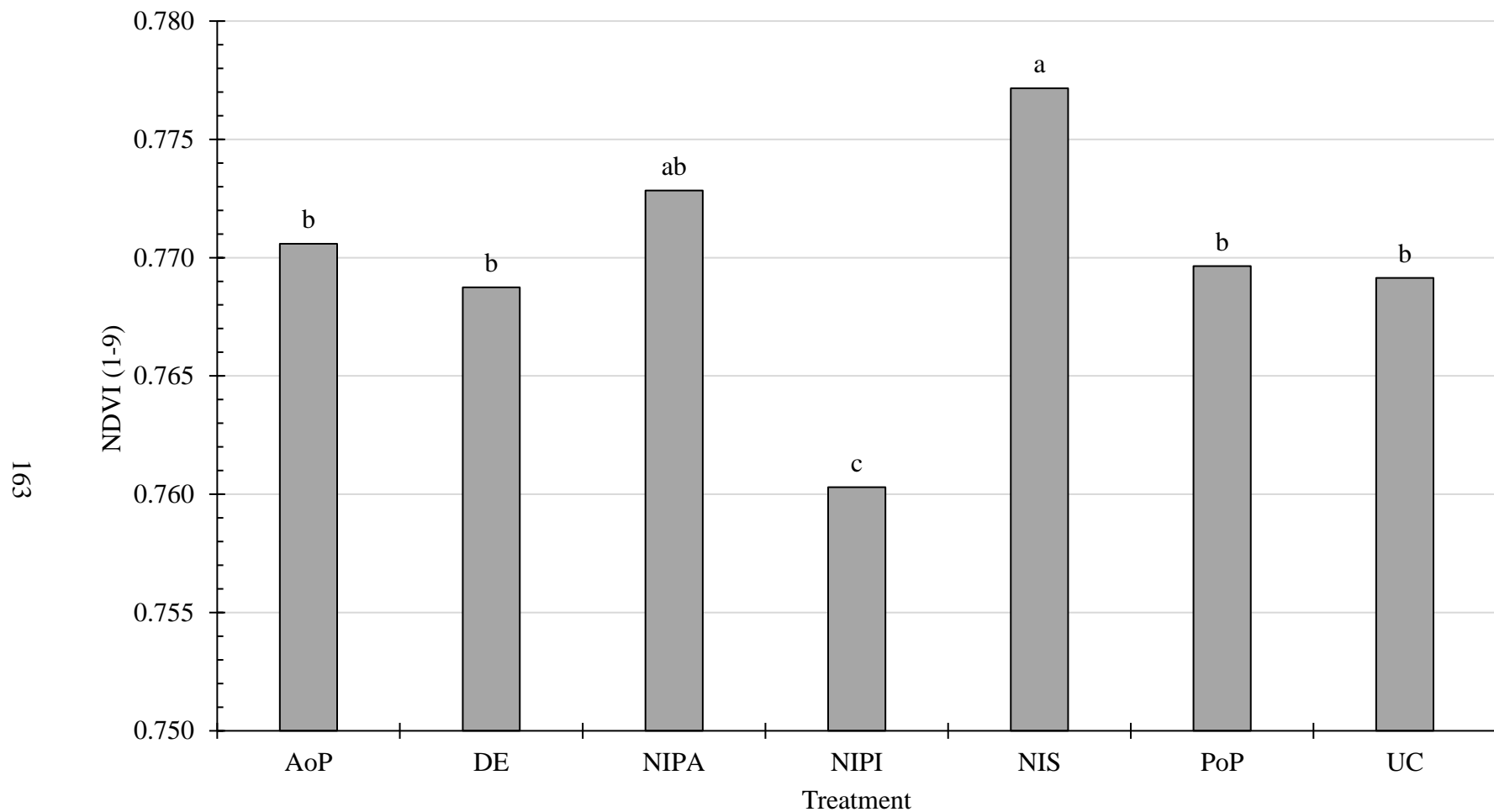


Figure 3.9. Normalized difference vegetation index (NDVI) of a '007' creeping bentgrass (*Agrostis stolonifera* L.) as influenced by wetting agents applied. No interaction between treatment and evaluation timing were found; hence, data were pooled over time. Bars labeled with different letters are significantly different based on Fisher's Protected LSD at $P \leq 0.05$.

Supplementary Table 3.1. Active ingredient, brand name, rate (L ha⁻¹), application timing and manufacture information of fungicides applied during the study on a creeping bentgrass (*Agrostis stolonifera* L.) putting green.

Chemical name	Brand name	Rate (L ha ⁻¹)	Application Timing	Manufacture
Azoxystrobin Difenoconazole	Briskway	2.3	14-May, 22-Jun	Syngenta, Greensboro, NC
Chlorothalonil	Daconil	17.5	14-May	Syngenta, Greensboro, NC
Iprodione Trifloxystrobin	Interface	12.7	1-Jun, 5-Oct	Bayer, Research Triangle Park, NC
Mefenoxam	Subdue Maxx	2.4	22-Jun, 25-Jul	Syngenta, Greensboro, NC
Propiconazole	Banner Maxx	4.8	25-Jul	Syngenta, Greensboro, NC
Azoxystrobin	Heritage	1.3	11-Jul, 13-Aug	Syngenta, Greensboro, NC
Boscalid	Emerald	0.6	11-Jul, 13-Aug	BASF, Research Triangle Park, NC
Penthiopyrad	Velista	1.6	22-Aug	Syngenta, Greensboro, NC

CHAPTER IV

Reduction of Bromide Soil Tracer Leaching and Increased Water Retention through Hydrophobic Sands due to Wetting Agent Application

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Abstract

The movement of water and nutrients in hydrophobic soils has been widely studied, as the formation of preferential flow pathways causes dramatic reductions in their availability. United States Golf Association (USGA) putting greens are prone to development of soil water repellency (SWR). Wetting agents are widely utilized to overcome SWR and aid in the retention or infiltration of water. To assess water and nutrient movement in water repellent soils, scientists have commonly utilized soil water tracers, such as bromide (Br^-) for their ease of detection and mobility in water. Studies that utilize soil tracers to assess the movement of water in wetting agent treated hydrophobic soils are limited. Hence, the objective of this study was to determine the movement of a Br^- tracer, at various depths, in wetting agent and non-wetting agent treated hydrophobic soils after multiple irrigation events. The three wetting agents selected demonstrated the ability to retain at least 317-fold the amount of Br^- in the hydrophobic soil as compared to treatment with water alone. Additionally, wetting agent application was able to increase the volumetric water content (VWC) in the hydrophobic sand columns after each irrigation event, compared to the application of water alone. Demonstrating the ability of wetting agents to increase water retention and reduce

leaching of potential nutrients and agrochemicals through a hydrophobic sand-based rootzone.

Abbreviations and key words: Br⁻, bromide; hydrophobicity; infiltration; leaching; preferential flow; USGA, United States Golf Association; SWR, soil water repellency; water retention; wetting agent; VWC, volumetric water content

Introduction

Throughout the world, all soil types can develop soil water repellency (SWR), but sandy soils are particularly prone (Dekker et al., 2005a; Tucker et al., 1990; Wallis and Horne, 1992). SWR is a condition in which a soil does not spontaneously wet after a drop of water is placed on the surface (Feng et al., 2002). When SWR conditions develop, it can affect a soil's effective water infiltration, retention or evaporation (DeBano, 1971; Letey et al., 1962a; Wang et al., 2000). Sand-based soils are more prone to developing SWR due to the small specific surface area of sand particles (Karnok and Tucker, 1989; Larsbo et al., 2008; Song et al., 2014a); As, United States Golf Association (USGA) putting greens are sand-based, they often develop SWR (Karnok and Tucker, 2001). When SWR is present in sand-based putting greens, rapid transport of water and solutes occurs through a small portion of the soil volume, creating an uneven wetting front and bypassing a majority of the unsaturated soil (Brown et al., 2000; Ritsema and Dekker, 1997; Wessolek et al., 2009). Preferential flow leads to an increased risk of pesticide and nutrient leaching from the soil profile into the ground water, causing a decrease in the efficacy of the amendments applied (Harris et al., 1994; Hendriks et al., 1999; Ritsema and Dekker, 2000).

To alleviate SWR within these sand-based root zones, a type of surface-active agent (surfactant) denoted as wetting agents, are utilized by 94% of golf course superintendents in the United States (Karnok and Tucker, 1989; Karnok, 2006; Kostka, 2000). Wetting agents are amphiphilic molecules that will adhere the hydrophobic, or nonpolar, portion of the molecule to the hydrophobic materials coating the sand particle surface, allowing the hydrophilic, or polar, portion of the molecule to protrude into the soil pore and attract water molecules to the soil surface (Müller and Deurer, 2011; Song

et al., 2014a). The application of wetting agents alters the hydrophobic surface and transforms the once water-repellent soil into a wettable growing media (Cisar et al., 2000; Dekker et al., 2005b; Karnok et al., 2004; Kostka, 2000; Song et al., 2014a). The functionality of wetting agents in water repellent soils has been disputed based on conflicting results, as some studies report increases or decreases regarding either water retention or water infiltration (Blodgett et al., 1993; Leinauer et al., 2001; Ruemmele and Amador, 1998; Wiecko and Carrow, 1992).

Previous studies have been conducted to evaluate water and solute movement through water repellent soils utilizing soil-water tracers, but a minimal number of studies have been conducted utilizing soil-water tracers to analyze the effect of wetting agents on water movement in water repellent soils (Clothier et al., 2000; Levy and Chamber, 1987; Ritsema and Dekker, 1998; Wang et al., 2008). Tracers have been widely utilized to determine water and nutrient movement through soils (Bowman, 1984; Davis et al., 1980; Patra and Rego, 1994). To effectively use soil water tracers, the tracers should not be significantly sorbed by the soil being evaluated, should not be commonly found in the soil, should be mobile in water and should not significantly degrade over the course of the experiment (Bowman, 1984; Davis et al., 1980; Levy and Chambers, 1987). Two of the most popular ions utilized in soil studies are chloride (Cl^-) and bromide (Br^-) due to their low cost, ease of detection and low sorption to soil particles (Davis et al., 1980; Levy and Chambers, 1987). However, due to naturally abundant concentrations of Cl^- in soil-water, it is not as suitable as Br^- (Bowman, 1984; Ahuja and Lehman, 1983; Germann et al., 1984; Levy and Chambers, 1987). Another benefit of utilizing Br^- is the similarity in charge and behavior to nitrate (NO_3^-) movement in soil and soil-water,

which is a major nutrient source for plants (Crawford, 1995; Geng et al., 2014; Patra and Rego, 1994). As USGA sand-based greens are prone to leaching, especially when SWR develops, the influence of wetting agents for their effect on water retention and leaching become crucial. To measure a wetting agent's effect on water movement, the water-soluble tracer potassium bromide (KBr) was chosen as it is commonly utilized in soil science studies to quantify water and nutrient movement through the hydrophobic sand column (Bowman, 1984; Clothier et al., 2000; Davis et al., 1980; Levy and Chambers, 1987; Patra and Rego, 1994). Therefore, the objective of this study was to utilize a water mobile soil tracer, KBr, to evaluate the influence of various wetting agents on water and Br⁻ movement through a water-repellent sand column, as it could indicate the potential effect wetting agents have on the reduction of leaching into ground waters.

Materials and Methods

In a laboratory study, three wetting agents were chosen based on their varying surface tensions (γ), with the control being water only. The wetting agents selected were: AE (Cascade Plus; 10% alcohol ethoxylates and 90% polyethylene-polypropylene glycol-block copolymer Precision Laboratories, Waukegan, IL) at a γ of 29.9 mN m⁻¹, MAP (Revolution; 100% modified alkylated polyols; Aquatrols, Paulsboro, NJ) at a γ of 36.9 mN m⁻¹, and AoP (Primer Select; 100% alkoxyated polyols; Aquatrols, Paulsboro, NJ) at a γ of 43.5 mN m⁻¹, representing the low, medium and high γ wetting agents, respectively, and water alone. Based on their label rate, all three wetting agents were applied at 177.44 mL in 9092.18 mL of water to cover 92.9 m².

Washed silica sand meeting the USGA specifications for putting green construction was utilized to create an artificial hydrophobic sand (AHS) (U.S. Golf Association, 2004; Song et al., 2014a). Utilizing the methods described by Bauters et al.

(1998), Bradford and Leij (1996), and Song et al. (2014a) the AHS was created by mixing 60 kg of sand with 4.6 g octadecylamine (Sigma-Aldrich, St. Louis, MO) in 18 L of tap water in a concrete mixer. The sand was mixed for 24 h and then dried in an oven at 75°C for 36 h. Once dry, the sand was rinsed three times with tap water to remove excess octadecylamine and dried again at 75°C for 36 h. After the second drying, the AHS was thoroughly mixed and stored in a sealed plastic container to eliminate potential changes in water repellency. The AHS was tested for hydrophobicity by the molarity of ethanol droplet (MED) test when the sand was packed to a bulk density (D_b) of 1.6 g cm⁻³ (Doerr, 1998; King, 1981; Roy and McGill, 2002; Watson and Letey, 1970). The AHS resulted in a MED value of 2.4, which is classified as moderately hydrophobic (King, 1981). This level of hydrophobicity was chosen based on putting green sand samples collected from various golf courses around Columbia, MO, where their hydrophobicity values ranged from 1.8 to 3.3 MED. In addition to the MED test to confirm the treated sands' hydrophobicity, tap water droplets were applied to confirm the non-penetration into the sand and, eventual evaporation from the sand surface. Particle distribution of the sands was determined to be 8.3% very coarse sand, 38.6% coarse sand, 47.3% medium sand, 4.8% fine sand and 1.0% very fine sand. Total porosity was determined to be 38.2%, with 23.2% being air-filled pores at a bulk density of 1.6 g cm⁻³ (Nimmo, 2004).

Following the procedure established by Song et al., (2014a) with modifications, Harvel Clear PVC tubes (Georg Fischer Harvel LLC, Easton, PA) with an inner diameter of 5.08 cm and a wall thickness of 0.48 cm, were used to build infiltration columns. PVC tubes were cut into 6.35 cm sections and a Stainless-Steel Woven Wire 200 Mesh (Edward J Darby & Son Inc, Philadelphia, PA) was adhered to the bottom of the

columns, to prevent any sand from passing through. The interior of the column walls were treated with Teflon Non-Stick Dry-Film Lubricant (DuPont, Wilmington, DE) to prevent preferential flow from occurring. Each PVC tube section was filled with 210.0 g of AHS, to achieve a D_b of 1.62 g cm^{-3} . Four column sections were attached together using 5.08 cm diameter no-hub rubber couplers which were 5.08 cm in length (Fernco Inc., Davison, MI), to create a 25.4 cm total column length. The column sections were tapped multiple times on a benchtop to ensure a consistent packing and D_b throughout the various column sections. Based on the porosity, the total pore volume of the 25.4 cm column was 196.7 mL. The various column sections were utilized to simulate depth in the sand-based rootzone, which is recommended to be 30.48 cm for USGA putting green rootzones (U.S. Golf Association, 2004). Each column section represents various depths in the profile to understand how the wetting agent treatment would influence water and Br^- tracer movement through the artificial hydrophobic soil.

After assembly, columns were suspended above 7 cm inner mouth diameter funnels, with a 0.5 cm inner stem diameter, that were inserted into 125 mL No. 6 flasks (Pyrex, Corning, NY) using a No. 6 rubber stopper with a hole in the middle for the funnel stem. This allowed for the seepage to be collected after application of water. To determine treatment effect on water movement over time, various infiltration events were applied over 1, 2, 3, 4 or 5 days after treatment application (DAT) to AHS columns. Each wetting agent solution was applied at 5 mL to the surface layer of the AHS columns utilizing a 55 mL mini mister spray bottles (Jastella, Hacienda Heights, CA), to simulate the spray application made to USGA putting greens. Untreated control columns received 5 mL of deionized (DI) water instead. The greater than 99.5% pure KBr (Sigma-Aldrich,

St. Louis, MO) was mixed at a rate of 3000 mg Br⁻ L⁻¹, based on previous studies (Clothier et al., 2000; Davis et al., 1980; McLead et al., 2001).

Wetting agent treatment was sprayed on their respective columns and then watered in using 100 mL KBr solution with a squeeze bottle at 1 DAT. Starting at 2 DAT and through 5 DAT, only 100 mL of DI water was applied each day. The KBr solution or DI water was applied to the columns at 25 mL or 1.22 cm ponding head (h_p) depth and allowed to recede into the column before applying the remaining solution, which would simulate irrigation from a sprinkler head on a USGA putting green. The solution or DI water was allowed to infiltrate and move through the column for 24 h before the next watering event was applied or the column was broken down to evaluate water and Br⁻ movement. Leachate seepage was collected prior to the next watering event and stored at 22°C in seal tight bottles to be later analyzed for leachate volume and Br⁻ concentration.

Treated columns were then destructively sampled at 1, 2, 3, 4, or 5 DAT. Columns were carefully disassembled and each column section was weighed to determine volumetric water content (VWC) after drying at 105°C for 48 h. After column sections were dried, the Br⁻ was extracted from the sand using modified methods established by Abdalla and Lear (1975) and Patra and Rego (1994). Each section of sand was transferred into 946 mL wide mouth mason jars (Ball, Broomfield, CO) and 150 mL of DI water and 2% or 3 mL of 5 M NaNO₃ Halide Ion Strengthen (Hanna Instruments, Woonsocket, RI) was added to the sand and vigorously shaken on a shaker table for 30 min. After the jars were shaken, the filtrate was extracted and stored in 100 mL bottles (Nalgene, Rochester, NY) and allowed to settle overnight to analyze for Br⁻ concentration. The following day the filtrate was collected and stored, then 40 mL of

filtrate was transferred into 50 mL centrifuge tubes (Thermo Fisher Scientific, Waltham, MA) and 0.5 mL of H₂O₂ (30% w/w) (Thermo Fisher Scientific, Waltham, MA) was added. Centrifuge tubes were submerged in a water bath at 85°C for 10 min. Once completed, the centrifuge tubes were taken out of the bath and allowed to cool to 23.5°C prior to measuring Br⁻ concentration.

Leachate Br⁻ extraction underwent a similar procedure to determine Br⁻ concentration. Depending on the leachate volume, a maximum of 40 mL of leachate was extracted and transferred into 50 mL centrifuge tubes, then 0.5 mL H₂O₂ (30% w/w) and 2% (v/v) or 0.8 mL of 5 M NaNO₃ Halide Ion Strengthen (Hanna Instruments, Woonsocket, RI) was added and put into a water bath at 85°C for 10 min. If less than 40 mL of leachate was available for extraction, the total volume of available leachate was added to the centrifuge tubes and an adjusted ratio of both H₂O₂ and 5 M NaNO₃ was added based on the leachate volume. Centrifuge tubes were removed from the water bath and allowed to cool to 23.5°C before testing for Br⁻ concentration. After Br⁻ concentration was determined, the centrifuge tube volume was added back to its corresponding leachate storage bottle, following which the total volume of leachate was measured.

Br⁻ concentration was measured utilizing a Laboratory Research Grade Two Channel Benchtop pH/mV/ISE meter (Hanna Instruments, Woonsocket, RI) based on previous studies (Clothier et al., 2000; Levy and Chambers, 1987; Patra and Rego, 1994). A Br⁻ Combination Ion Selective Electrode (Br⁻ ISE; Hanna Instruments, Woonsocket, RI) with a detection range of 0.08 to 79910 mg Br⁻ L⁻¹ was utilized to measure the Br⁻ concentration in either the sand filtrate or leachate. The Br⁻ ISE was standardized based on the procedures established by Hanna Instruments, by utilizing 0.1M Br⁻ ISE

Standardizing solution (Hanna Instruments, Woonstock, RI) and creating 10-fold dilutions that bracketed the Br^- concentrations utilized in the study. The ISE was cleaned between each sample measurement by spraying DI water on the ISE and wiping it clean with Kimwipes EX-L (Kimberly-Clark Corporation, Irving, TX) until the pH/mV/ISE meter did not register any Br^- concentration. Throughout this study, the data collected included: individual column section VMC, whole column VMC, leachate volume, leachate Br^- concentration, and sand filtrate Br^- concentration.

Treatments in this experiment were arranged as a factorial combination of wetting agents, including control, column section, and destructive sampling dates, in a completely randomized design with 4 replications. The entire experiment was repeated once.

Analysis of variance (ANOVA) was conducted using the Proc Mixed procedure of SAS 9.4 (SAS Institute, Cary, NC). Experimental run was found to significantly interact with other fixed terms for all response variables and hence, data were analyzed separately for each run. Proc GLM procedure was then used for ANOVA with data collected for each run. Significant means were separated based on Fisher's Protected LSD at $P = 0.05$.

When an interaction was detected, a multiple comparison was performed accordingly.

Results and Discussions

Volumetric water content

The VWC data were presented for individual column sections as well as the whole column. For the individual column sections, interactions between treatment, DAT, and column section were observed in both runs of the study (Table 4.1, 4.2, and 4.3).

Consistently, AE maintained a significantly higher overall column section VWC in both runs, over all 5 DAT and among all treatments, except for one event (Table 4.1).

In both runs, column sections treated with AE held a range of VWC from 18.8% to 21.3% over all 5 DAT. Overall, the average VWC held in AE treated columns were 20.5% and 19.5% over the 5 DAT, which is 10.4% or 7.2% greater than other wetting agent treatments, in run 1 and 2, respectively (Table 4.1). Column sections treated with MAP maintained the next highest average column section VWC of 18.4% and 18.1%, in run 1 and 2 respectively, compared to AoP and UC treated column sections (Table 4.1). The sole exception, in both runs, was where MAP and AoP treated column sections had similar VWC at 4 DAT. Application of AoP maintained significantly lower average column section VWC, of 17.18% and 17.37% for run 1 and 2 respectively, compared to other wetting agent treatments (Table 4.1). Regardless of wetting agent application, 62% or greater VWC was maintained compared to columns treated with water alone. Columns treated with only water maintained the lowest column VWC, an average of 6.0% over all 5 DAT in both runs, among all treatments (Table 4.1).

Various treatments influenced VWC differently over the 5 DAT. Columns sections treated with AE maintained higher VWC at 4 DAT over both runs (Table 4.1). Over both runs, the lowest VWC, numerically, was after the initial infiltration event. The range of VWC in AE treated columns sections, over both runs, ranged from 18.8% to 21.27% (Table 4.1). Columns treated with AoP, in both runs, generally maintained significantly greater VWC at 4 and 5 DAT by at least 8.6%, which ranged from 17.0% to 17.6% (Table 4.1). The lowest column section VWC was from 1 to 3 DAT, which had a range of 14.8% to 16.4%. Following application of MAP, column sections generally, in both runs, resulted in higher column section VWC at 2 and 5 DAT (Table 4.1). The lowest column section VWC was seen after the first infiltration event, being either 17.4%

or 16.0% in run 1 or 2 respectively. Overall, the MAP treated column sections ranged from 17.2% to 19.4%, in both runs, over the 5 DAT study. Compared to all other treatments, column sections treated with water alone resulted in the lowest range of VWC, from 5.9% to 6.5%, over all five infiltration events. Over the 5 DAT, application of AE resulted in a higher average VWC than all other wetting agent treatments, by 7.2% or greater. In contrast, application of AoP resulted in the lowest average VWC compared to all other wetting agent treatments, by 21.5% or less (Table 4.1).

Overall, the study demonstrated that various wetting agent treatments affect the movement and retention of water differently over time. Certain wetting agents, such as AE, are able to maintain increased VWC over time. Other wetting agents, such as AoP, after the initial application, maintain lower VWC; however, after additional water infiltration events, increased VWC is held in the soil profile. These results are similar to those found by Leinauer et al., (2001), where sand columns treated with Primer 604 maintained 15.1% or greater VWC than columns treated with Midorich over three months. However, regardless of the applied wetting agent treatment, hydrophobic sands held significantly more water than sands not receiving wetting agent applications. These results are similar to the Leinauer et al. (2001), who reported that wetting agent treated sand columns maintained 1.2-fold higher VWC than columns treated with water alone.

The VWC retained in various column sections is influenced by the treatments applied (Table 4.2). Over both runs, all wetting agent treatments held significantly higher VWC in the upper three column sections, from 0.0 cm to 19.05 cm, than the water only by $\geq 42.3\%$. In the upper column section, all three wetting agent treatments maintained similar VWC values, ranging from 24.0% to 26.7% (Table 4.2). In comparison, the upper

column treated with water alone ranged from 3.9 to 4.4%. However, in the upper middle column section, at 6.36 cm to 12.70 cm, treated with AE resulted in up to 12% higher VWC than other treatments. In contrast, treatment of AoP resulted in significantly lower VWC than other wetting agent treatments, by 24.0% or less (Table 4.2). The lower middle column section, from 12.71 cm to 19.05 cm, showed a similar trend as the upper middle column. In the lowest column section, at 19.06 cm to 25.40 cm, AE treatment resulted in either similar or higher VWC than all other wetting agent treatments (Table 4.2). Among all treatments, columns treated with water alone resulted in a 6.6-fold or lower decrease in VWC compared to all wetting agent treatments.

Overall, AE maintained a higher VWC in all column sections than all other treatments (Table 4.2). Column sections treated with AoP maintained lower VWC than other wetting agent treatments. The upper three column sections treated with water alone maintained significantly lower VWC after five irrigation events as compared to all other treatments (Table 4.2). This agrees with Leinauer et al., (2001), where application of Primer 604 maintained equally similar or higher VWC than either Midorich or water alone from 5 cm to 25 cm in depth. In contrast, Leinauer et al., (2001) saw increased VWC in wetting agent treated columns at deeper depths, such as 15 cm, while in our study, the VWC in wetting agent treated columns was greater in the upper portions of the columns. The trends were similar between the studies, where columns treated with water alone had a greater VWC at deeper column depths. These results demonstrated that hydrophobic sand treated with certain wetting agents, such as AE, were able to maintain significantly higher VWC across all depths of the soil column profile when compared to all other treatments. The application of other wetting agents, such as AoP, on

hydrophobic sand maintained significantly lower VWC than other wetting agent treatments. However, wetting agent treatments significantly increased the VWC held across the various depths of the soil column profile as compared to the treatment of water alone.

The VWC varied across the column sections based on the amount of infiltration events applied (Table 4.3). In both runs, the two upper column sections, from 0 to 12.70 cm, maintained higher VWC than the two lower column sections, regardless of the number of infiltration events applied. In both runs, the upper column sections maintained a range of 19.6% to 21.4% across all 5 DAT, which was up to 3.7-fold less than the other column sections (Table 4.3). Additionally, the upper two sections accounted for 1.5-fold more VWC than the lower two sections across all DAT (Table 4.3). Regardless of the DAT, the lowest column section held the lowest VWC as compared to the other three column sections in both runs (Table 4.3).

Over the 5 DAT, the VWC varied depending on the infiltration events applied. In both runs, the upper column section maintained a higher VWC, by $\geq 5.1\%$, after the last infiltration event. In the upper middle column section, from 6.36 cm to 12.70 cm, a higher VWC, by 5.1% or greater, was maintained after the four infiltration events compared to all other days. On all other days, VWC was not significantly different from each other. The VWC in the lower middle column section maintained higher VWC after the first and second infiltration event by 13.1% or less, in both runs (Table 4.3). In the lowest column section, 1 DAT maintained significantly lower VWC, by 13.0% or greater, than all other DAT compared to all other days (Table 4.3).

Overall, both runs demonstrated that the upper column section held more water at 4 and 5 DAT, while the lower middle column section held more water at 1 and 2 DAT. Based on these data, it would seem that preferential flow still occurred and moved water deeper in the hydrophobic soil profile initially after the first and second infiltration event. As more infiltration events occurred over time, the VWC in the upper column sections increased and held significantly more water than the lower sections, demonstrating that as the upper soil profiles were exposed to repeated wetting and the VWC increased.

Column section Br⁻ concentration

Recovery of Br⁻ in the column sections varied among treatments and over the various infiltration events in both runs (Table 4.4). Overall, wetting agent treatments held a higher amount of Br⁻ in the column sections compared to water alone, by 4.2-fold from 1 to 4 DAT. At 5 DAT, the Br⁻ recovered from the water only treated column section was only 0.04 mg or less, a 786-fold reduction in Br⁻ compared with wetting agent treatments in which Br⁻ concentrations ranged from 23 mg to 33 mg of Br⁻ (Table 4.4). In both runs, column sections treated with AE retained the greatest amount of Br following the first infiltration event, by 11.2% or less, compared to the other wetting agent treatments. When the amount of Br⁻ recovered from all wetting agent treatments ranged from 63 mg to 71.5 mg at 1 DAT, while columns treated with water only held only 36 mg. Following two infiltration events, column sections treated with MAP maintained significantly higher recovered Br⁻ amounts than all other wetting agent treatments, with the trend continuing, throughout the remainder of the study (Table 4.4).

Overall, the amount of Br⁻ progressively decreased after more infiltration events were applied. However, the greatest reduction in recovered Br⁻ amounts occurred in AE

treated columns where a reduction of $\geq 38.5\%$ from 1 to 2 DAT, from 71 mg to 43 mg was observed (Table 4.4). This result coincides with the amount of Br^- recovered from the leachate after 2 infiltration events (Table 4.8). In comparison, both AoP and MAP reduced recovered Br^- amounts by 28.2% or less at 1 to 2 DAT. The recovered Br^- amounts steadily decreased each day throughout the study in the wetting agent and water alone treated column sections. This demonstrates that wetting agent applications on hydrophobic sands consistently maintained higher amounts of Br^- recovered over a longer period of time, than just water alone, before being leached and washed out into ground water sources. Previous studies have demonstrated that the movement of Br^- is similar to NO_3^- under field conditions (Onken et al., 1977; Parta and Rego, 1994; Smith and Davis 1974). As Br^- movement closely mimics the movement of NO_3^- , this shows that certain nutrients may be more available to growing plants in wetting agent treated hydrophobic sands compared to the application of water alone.

Recovery of Br^- varied among the various column section depths based on the treatment applied (Table 4.5). Across both runs, significantly lower Br^- amounts were recovered in all column sections treated with water alone as compared to those that were treated with a wetting agent, by ≥ 1.71 -fold (Table 4.5). In both runs, in the two upper column sections higher Br^- amounts were recovered when treated with MAP as compared to all other wetting agent treatments, by $\geq 7.3\%$. Application of both AoP and MAP demonstrated greater Br^- amounts recovered from the lower middle column section, from 12.71 cm to 19.05 cm, than when treated with AE by 3.4% or greater. In both runs, the lowest column section held significantly higher Br^- amounts than both AE or MAP, by $\geq 11.9\%$ (Table 4.5). Following the application of AE, except for the upper most column

section, all other column sections maintained the lowest amount of Br^- recovered as compared to the other wetting agent treatments. Overall, the three upper sections of the column treated with MAP maintained equally similar or higher amounts of Br^- recovered than all other treatments.

Only water treated hydrophobic sand columns had significantly higher amounts of Br^- in the lowest column section after which, the amount of recovered Br^- progressively decreased with the upper column sections (Table 4.5). However, the MAP treated column resulted in greater amounts of recovered Br^- in the middle two sections by $\geq 52.7\%$ of the total Br^- retained in the column section. Similarly, 54.1% of the Br^- amount recovered from AE treated columns was held in the middle two column sections, from 6.36 cm to 19.05 cm (Table 4.5). In comparison, AoP treated columns held significantly higher amounts of Br^- in the lower two column sections, by $\geq 57.0\%$, compared to the upper two sections. These results demonstrated that application of MAP retained a greater amount of Br^- in the upper three-quarters of the soil profile compared to other treatments. Greater amounts of Br^- in AoP treated column sections moved further through the hydrophobic soil, which could limit access of nutrients similar to Br^- to plants.

Recovery of Br^- in column sections varied based on the number of infiltration events conducted (Table 4.6). Higher amounts of Br^- were detected in the upper three column sections, from 0 cm to 19.05 cm, after the first infiltration event by $\geq 12.8\%$ (Table 4.6). Progressively, as more infiltration events occurred, the amount of Br^- in the upper three column sections decreased through the end of the study. The largest decrease in Br^- amount was seen in all column sections from 1 to 2 DAT (Table 4.6). The upper most column section, from 0 cm to 6.35 cm, resulted in the highest reduction in amount

of recovered Br^- by $\geq 63.0\%$ (Table 4.6). The lower middle column section only saw a Br^- decrease of 13.1% or less from 1 to 2 DAT and the lowest column section held the lowest amount of Br^- after the first infiltration event, by 6.0% or greater when compared to all other days (Table 4.6). The highest amount of recovered Br^- was seen in the lowest column section after the second infiltration event, by $\geq 4.8\%$ compared to all other days (Table 4.6). However, after the third infiltration cycle, the amount of Br^- gradually decreased until the conclusion of the study.

Following the initial infiltration event $\geq 62.4\%$ the amount of recovered Br^- was held in the upper two column sections compared to the lower 2 column sections (Table 4.6). After 2 infiltration events, the Br^- amount was significantly greater in the lower middle column section by 12.0% or greater, as compared to the other sections (Table 4.6). With more infiltration events, greater amounts of Br^- were seen in the lower two column sections, where 61.8%, 69.5%, and 73.7% of the amount of Br^- were detected, in all sections combined, at 3, 4 and 5 DAT, respectively (Table 4.6). After the fourth and fifth infiltration event, the lowest column section held the highest amount of Br^- , by $\geq 16.4\%$ at 4 DAT and $\geq 27.3\%$ at 5 DAT. The amount of recovered Br^- progressively moved deeper through the hydrophobic soil profile as more infiltration events occurred, concurring with Ritsema and Dekker (1998b) and Hendriks et al. (1999), who reported significant movement of bromide deeper in the sand profile following rain events. After the initial application of Br^- , over 95% of the Br^- was found in the upper 5 cm of the soil. Following a rain event, over 80% of the Br^- applied moved deeper in the soil from 15 cm to 25 cm. As the study continued and more rain events occurred, Br^- continued to move

deeper in the soil profile, and significantly less Br⁻ was found in upper depths of the soil (Ritsema and Dekker. 1998b; Hendriks et al., 1999).

Leachate

Leachate volume

Leachate amounts collected at the bottom of the hydrophobic sand columns were significantly influenced by the interaction between treatments and infiltration event dates and occurred in both runs (Table 4.7). Among the wetting agent treatments, the leachates collected at 1 DAT were substantially low, accounting for 16.8% or less, than leachates collected at a later date. A similar pattern was found in control columns, although leachates collected at 1 DAT accounted for 73.6% or less compared to leachates collected in a later date. As the total porosity of the sand columns was determined to be 197.7 mL and the treatments, including water, were applied at 100 mL, those results suggested that all treated sand columns, including wetting agent treatments, formed preferential flow before reaching saturation. These data, however, indicated that application of wetting agents substantially reduced water loss through preferential flow immediately after treatment application, compared to the water alone application. Regardless of the treatment, however, the overall trend showed that leachate collected increased in volume at 2 DAT, and reached a plateau of 82 mL or greater at 4 or 5 DAT in both runs. This trend was expected as the sand columns contained no moisture initially, agreeing with similar results reported by Song et al., (2021).

Among treatments, leachates collected from control columns showed consistently the highest volume following all infiltration events in both runs (Table 4.7). This result suggested that the selected wetting agents all improved water retention in the hydrophobic sands compared to the untreated control. This effect was especially

noticeable at 1 DAT where ≥ 4.8 -fold of leachates were collected from control columns compared to wetting agents-treated columns. At 2 DAT and later, greater amounts of leachate were still recovered from control columns although the disparity with leachates from wetting agent-treated columns were reduced to ≤ 1.2 -fold. One of the major purposes of using wetting agents is to improve water retention of hydrophobic soil in order to conserve water, suggesting that these results demonstrated such a function by the selected wetting agents.

Among the wetting agents, columns treated with AE resulted in zero leaching at 1 DAT, and 76 mL or less leachates at 2 DAT in both runs, suggesting a greater water retention compared to other selected wetting agents. Although leachates collected from AE-treated columns were comparable to other wetting agents at 3 DAT or later, ultimately more water was retained in AE-treated sand columns after the five infiltration events. An earlier report found that AE application to hydrophobic sands resulted in the fastest seepage time among other wetting agent treatments (Song et al., 2014a). Collectively, these results suggest that application of AE to hydrophobic sands could result in a greater probability of preferential flow before the sand profile becomes saturated. In comparison, columns treated with AoP or MAP showed steady seepage at 2 DAT or later in the range of 81—89 mL in both runs.

Br⁻ recovery in leachate

Recovery of Br⁻ in leachates varied among treatments applied and infiltration events in both runs (Table 4.8). At 1 DAT, Br⁻ recovered from control column leachates reached 128 or 126 mg in run 1 and 2, respectively. Starting at 2 DAT, Br⁻ recovery showed a steady decrease and dropped by 53% or greater at 2 DAT compared to 1 DAT.

By 5 DAT, Br⁻ recovery in control column leachates was only 11% or less compared to Br⁻ recovered at 1 DAT in both runs. These results clearly showed that without using wetting agents, water alone would cause significant risk of leaching in hydrophobic soil, especially within the first couple of days after an application. Various studies, such as Bauters et al. (1998), McLeod et al. (2001), and Ritsema and Dekker (1996), have demonstrated that movement of Br⁻ in hydrophobic soils can be up to three times faster than through wettable soils. This phenomenon was determined to be due to preferential flow pathways bypassing a majority of the bulk hydrophobic soil and moving through the soil more quickly (Brown et al., 2000; Ritsema and Dekker, 1996). Unlike the untreated control, Br⁻ recovered from the treated column leachates were 16 mg or less at 1 DAT, but reached the highest amount at 71 mg or greater at 2 DAT among the wetting agents in both runs. By 3 DAT, Br⁻ recovered from treated column leachates ranged between 30 to 40 mg in both runs, and continued to decrease at 4 and 5 DAT. Collectively, these results demonstrated a delayed effect of leaching following wetting agent application compared to water alone.

Among the wetting agents, application of AE led to zero Br⁻ recovery in the leachates at 1 DAT in both runs (Table 4.8), which is due to the absence of leaching occurring at this event (Table 4.7). By 2 DAT, however, the highest concentrations of leachate Br⁻ were recovered from AE-treated columns, accounting for 1.38-fold or greater compared to AoP- or MAP-treated columns. This trend continued and except for one event, Br⁻ recovery from AE-treated column leachates were similar to or greater than leachate Br⁻ recovered from AoP or MAP applications in 3, 4, and 5 DAT in both runs. At 2 DAT, relatively fewer leachates were found following AE application compared to

the other two wetting agents (Table 4.7), indicating AE application resulted in a higher concentration of Br⁻ in the leachates. This more concentrated movement of Br⁻ from AE could potentially be due to anion exclusion, where the Br⁻ anion is repelled from negative particle surfaces leading to an increased concentration in the water in the middle of the soil pore, which is normally more mobile (James and Rubin, 1986; Porro and Wierenga, 1993; Wang et al. 2008). Once application of AE resulted in negligible leachate volume or detectable Br⁻ after the first infiltration event, an increase of Br⁻ concentration could have occurred in the lower section of the columns soil water. Following the second infiltration event, the higher Br⁻ concentrated soil water in the lower section of the column could be leached out resulting in the higher Br⁻ concentration detected at 2 DAT. In comparison, equal or relatively less Br⁻ were recovered from leachates following MAP application, compared to other wetting agents in most infiltration events in both runs.

Total Br⁻ Recovery

Leachate

The amount of Br⁻ concentration recovered from either the leachate or hydrophobic sand columns varied based on the treatment and infiltration events applied (Table 4.9). In both runs, after the first infiltration event, hydrophobic columns treated with water alone resulted in 7.8-fold more Br⁻ recovered in the leachate compared to wetting agent treated columns (Table 4.9). The columns treated with water alone resulted in $\geq 42.3\%$ of the total applied Br⁻ recovered in the leachate after the first infiltration event. In comparison, after the first infiltration event, wetting agent treated hydrophobic sand columns resulted in a range of only 0.0% to 5.4% of the total Br⁻ applied. However, from 1 to 2 DAT, the wetting agent columns saw a dramatic increase of Br⁻ recovered, by

≥ 5.3 -fold, in the leachate (Table 4.9). For the remainder of the study, the Br^- concentration progressively increased in the leachate across all treatments, although not as dramatic as from 1 to 2 DAT. The highest recovery of leachate Br^- concentration occurred in the columns treated with water alone, where $\geq 90.2\%$ of the total Br^- applied was recovered in the leachate after the last infiltration event (Table 4.9). In columns treated with wetting agents, after the last infiltration event, Br^- concentration recovered ranged from 46.3% to 58.7% of the total Br^- applied.

Among the wetting agent treated columns, AE had zero Br^- recovered after the first infiltration, due to no leachate being collected from this event (Table 4.7). After the second infiltration event AE treated columns saw the largest increase in Br^- recovered in the leachate, going from 0.0% to 34.0% or greater. Following two infiltration events, the Br^- recovered from AE treated columns was 10.9% higher than other wetting agent treatments (Table 4.9). Columns treated with MAP resulted in the lowest amount of Br^- recovered in the leachate, after two infiltration events, by 2.8% or greater in both runs. Both of these trends continued throughout the remainder of the study. After the final infiltration event, AE treated columns had greater Br^- recovered in the leachate, by $\geq 6.7\%$ or higher, than all other wetting agent treatments. After the final infiltration event, MAP treated columns resulted in significantly lower Br^- recovered in the leachate, by 21.2% or less.

Hydrophobic sand

Based on the Br^- recovered from the hydrophobic sand being mutually dependent on the amount recovered in the leachate, the amount of Br^- recovered from the sand columns was lowest in water only treatments (Table 4.9). Wetting agent treated

hydrophobic sand columns maintained 43.7% or greater Br^- recovery after the first infiltration event, as compared to just water alone. After the first infiltration event, the amount of Br^- retained in wetting agent treated sand ranged from 85.3% to 95% of the total Br^- applied (Table 4.9). Following the second infiltration event, a 39.5% or less decrease of Br^- recovered from wetting agent treated sand columns was seen in all wetting agent treatments at 1 to 2 DAT. This trend continued throughout the remainder of the study, although decreases in recovered Br^- concentration were not as great as that observed in the initial events. After the last infiltration event, the amount of Br^- retained in the wetting agent treated sand columns ranged from 31.4% to 43.6%, which was 314-fold more Br^- retained than in columns treated with water alone (Table 4.9).

After the first infiltration event, AE treated columns retained significantly more Br^- than all other wetting agent treatments, 3.3% or greater. However, after the second infiltration event, AE treated columns had the largest decrease in Br^- held in the sand column, by ≥ 1.6 -fold, compared to the other wetting agent treatments (Table 4.9). Additionally, AE treated columns retained a lower amount of Br^- compared to AoP and MAP, by 7.3% or greater. Columns treated with MAP maintained significantly more Br^- than AE and AoP after the second infiltration event. These trends continued throughout the remainder of the study. After the final infiltration event, AE treated columns held 31.4% to 32.5% of the total Br^- applied, while MAP treated columns held 43.1% to 43.6% of the total Br^- applied (Table 4.9).

Overall, 91.9% of the total Br^- applied was recovered in this study (Table 4.9). Previous studies showed Br^- recovery rates from 90% to 97% (Parta and Rego, 1994; Ritsema and Dekker, 1998). From the Br^- recovered in both the leachate and hydrophobic

sand columns, regardless of the wetting agent treatment applied, a greater amount of Br^- was recovered in the hydrophobic sand compared to when treated with water alone. Similarly, wetting agent treated columns showed a reduced amount of Br^- that leached through the columns when compared to those columns where water alone was applied. These results demonstrated again the ability of wetting agents to influence the potential movement of nutrients or agrochemicals in soil by either maximizing the amount retained or reducing the amount that leached through a hydrophobic sand media (Brown et al., 2000; Hendriks et al., 1999; Onken et al., 1977; Ritsema and Dekker, 2000).

Conclusions

Wetting agents applied demonstrated increased VWC and reduced Br^- concentrations leached through hydrophobic soil columns as compared to application of water alone. The columns treated with water alone resulted in greater than 91% of the applied Br^- leach out of the column after five infiltration events, while wetting agent treated columns reduced the amount of Br^- leached by 1.5-fold or greater. Additionally, application of wetting agents retained 31.4% or greater of the applied Br^- within the hydrophobic soil columns after the fifth infiltration event, compared to 0.1% remaining in columns treated with water alone. This demonstrates that wetting agents reduce leaching through hydrophobic soils by mitigating the amount of preferential flow that occurs.

The application of wetting agents also significantly increased the VWC by 57.3% or greater, over the five infiltration events, compared to water alone. In general, wetting agent treated hydrophobic sand columns maintained 2-fold greater VWC in the upper 0 cm to 19.05 cm portion, compared to when there was no treatment. This demonstrates the ability of wetting agents to more effectively create a uniform wetting front in

hydrophobic sands compared to application of only water. The ability of wetting agents to retain more water in the upper portions of the soil profile aid in plant available water, leading to reduction of localized dry spot and potentially increasing the efficacy of nutrients or agrochemicals.

Variation among leachate and water movement based on the wetting agent treatment applied was seen, demonstrating that all wetting agents do not perform the same. However, wetting agents influence on leaching and water movement was not correlated to their surface tension values. This indicates that wetting agent performance cannot be predicted solely based on their influence on water's surface tension value.

Overall, all wetting agents do not perform the same and this should be considered when golf course superintendents utilize these products. However, regardless of the wetting agent applied, water retention was increased and the amount of Br^- leached was significantly reduced compared to the application of water alone. This demonstrates the ability of wetting agents to increase the water retention and the potential reduction of nutrient or agrochemicals leaching into ground waters.

References

- Abdalla, N.A., and B. Lear. 1975. Determination of inorganic bromide in soils and plant tissues with a bromide selective-ion electrode. *Commun. Soil Sci. Plant Anal.* 6:489-494.
- Ahuja, L.R., and O.R. Lehman. 1983. The extent and nature of rainfall-soil interaction in the release of soluble chemicals to runoff. *J. Envir. Quality.* 12(1):34-40.
- Bauters, T.W.J., D.A. DiCarlo, T.S. Steenhuis, and J.Y. Parlange. 1998. Preferential flow in water repellent sands. *Soil Sci. Soc. Am. J.* 62:1185-1190.
- Blodgett, A.M., D.J. Beattie, and J.W. White. 1993. Hydrophilic polymers and wetting agents affect absorption and evaporative water loss. *Hort. Sci.* 28(6):633-635.
- Bowman, R.S. 1984. Evaluation of some new tracers for soil water studies. *Soil Sci. Soc. Am. J.* 48:987-993.
- Bradford, S.A., and F.J. Leij. 1996. Predicting two- and three-fluid capillary pressure-saturation relationships of porous media with fractional wettability. *Water Resour. Res.* 32:251-259.
- Brown, C.D., J.M. Hollis, R.J. Bettinson, and A. Walker. 2000. Leaching of pesticides and a bromide tracer through lysimeters from five contrasting soils. *Pest Manag. Sci.* 56:83-93.
- Carrillo, M.L.K., J. Letey, and S.R. Yates. 2000. Unstable water flow in a layered soil: I. Effects of a stable water-repellent layer. *Soil Sci. Soc. Am. J.* 64:450-455.
- Cisar, J.L., K.E. Williams, H.E. Vivas, and J.J. Haydu. 2000. The occurrence and alleviation by surfactants of soil-water repellency on sand-based turfgrass systems. *J. Hydrol.* 231-232:352-358.

- Clothier, B.E., I. Vogeler, and G.N. Magesan. 2000. The breakdown of water repellency and solute transport through a hydrophobic soil. *J. Hydrol.* 231-232:255-264.
- Crawford, N.M. 1995. Nitrate: nutrient and signal for plant growth. *Plant Cell.* 7:859-868.
- Davis, S.N., G.M. Thompson, H.W. Bentley, and G. Stiles. 1980. Ground-water tracers – a short review. *Ground Water.* 18:14-23.
- DeBano, L.F. 1971. The effect of hydrophobic substances on water movement in soil during infiltration. *Soil Sci. Soc. Amer. Proc.* 35:341-343.
- Dekker, L.W., K. Oostindie, and C.J. Ritsema. 2005a. Exponential increase of publications related to soil water repellency. *Aust. J. of Soil Res.* 43:403-441.
- Dekker, L.W., K. Oostindie, S.J. Kostka, and C.J. Ritsema. 2005b. Effects of surfactant treatments on the wettability of water repellent grass-covered dune sand. *Aust. J. Soil Res.* 43:383-395.
- Doerr S.H. 1998. On standardizing the ‘Water Drop Penetration Time’ and the ‘Molarity of an Ethanol Droplet’ techniques to classify soil hydrophobicity: A case study using medium textured soils. *Earth Surf. Process. Landforms.* 23: 663-668.
- Feng, G.L., J. Letey, and L. Wu. 2002. The influence of two surfactants on infiltration into a water-repellent soil. *Soil Sci. Soc. Am. J.* 66:361-367.
- Geng, X., K. Guillard, and T.F. Morris. 2014. Relating turfgrass growth and quality to frequently measured soil nitrate. *Crop Sci.* 54:366-382.
- Germann, P.F., W.M. Edwards, and L.B. Owens. 1984. Profiles of bromide and increased soil moisture after infiltration into soils with macropores. *Soil Sci. Soc. Am. J.* 48:237-244.

- Harris, G.L., P.H. Nicholls, S.W. Bailey, K.R. Howse, and D.J. Mason. 1994. Factors influencing the loss of pesticides in drainage from a cracking clay soil. *J. Hydro.* 159:235-253.
- Hendriks, R.F.A., K. Oostindie, and P. Hamminga. 1999. Simulation of bromide tracer and nitrogen transport in a cracked clay soil with the FLOCR/ANIMO model combination. *J. Hydro.* 215:94-115.
- James, R.V., and J. Rubin. 1986. Transport of chloride ion in a water unsaturated soil exhibiting anion exclusion. *Soil Sci Soc of Am J.* 50(5): 1142-1149.
- Karnok, K.J. 2006. Which wetting agent is best? *Golf Course Manag.* 74:82-83.
- Karnok, K.J., and K.A. Tucker. 1989. The cause and control of localized dry spots on bentgrass greens. *Golf Course Manage.* 57:28-34.
- Karnok, K.J., and K.A. Tucker. 2001. Wetting agent treated hydrophobic soil and its effect on color, quality and root growth of creeping bentgrass. *Int. Turfgrass Soc. Res. J.* 9:537-541.
- Karnok, K.J., K. Xia, and K.A. Tucker. 2004. Wetting agents: What are they, and how do they work? *Golf Course Manage.* 72:84-86.
- King, P.M. 1981. Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect measurement. *Aust. J. Soil Res.* 19:275–285.
- Kostka, S.J. 2000. Amelioration of water repellency in highly maintained soils and the enhancement of turfgrass performance through the systematic application of surfactants. *J. Hydrol.* 231-232:359-368.

- Larsbo, M., T.S. Aamlid, L. Persson, and N. Jarvis. 2008. Fungicide leaching from golf greens: Effects of root zone composition and surfactant use. *J. Environ. Qual.* 37:1527-1535.
- Leinauer, B., P.E. Rieke, D. VanLeeuwen, R. Sallenave, J. Makk, and E. Johnson. 2001. Effects of soil surfactants on water retention in turfgrass rootzones. *Int. Turf. Soc. Res. J.* 9:542-547.
- Letey, J., J. Osborn, and R.E. Pelishek. 1962. The influence of the water-solid contact angle on water movement in soil. *Int. Ass. Sci. Hydrol. Bull.* 3:75-81.
- Levy, B.S., and R.M. Chambers. 1987. Bromide as a conservative tracer for soil-water studies. *Hydrol. Proc.* 1:385-389.
- McLeod, M., J. Aislabie, J. Smith, R. Fraser, A. Roberts, and M. Taylor. 2001. Viral and chemical tracer movement through contrasting soils. *J. Environ. Qual.* 30:2134-2140.
- Müller, K., and M. Deurer. 2011. Review of the remediation strategies for soil water repellency. *Agriculture, Ecosystems and Environment.* 144:208-221.
- Nimmo, J.R. 2004. Porosity and pore size distribution. In: D. Hillel, editor, *Encyclopedia of soils in the environment.* Elsevier, London. p. 295–303.
- Onken, A.B., C.W. Wendt, R.S. Hargrove, and O.C. Wilke. 1977. Relative movement of bromide and nitrate in soils under three irrigation systems. *Soil Sci. Soc. Am. Proc.* 41: 50-52.
- Patra, A.K., and T.J. Rego. 1994. Modified procedure for bromide estimation with ion-selective electrode for predicting nitrate movement in soil. *Current Science.* 67(7):545-546.

- Porro, I., and P.W. Wierenga. 1993. Transient and steady-state solute transport through a large unsaturated soil column. *Ground Water*. 31(2): 193-200.
- Ritsema, C.J., and L.W. Dekker. 1996. Water repellency and its role in forming preferred flow paths in soils. *Aust. J. Soil Res.* 34:475-487.
- Ritsema, C.J., and L.W. Dekker. 1998a. Three-dimensional patterns of moisture, water repellency, bromide and pH in a sandy soil. *J. Contaminant Hydro.* 31:295-313.
- Ritsema, C.J., and L.W. Dekker. 1998b. Stable or unstable wetting fronts in water repellent soils – effect of antecedent soil moisture content. *Soil Tillage Res.* 47:111-123
- Ritsema, C.J., and L.W. Dekker. 2000. Preferential flow in water repellent sandy soils: principles and modeling implications. *J. Hydro.* 231-232:308-319.
- Ruemmele, B.A., and J.A. Amador. 1994. Plant and soil responses to soil wetting agents. p. 180. In 1994 *Agron. Abst.* ASA, Madison, WI.
- Roy, J.L., and W.B. McGill. 2002. Assessing soil water repellency using the Molarity of Ethanol Droplet (MED) test. *Soil. Sci.* 167(2): 83-97.
- Smith, S.J., and R.J. Davis. Relative movement of bromide and nitrate through soils. *Jour. Environ. Qual.* 3(2): 152-155.
- Song, E., K.W. Goyne, R.J. Kremer, S.H. Anderson, and X. Xiong. 2021. Certain soil surfactants could become a source of soil water repellency after repeated application. *Nanomaterials.* 11:2577.
- Song, E., J.G. Schneider, S.H. Anderson, K.W. Goyne, and X. Xiong. 2014a. Wetting agent influence on water infiltration into hydrophobic sand: I. Rewettability. *Agron. J.* 106(5):1873-1878.

- Tucker, K.A., K.J. Karnok, D.E. Radcliffe, G. Landry, R.W. Roncadori, and K.H. Tan. 1990. Localized dry spots as caused by hydrophobic sands on bentgrass greens. *Agron. J.* 82:549-555.
- Wallis, M.D., and D.J. Horne. 1992. Soil water repellency. *Adv. Soil Sci.* 20:91-146.
- Wang, B., M. Jin, J.R. Nimmo, L. Yang, and W. Wang. 2008. Estimating groundwater recharge in Hebei Plain, China under varying land use practices using tritium and bromide tracers. *J. Hydro.* 356:209-222.
- Wang, Z., Q.J. Wu, L. Wu, C.J. Ritsema, L.W. Dekker, J. Feyen. 2000. Effects of soil water repellency on infiltration rate and flow instability. *J. Hydro.* 231-232:265-276.
- Watson, C.L., and J. Letey. 1970. Indices for characterizing soil water repellence based upon contact angle-surface tension relationships. *Soil Sci. Soc. Am. Proc.* 34:841-844.
- Wessolek, G., H. Stoffregen, and K. Täumer. 2009. Persistency of flow patterns in a water repellent sandy soil – conclusions of TDR readings and a time-delayed double tracer experiment. *J. Hydro.* 375:524-535.
- Wiecko, G. and R.N. Carrow. 1992. Wetting agent effects on soil physical properties and turfgrass growth. p. 178. In 1992 *Agron. Abst. ASA*, Madison WI.

Table 4.1. Volumetric water content (VWC; %) of hydrophobic sands influenced by treatments that include three wetting agents and a water control, and infiltration events applied at 1, 2, 3, 4, and 5 days after treatment (DAT).

Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
-----Volumetric Water Content (%) -----					
----Run 1----					
AE [†]	19.0 a3 [‡]	20.8 a12	21.3 a1	21.2 a1	20.2 a2
AoP	16.4 c2	14.8 c3	14.5 c3	17.6 b1	17.2 c12
MAP	17.4 b3	19.4 b1	17.7 b23	18.6 b12	18.8 b1
UC	5.9 d1	6.0 d1	6.2 d1	6.2 c1	5.9 d1
----Run 2----					
AE	18.8 a2	19.1 a2	19.4 a2	20.5 a1	19.7 a12
AoP	15.9 c2	15.5 b2	15.6 c2	17.5 b1	17.4 c1
MAP	17.2 b3	19.1 a1	17.8 b23	18.1 b2	18.3 b12
UC	6.2 d1	6.1 c1	6.1 d1	6.5 c1	6.1 d1

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.2. Volumetric water content (VWC; %) of hydrophobic sands influenced by wetting agents applied and different column depths.

Column Section	AE [†]	AoP	MAP	UC
-----Volumetric Water Content (%) -----				
----Run 1----				
1 [§]	25.7 a1 [‡]	25.0 a1	25.9 a1	3.9 c2
2	25.7 a1	19.8 b3	22.7 b2	7.3 a4
3	20.1 b1	12.6 c3	15.9 c2	6.4 b4
4	10.4 c1	7.1 d3	9.0 d2	6.5 ab3
----Run 2----				
1	25.5 b2	24.0 a3	26.7 a1	4.4 c4
2	26.3 a1	20.0 b3	22.5 b2	7.0 b4
3	18.6 c1	14.9 c2	15.4 c2	8.6 a3
4	7.6 d1	6.7 d2	7.9 d1	4.9 c3

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxyated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[§]Column sections: 1 is equivalent to 0 to 6.35 cm, 2 is equivalent to 6.36 to 12.70 cm, 3 is equivalent to 12.71 to 19.05 cm, and 4 is equivalent to 19.06 to 25.4 cm.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.3. Volumetric water content (VWC; %) of hydrophobic sands influenced by the column depth and infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Column Section	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
-----Volumetric Water Content (%) -----					
----Run 1----					
1 [§]	19.7 a2 [‡]	19.6 a2	19.6 a2	20.3 a2	21.4 a1
2	18.8 a2	18.1 b2	18.8 a2	19.9 a1	18.8 b2
3	14.5 b1	14.2 c1	12.6 b2	14.7 b1	12.9 c2
4	5.7 c2	9.0 d1	8.7 c1	9.0 c1	8.9 d1
----Run 2----					
1	19.9 a12	19.8 a2	19.8 a2	20.6 a12	20.7 a1
2	17.9 b3	18.7 b23	19.2 a12	20.0 a1	19.0 b2
3	15.0 c1	14.9 c12	13.6 b3	14.0 b23	14.2 c123
4	5.4 d3	6.4 d2	6.4 c2	8.0 c1	4.7 d4

[§]Column sections: 1 is equivalent to 0 to 6.35 cm, 2 is equivalent to 6.36 to 12.70 cm, 3 is equivalent to 12.71 to 19.05 cm, and 4 is equivalent to 19.06 to 25.4 cm.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.4. Bromide (Br⁻; mg) recovered in hydrophobic sands influenced by wetting agent applications and infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Column Section	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
	----- Bromide (mg) -----				
----Run 1----					
AE [†]	71.3 a1 [‡]	43.8 c2	36.0 c3	28.5 c4	23.6 c5
AoP	63.3 c1	47.2 b2	40.3 b3	32.7 b4	30.3 b5
MAP	68.9 b1	48.6 a2	41.6 a3	34.0 a4	32.7 a5
UC	35.7 d1	20.1 d2	14.9 d3	6.8 d4	0.03 d5
----Run 2----					
AE	71.3 a1	43.2 c2	36.3 c3	28.8 c4	24.4 c5
AoP	64.0 c1	47.1 b2	39.5 b3	32.3 b4	30.4 b5
MAP	67.0 b1	48.1 a2	41.2 a3	34.1 a4	32.3 a5
UC	36.1 d1	21.3 d2	15.0 d3	7.2 d4	0.04 d5

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.5. Bromide (Br⁻; mg) recovered in hydrophobic sand columns influenced by wetting agents applied and column depth.

Column Section	AE [†]	AoP	MAP	UC
----- Bromide (mg) -----				
----Run 1----				
1 [§]	34.2 c2 [‡]	31.0 d3	43.4 c1	8.1 d4
2	41.2 b3	42.5 c2	45.9 b1	12.3 c4
3	46.7 a2	49.8 a1	49.2 a1	18.1 b3
4	40.4 b3	47.7 b1	42.1 d2	23.6 a4
----Run 2----				
1	34.2 d2	31.3 d3	42.1 c1	8.4 d4
2	41.3 b3	42.1 c2	45.7 b1	13.0 c4
3	47.4 a2	49.6 a1	49.1 a1	18.7 b3
4	40.3 c3	47.6 b1	41.3 d2	23.5 a4

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[§]Column sections: 1 is equivalent to 0 to 6.35 cm, 2 is equivalent to 6.36 to 12.70 cm, 3 is equivalent to 12.71 to 19.05 cm, and 4 is equivalent to 19.06 to 25.4 cm.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.6. Bromide (Br⁻; mg) recovered in hydrophobic sands at different column sections and infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Column Section	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
	----- Bromide (mg) -----				
----Run 1----					
1 [§]	79.9 a1 [‡]	28.8 c2	20.5 d3	10.8 d4	6.0 d5
2	69.8 b1	41.4 b2	29.5 c3	19.9 c4	16.8 c5
3	54.8 c1	47.6 a2	43.0 a3	32.4 b4	26.9 b5
4	34.8 d4	41.9 b1	39.8 b2	38.7 a2	37.0 a3
----Run 2----					
1	78.2 a1	28.9 c2	20.6 d3	10.8 d4	6.3 d5
2	70.4 b1	41.1 b2	29.8 c3	20.4 c4	16.0 c5
3	55.2 c1	48.2 a2	43.4 a3	32.2 b4	27.1 b5
4	34.5 d4	41.5 b1	38.2 b2	39.0 a2	37.7 a3

[§]Column sections: 1 is equivalent to 0 to 6.35 cm, 2 is equivalent to 6.36 to 12.70 cm, 3 is equivalent to 12.71 to 19.05 cm, and 4 is equivalent to 19.06 to 25.4 cm.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.7. Leachate volume (mL) through hydrophobic sand columns following each infiltration event at 1, 2, 3, 4, and 5 days after treatment (DAT).

Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
----- Leachate (mL) -----					
----Run 1----					
AE [†]	0.0 d3 [‡]	72.6 d2	86.0 ab1	88.8 ab1	88.0 b1
AoP	13.6 b3	80.8 c2	83.3 b1	86.0 b1	82.0 c12
MAP	8.5 c3	83.9 b2	87.7 a1	86.6 b12	86.3 bc12
UC	65.3 a3	91.7 a1	88.7 a2	90.4 a12	94.3 a1
----Run 2----					
AE	0.0 d4	76.3 c3	85.1 c2	88.8 bc1	86.3 b12
AoP	12.9 b4	84.5 b3	87.5 b2	89.9 b1	89.0 b12
MAP	9.0 c3	84.1 b2	85.3 c12	87.3 c1	86.0 b12
UC	64.2 a3	90.6 a2	91.4 a2	93.9 a1	94.8 a1

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.8. Bromide (Br⁻; mg) recovered in leachates following infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
----- Bromide (mg) -----					
----Run 1----					
AE [†]	0.0 d5 [‡]	100.5 a1	38.9 a2	21.7 ab3	14.0 a4
AoP	15.7 b4	70.5 c1	36.4 b2	19.0 b3	10.2 ab5
MAP	7.3 c4	72.6 b1	31.2 c2	21.1 ab3	7.7 b4
UC	127.8 a1	60.4 d2	39.7 a3	24.1 a4	14.2 a5
----Run 2----					
AE	0.0 d5	102.6 a1	35.3 c2	21.7 b3	13.6 ab4
AoP	14.9 b4	73.1 b1	39.6 b2	20.2 b3	10.8 bc5
MAP	7.7 c4	74.0 b1	30.2 d2	21.4 b3	7.7 c4
UC	126.3 a1	59.7 c2	42.5 a3	24.3 a4	14.5 a5

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Table 4.9. Cumulative bromide (Br⁻) recovered (%) from hydrophobic sands, and the combined total influenced by wetting agents applied and the following infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Recovery Source	Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
----- Total Bromide (%) -----						
----Run 1----						
Leachate						
	AE [†]	0.0 d5 [‡]	34.0 b4	44.3 b3	55.1 b2	58.7 b1
	AoP	4.7 b4	30.3 c3	39.3 c2	48.7 c1	49.5 c1
	MAP	2.5 c4	27.4 d3	35.9 d2	44.7 d1	46.3 d1
	UC	42.7 a5	62.5 a4	75.1 a3	83.4 a2	90.2 a1
Sand						
	AE	95.0 a1	58.4 c2	48.0 c3	38.0 c4	31.4 c5
	AoP	84.4 c1	63.0 b2	53.8 b3	43.6 b4	40.4 b5
	MAP	91.9 b1	64.7 a2	55.4 a3	45.3 a4	43.6 a5
	UC	47.6 d1	26.8 d2	19.9 d3	9.0 d4	0.1 d5
Total						
	AE	95.0 a1	92.4 a2	92.3 b23	93.0 a12	90.1 a3
	AoP	89.2 b2	93.2 a1	93.0 ab1	92.3 a1	90.0 a2
	MAP	94.4 a1	92.1 a2	91.4 b23	90.0 b23	89.9 a3
	UC	90.3 b3	89.3 b3	95.0 a1	92.4 a2	90.3 a3
----Run 2----						
Leachate						
	AE	0.0 d5	36.8 b4	46.3 b3	51.2 b2	56.7 b1
	AoP	5.4 b5	28.4 c4	42.3 c3	50.1 b2	52.9 c1
	MAP	2.1 c5	27.6 c4	37.0 d3	44.2 c2	47.4 d1
	UC	42.3 a5	60.9 a4	75.0 a3	84.4 a2	90.8 a1
Sand						
	AE	95.0 a1	57.5 c2	48.5 c3	38.4 c4	32.5 c5
	AoP	85.3 c1	62.9 b2	52.7 b3	43.1 b4	40.6 b5
	MAP	89.3 b1	64.2 a2	54.9 a3	45.4 a4	43.1 a5
	UC	48.1 d1	28.4 d2	19.9 d3	9.7 d4	0.1 d5
Total						
	AE	95.0 a1	94.4 a1	94.7 a1	89.6 b2	89.2 c2
	AoP	90.7 b3	91.2 b3	94.9 a1	93.2 a2	93.4 a2
	MAP	91.4 b12	91.8 b1	91.9 b1	89.6 b3	91.5 bc23
	UC	90.3 b23	89.3 c3	95.0 a1	94.1 a1	90.9 b2

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each recovery source column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each recovery source row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Supplementary Table 4.1. Deionized water volume (mL) in hydrophobic sands influenced by treatments that include three wetting agents and a water control, and infiltration events applied at 1, 2, 3, 4, and 5 days after treatment (DAT).

Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
	----- Volume (mL) -----				
----Run 1----					
AE [†]	24.5 a3 [‡]	26.7 a12	27.4 a1	27.3 a1	26.0 a2
AoP	21.1 c2	19.1 c3	18.7 c3	22.7 b1	22.1 c12
MAP	22.4 b3	24.9 b1	22.8 b23	23.9 b12	24.1 b1
UC	7.6 d1	7.7 d1	7.9 d1	7.9 c1	7.6 d1
----Run 2----					
AE	24.2 a2	24.6 a2	25.0 a2	26.4 a1	25.3 a12
AoP	20.5 c2	20.0 b2	20.1 c2	22.5 b1	22.4 c1
MAP	22.2 b3	24.5 a1	23.0 b2	23.3 b23	23.6 b12
UC	8.0 d1	7.8 c1	7.9 d1	8.4 c1	7.9 d1

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Supplementary Table 4.2. Deionized water volume (mL) in hydrophobic sands influenced by wetting agents applied and different column depths.

Column Section	AE [†]	AoP	MAP	UC
	----- Volume (mL) -----			
----Run 1----				
1 [§]	33.0 a1 [‡]	32.1 a1	33.4 a1	5.0 d2
2	33.1 a1	25.5 b3	29.2 b2	9.4 a4
3	25.9 b1	16.2 c3	20.4 c2	8.2 b4
4	13.4 c1	9.1 d3	11.5 d2	8.4 ab3
----Run 2----				
1	32.8 b2	30.9 a3	34.3 a1	5.7 c4
2	33.9 a1	25.7 b3	29.0 b2	9.0 b4
3	24.0 c1	19.1 c2	19.8 c2	11.0 a3
4	9.8 d1	8.6 d2	10.2 d1	6.3 c3

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxyated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[§]Column sections: 1 is equivalent to 0 to 6.35 cm, 2 is equivalent to 6.36 to 12.70 cm, 3 is equivalent to 12.71 to 19.05 cm, and 4 is equivalent to 19.06 to 25.4 cm.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Supplementary Table 4.3. Deionized water volume (mL) in hydrophobic sands influenced by the column depth and infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Column Section	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
	----- Volume (mL) -----				
----Run 1----					
1 [§]	25.4 a2 [‡]	25.2 a2	25.2 a2	26.2 a2	27.5 a1
2	24.2 a2	23.3 b2	24.1 a2	25.5 a1	24.3 b2
3	18.6 b1	18.3 c1	16.3 b2	18.6 b1	16.5 c2
4	7.3 c2	11.5 d1	11.2 c1	11.5 c1	11.5 d1
----Run 2----					
1	25.6 a12	25.4 a2	25.4 a2	26.5 a12	26.6 a1
2	23.0 b3	24.1 b23	24.7 a12	25.8 a1	24.4 b2
3	19.3 c1	19.2 c12	17.5 b3	18.1 b23	18.2 c123
4	6.9 d3	8.2 d2	8.3 c2	10.3 c1	9.9 d4

[§]Column sections: 1 is equivalent to 0 to 6.35 cm, 2 is equivalent to 6.36 to 12.70 cm, 3 is equivalent to 12.71 to 19.05 cm, and 4 is equivalent to 19.06 to 25.4 cm.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Supplementary Table 4.4. Deionized water volume (mL) in hydrophobic sand columns influenced by treatments that include three wetting agents and a water control, and infiltration events applied at 1, 2, 3, 4, and 5 days after treatment (DAT).

Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
----- Volume (mL)-----					
----Run 1----					
AE [†]	97.9 a3	106.9 a1	109.5 a1	109.1 a1	104.0 a2
AoP	84.3 c2	76.3 c3	74.8 c3	90.8 c1	88.4 c1
MAP	89.4 b3	99.6 b1	91.1 b3	95.6 b2	96.5 b2
UC	30.2 d1	30.8 d1	31.7 d1	31.8 d1	30.3 d1
----Run 2----					
AE	96.8 a4	98.6 a34	100.0 a23	105.7 a1	101.3 a2
AoP	81.9 c2	79.9 b2	80.3 c2	90.1 c1	89.4 c1
MAP	88.8 b3	98.1 a1	91.8 b2	93.4 b2	94.3 b2
UC	32.1 d1	31.1 c1	31.4 d1	33.5 d1	31.5 d1

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

Supplementary Table 4.5. Cumulative total bromide (Br⁻; mg) recovered from hydrophobic sands, leachate, and the combined total influenced by wetting agents applied and the following infiltration events at 1, 2, 3, 4, and 5 days after treatment (DAT).

Recovery Source	Treatment	1 DAT	2 DAT	3 DAT	4 DAT	5 DAT
----- Total Bromide (mg) -----						
----Run 1----						
Leachate						
	AE [†]	0.0 d5 [‡]	102.0 b4	132.9 b3	165.2 b2	176.0 b1
	AoP	14.2 b4	90.9 c3	117.9 c2	146.2 c1	148.7 c1
	MAP	7.4 c4	82.1 d3	107.8 d2	134.1 d1	138.8 d1
	UC	128.1 a5	187.5 a4	225.4 a3	250.2 a2	270.7 a1
Sand						
	AE	285.0 a1	175.2 c2	143.9 c3	113.9 c4	94.3 c5
	AoP	253.3 c1	188.9 b2	161.3 b3	130.7 b4	121.3 b5
	MAP	275.7 b1	194.2 a2	166.3 a3	135.8 a4	130.7 a5
	UC	142.7 d1	80.5 d2	57.8 d3	27.1 d4	0.1 d5
Total						
	AE	285.0 a1	277.1 a2	276.8 b23	279.1 a12	270.4 a3
	AoP	267.5 b2	279.7 a1	279.1 ab1	276.9 a1	269.9 a2
	MAP	283.1 a1	276.3 a2	274.1 b23	269.9 b23	269.5 a3
	UC	270.8 b3	268.0 b3	285.1 a1	277.3 a2	270.8 a3
----Run 2----						
Leachate						
	AE	0.0 d5	110.6 b4	138.9 b3	153.7 b2	170.1 b1
	AoP	16.2 b5	85.1 c4	126.8 c3	150.3 b2	158.6 c1
	MAP	6.2 c5	82.9 c4	111.1 d3	132.7 c2	142.3 d1
	UC	126.8 a5	182.8 a4	225.1 a3	253.3 a2	272.5 a1
Sand						
	AE	285.0 a1	172.6 c2	145.4 c3	115.1 c4	97.7 c5
	AoP	255.9 c1	188.6 b2	158.0 b3	129.2 b4	121.7 b5
	MAP	268.0 b1	192.5 a2	164.6 a3	136.2 a4	129.2 a5
	UC	144.3 d1	85.2 d2	59.8 d3	29.0 d4	0.1 d5
Total						
	AE	285.0 a1	283.2 a1	284.2 a1	268.8 b2	267.7 c2
	AoP	272.1 b3	273.6 b3	284.8 a1	279.6 a2	580.3 a2
	MAP	274.2 b12	275.4 b1	275.7 b1	268.9 b3	271.4 bc23
	UC	271.0 b23	268.0 c3	285.0 a1	282.3 a1	272.7 b2

[†]AE, Alcohol ethoxylates, Cascade; AoP, Alkoxylated polyols, Primer Select; MAP, Modified alkylated polyol, Revolution; UC, Untreated control.

[‡]Means in each recovery source column, within each run, labeled by different letters are significantly different based on Fisher's Protected LSD ($P \leq 0.05$); means in each recovery source row, within each run, labeled by different numbers are significantly different based on Fisher's Protected LSD ($P \leq 0.05$).

CHAPTER V

Dissertation Study Conclusion

The studies in this dissertation were performed to determine the potential of utilizing wetting agents influence on water's surface tension value to be able to predict their function in a hydrophobic sand. Based on the determination of 23 selected wetting agents surface tension values it was shown that each influences surface tension values differently, therefore, we hypothesized that three categories could be created. Wetting agents surface tension values either fell into under 30 mN m^{-1} , which were hypothesized to have greater influences on water infiltration, from 30 to 40 mN m^{-1} , hypothesized to have a dual influence on both water infiltration and water retention, and then greater than 40 mN m^{-1} , which were hypothesized to have a greater influence on water retention.

Based on that preliminary study, six wetting agent, spanning the various categories, were selected to determine if our hypothesis of differences on water infiltration and rewettability based on their surface tension values. In the laboratory study, we determined that the selected wetting agents did influence infiltration and rewettability differently. Various wetting agents were able to maintain their infiltration rate throughout the entirety of study while other wetting agents had a gradual reduction and evenly loss of infiltration. However, even though differences were seen, no correlation was seen between wetting agent surface tension values and their influence on infiltration and rewettability.

These same six selected wetting agents were tested under field condition, to assess if the results seen in the laboratory study were similar. Between the two locations tested, there was no correlation seen between the wetting agents surface tension values

and their field infiltration rates or water retention. However, it was shown that variations between the locations soil properties, such as porosity and organic matter content, may affect wetting agent performance to a greater effect than previously thought.

Demonstrating why this research is necessary, as dramatic differences in wetting agent performance can be seen location to locations.

Finally, three wetting agents, based on the hypothesized surface tension categories, were selected to assess the influence on water movement through hydrophobic sand columns via a bromide soil tracer. All wetting agents tested did significantly maintain or reduce the amount of leachate as compared to the control of water alone. Additionally, the amount of bromide and water retained in the hydrophobic sand columns were significantly increased in wetting agent columns as compared to water alone. Among wetting agent treatments differences in their ability to reduce leachate and retain increased water and bromide was seen. However, no correlation was seen between the wetting agents surface tension values and their influence on water movement.

Overall, various wetting agents influence surface tension values differently, however, the study performed contradicted our hypothesis that they can predict their performance on water infiltration, rewettability, or retention. Future studies to predict wetting agent performance should focus on other characteristics, such as determining their hydrophilic-lipophilic balance. As well as, the influence of varying soil properties on the performance of wetting agents.

VITA

Matthew C. Fleetwood was born in Morristown, NJ on June 9th, 1993 to Patricia Kelley Fleetwood and Scott Curtis Fleetwood. He moved around throughout his life from New Jersey to Kansas and then to Wisconsin, where he attended high school. In high school he was extremely dedicated to school and sports, including baseball, football and wrestling. He graduated from Pewaukee High School in 2011 and was one of the few students in his class to attend college out of state at the University of Missouri.

When Matt arrived at the University of Missouri, he pledged to the fraternity of Phi Gamma Delta, and started his pursuit of his B.S. degree. While in the fraternity, Matt took on roles on the executive board and formed lifelong friendships with many of his fraternity brothers. In 2015, Matt graduated with the University of Missouri with a Plant Science degree with a double emphasis in Breeding, Biotechnology, and Biology and Crop Management. He then decided to further his education and pursue his Master's degree in Plant, Insect and Microbial Sciences focusing on turfgrass research with Dr. Xi Xiong. During his pursuit of the Master's, Dr. Xiong and Matt decided to combine his Master's work into a Ph.D. focused on the prediction of wetting agent functions based on their influence on water's surface tension. He also was able to take on the role of lab technician which allowed him to experience working with industry cooperator trials and developing turfgrass IPM programs. After receiving his Ph.D., Matt plans to pursue an industry career in either Research and Development or Product Development within the turf and ornamental industry.