

**SOIL WETTING AGENTS INFLUENCES ON SOIL  
HYDROPHOBICITY: THE EFFECTS AND MECHANISMS**

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Doctor of Philosophy

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By  
ENZHAN SONG

Dr. Xi Xiong, Dissertation Supervisor

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The undersigned, appointed by the dean of the Graduate School, have examined the Dissertation entitled:

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HYDROPHOBICITY: THE EFFECTS AND MECHANISMS**

Presented by Enzhan song

A candidate for the degree of

Doctor of Philosophy

And hereby certify that, in their opinion, it is worthy of acceptance.

---

Dr. Xi Xiong

Assistant Professor

---

Dr. Keith Goyne

Associate Professor

---

Dr. Robert Kremer

Professor

---

Dr. Stephen Anderson

Professor

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# **Chapter One**

## **Literature Review**

### **A historical review on soil water repellency**

Soil water repellency (SWR) has been a land management concern since drawing the attention of scientists over a century ago. Initial interests in SWR were purely of scientific curiosity but quickly developed into a practical scientific endeavor worldwide. Previous research related to SWR showed an extreme wide range of topics in various scientific disciplines.

Early studies (before 1900) on the discovery and identification of soil organic matter (humus) (SOM), as well as its decomposition by fungi established the fundamental milestone of later research interests on SWR. As matter of fact, SWR can never be discussed alone without considering SOM. As the most important part of SOM, humic substances were believed to be initially investigated by Achard who attempted to isolate humic substances from SOM in 1786 (Stevensen, 1994). Soon the words ‘humus’ and ‘humic acids’ were introduced by DeSaussure in 1804 and by Dobereiner in 1822 (DeBano, 2000), respectively. The phenomenon known as ‘fairy rings’ was brought up during the early 1900s with studies that investigated fungal decomposition of organic matter (Bayliss, 1911) and discussed the influences of mycelium growth on soil water sorption. The term ‘fairy ring’ was used to describe the particular circular arrangement of plants with enhanced plant growth on the inside of the circle. The extreme case of fairy ring phenomena was often reported to substantially affect plant yield. Decades later, researchers were able to collect quantitative data showing more soil moisture in the healthy ring of plants than the surrounding area (Lawes et al., 1883), suggesting observation of the phenomenon of SWR as what we know today.

Due to the SWR prone nature of sandy soil, scientists from Australia and arid regions of the United States led a wide range of studies during the mid-20th century. Topics on the stability and wetting of soil aggregates, especially the influences from organic matter and microbial activity (Kanivetz and Korneva, 1937; Martin and Waksman, 1940; Swaby, 1949; Waksman, 1938), started to draw greater interest. The Australian scientist Bond (1959) successfully examined the glue-like effect of microbial filaments on the aggregation of sand grains via microscopic techniques. The relationships among SOM, soil microorganisms, and SWR were extensively studied in the 1960s. Australian scientists dedicated their efforts on topics related to microbial filament influences on soil properties (Bond, 1962). Field studies conducted on water-repellent sandy soils (Bond, 1964) revealed a major inducing effect of filamentous algae and fungi on water repellency (Bond and Harris, 1964). Production of water repellency by fungi were also validated by United States scientists (Savage et al., 1969b), who also evaluated the roles of humic acids and polysaccharides on SWR (Savage et al., 1969a). Meanwhile, wildfires emerged as a big concern in southern California regions, particularly in the Los Angeles Basin. Heating processes on fire exposed land were found to intensify/induce SWR and dramatically decrease water infiltration in erosive watersheds (DeBano and Krammes, 1966; Krammes and DeBano, 1965; Scott and Burgy, 1956). Fire induced SWR was also reported in other landscape environments throughout the western United States (DeBano, 1969), such as the forests of Nevada and California (Hussain et al., 1969). Further, significant interactions between soil fungi activities and soil heating during fire were discovered (Savage et al., 1969b).

Additionally, growth of the soil physics discipline contributed significantly to the understanding of water repellency. At the beginning of 20th century, soil physics, especially soil hydrology, began thriving as an important practical science. Soil physicists were able to quantify the concept of water movement in soil, and established the important role of capillary forces in soil hydrology (Richards, 1931; Zunker, 1930). Additionally, with the inspiration by physical–chemical engineering, the nature of low surface tension solids was investigated from a soil science perspective (Bartell and Zuidema, 1936; Wenzel, 1936), along with increasing interests in characterizing contact angles (Bikerman, 1941; Barr et al., 1948). Sequentially, theoretical concepts were developed, including describing capillarity (Miller and Miller, 1956), influences of contact angles and soil water energetics on infiltration (Bodman and Colman, 1943; Fletcher, 1949), and the numerical solution of concentration dependent diffusion equations (Philip, 1957). The most important contribution of these studies was the development of physical quantification methods for characterizing SWR via contact angle methodology. Two significant papers published by Letey et al. in 1962 at the University of California, Los Angeles, established the standard of liquid–solid contact angles measurement (Letey et al., 1962a), and validated the influence of water–solid contact angles on soil water movement (Letey et al., 1962b). One year later, Emerson and Bond (1963) from Australia published a paper which introduced the concept of water entry rate into dry sand and correlated this new index with liquid–solid contact angles. Characterization of water repellency was further standardized using indices such as contact angle–surface tension relationships (Watson and Letey, 1970) and solid–air surface tensions of porous media (Miyamoto and Letey, 1971). More efficient

measurements such as molarity of ethanol droplet (MED) test (King, 1981; Watson and Letey, 1970) and water droplet penetration test (WDPT) (Bisdorf et al., 1993; Dekker and Ritsema, 1994; Van't Woudt, 1959) for quick assessments were also developed. While WDPT determines the persistence of water repellency, the MED test indirectly represents the surface tension of a soil surface based on ethanol concentration.

### **Characteristics, causes and impacts of SWR**

Water repellency or hydrophobicity is the phenomena where a surface repels water into individual droplets (Adam, 1963), thus inhibiting water infiltration into porous medium such as soil. This 'repelling force' is actually not a true physical force but caused by a strong cohesive force within the water body, which is called surface tension or surface-free energy. Under normal conditions (at 20°C), surface tension of water is  $72.75 \times 10^{-3}$  N/m (Parker, 1987), while the surface tension of a hard-solid surface is usually significantly higher and ranges from 500 to  $5000 \times 10^{-3}$  N/m (Zisman, 1964). Surfaces with a surface-free energy  $>72.75 \times 10^{-3}$  N/m possess stronger adhesive forces than cohesive forces within water which sequentially forces attraction and spreading of the contacting water molecules, thus enabling a hydrophilic situation. Most soil minerals have a much higher surface tension than water (Tschapek, 1984), whereas organic materials such as waxes, fatty acids, and other organic polymers often have surface tension  $< 72.75 \times 10^{-3}$  N/m and thus lead to hydrophobicity (Zisman, 1964).

It is well demonstrated by numerous studies that SWR is usually caused by organic matter originating from living or decomposing soil organisms, including plants and microorganisms (Horn et al., 1963; Kolattukudy et al., 1976; Tulloch, 1976).

Hydrophobic organic compounds (HOC) can be divided into two main groups: the

complete hydrophobic hydrocarbons and organic compounds with amphiphilic structure. Substances in the first group have an elongated non-polar carbon chain structure with no positive or negative charges throughout the whole chain and are almost insoluble in water. The water repellent property of the second group is mainly represented by the non-polar end (hydrophobic) of an amphiphilic structure which also has a polar end (hydrophilic) that is often occupied by charged functional groups (e.g., R-COO<sup>-</sup>). Despite being potentially water soluble, amphiphilic molecules can also effectively create hydrophobicity by bonding their polar ends to the original hydrophilic surface and facing their non-polar ends into solution, thus producing a hydrophobic coating (McIntosh and Horne, 1994). Nevertheless, non-polar molecules such as fatty acids, certain waxes, and more complicated humic substances are believed to be the main sources that contribute to hydrophobic coating on water-repellent sands (Franco et al., 2000; Hudson et al., 1994; Ma'shum et al., 1988). It is commonly accepted that fungi are the prime producer of SWR. This relationship was first reported early in 1960s by Bond (1964) and research interests have continued to grow since then. Fungal groups are generally acknowledged microbial factor in the development of soil aggregates (Tisdall and Oades, 1982; Six et al., 2004; Rillig and Mummey, 2006). Fungal mycelium/hyphae was observed to stabilize soil aggregation, while the secretion of hydrophobic substances such as n-alkanes and olefines has been reported (Horn et al., 1963; Kolattukudy et al., 1976; Tulloch, 1976). Fungi group also produces extensive amount of biomass that may be even higher than aboveground biomass production (Fogel and Hunt, 1979). Later work focused on more specific topics such as identification of the role of individual fungal species (Hallett et al.

2006) and the link between basidiomycetes fungi and development of fairy rings on sandy soils (Feeney et al. 2006; York and Canaway, 2000).

Microscopic techniques have been used to better investigate surface hydrophobic coatings; however, inconsistent results were reported. Some studies observed distinctive coatings on hydrophobic particles (Franco et al., 1995) but others did not (Jungerius and de Jong, 1989). Further, coatings were observed on both hydrophobic and hydrophilic particles (Jex et al., 1985; Doerr, 1997). This coating phenomena on soil particles is commonly observed on different soil types with or without SWR, thus the existence of coatings may be irrelevant to SWR (Tschapek, 1984). In the case of absence of coatings on hydrophobic particles, organic coatings may actually exist but are not observable because of extremely thin molecular monolayers which may be undetectable even with scanning electron microscopy (SEM). Ma'shum et al. (1988) reported that several monolayers of organic matter may be required for comprehensive coverage of a mineral grain. However, the actual required mass is very small and the authors were able to induce severe water repellency on sand with only 0.35% by weight of hydrophobic compounds. Others reported induction of severe water repellency via mixing 2 to 5% by weight of organic matter with hydrophilic sand (McGhie and Posner, 1981).

Fire-induced SWR emerged as a thriving concern in the 1960s and 1970s in North America (DeBano, 1981) and the concept of heating processes during wildfire that induce/intensify SWR has been widely established. Based on the results of many laboratory studies, SWR starts to intensify at soil temperatures 175 °C and above, and HOCs are fixed to the soil particles at approximately 250 °C. However, further increases of the soil temperature will facilitate physical-chemical degradation of HOCs (DeBano et

al., 1976; Savage, 1974). In contrast, others observed that SWR was affected (increased) by heating soil at much lower temperatures of 43 °C or 70 °C (Crockford et al., 1991; Dekker et al., 1998). Inconsistent data were observed in different studies, possibly the results of different heating time, soil type, water content, SOM content, and methodology (Nakaya, 1982). The increased SWR during heating was suspected to be caused by either enhanced alignment of the hydrophobic molecules under abnormal high temperature, or release of more HOC such as waxes from organic matter in the soil system onto mineral particle surfaces (Franco et al., 1995).

As discussed previously, SWR-related studies were mainly conducted in areas with sandy soils where maintenance of soil moisture is a concern, such as the southwestern USA (Krammes and Osborn, 1969; Scholl, 1975), Southern and Western Australia (Bond, 1969; Roberts and Carbon, 1971), drier regions in Africa (Rietfeld, 1978; Bishay and Bakhati, 1976), and the Mediterranean (Giovannini and Lucchesi, 1984). However, to present, reporting/monitoring of SWR is usually not incorporated in general soil surveys/analysis, even though scientific research/surveys have proven that water repellency can affect large areas of agriculture lands in arid/semi-arid regions. For instance, it had been reported that 5 million ha of land in Australia was affected by SWR with up to 80% losses in agriculture production (House, 1991; Blackwell, 1993); similarly, 75% of the crop- and grass-land in the Netherlands also exhibited SWR (Dekker and Ritsema, 1994).

Impacts of SWR on soil properties are mainly viewed from the aspect of soil hydrology and can be summarized into three categories:

1. Reduced water infiltration and increased runoff

The most noticed impacts of water are reduced soil infiltration rate (Van Dam et al., 1990; Imeson et al., 1992) and sequentially increased surface flow/runoff (McGhie and Posner, 1980; Crockford et al., 1991; Witter et al., 1991). Example studies include: DeBano (1971) reported 25 times less infiltration capacity of a water-repellent soil, compared to similar but hydrophilic soil; Wallis et al. (1990) also observed that the infiltration capacity on a water-repellent sandy soil was six times less than on the adjacent but less water-repellent soil; Burch et al. (1989) reported a three-fold increase of surface runoff in an Australian eucalyptus forest soil, after water repellency was induced by natural wet-dry process; and Scott and Van Wyk (1990) discovered a subsurface water-repellent layer in a burnt pine forest in South Africa, leading to topsoil saturation and an 2.2 to 7.5% increase in the stormflow response index, compared with the nearby unburnt wettable terrain.

2. Promoted preferential flow

Preferential flow is usually a condensed vertical movement of water in the soil matrix through preferred pathways such as cracks, tunnels, macropores, and unstable wetting fronts (Ritsema et al., 1993). Although this phenomenon is not limited uniquely in water-repellent soil, SWR enhances uneven water movement in the soil profile and forces it into structural or textural preferred flow patterns (Kung, 1990; Ritsema and Dekker, 1994a). Consequently, an uneven wetting front is often created (DeBano, 1971), where water will be channeled via macropores, tunnels, and cracks, by-passing the soil matrix (Burch et al., 1989). Such by-passing but rapid flow routes can potentially limit surface flow even during large precipitation events yet prevent complete wetting of the soil (Walsh

et al. 1995). Bauters et al. (1998) found that sandy soils with SWR often exhibited fingered flow; whereas uniform horizontal infiltration occurred only when ponding head exceeded water-entry pressure of the water-repellent soil. Additionally, the finger flow rate increased with SWR severity.

### 3. Increased soil erosion

Because of reduced infiltration capacity, hydrophobic soils tend to have increased surface flow during rainfall/irrigation events and consequently enhance soil erosion. Many studies have reported increased soil loss on water-repellent land (Megahan and Molitor, 1975; Wells et al., 1979; Morris and Moses, 1987; Shakesby et al., 1993), although it is difficult to isolate and quantify the contribution of SWR on erosion from other factors. Osborn et al. (1964) compared soil losses in burnt and water-repellent plots with adjacent wetting agent-treated, thus less water-repellent plots, under the same conditions. They found at least 12-fold more soil sediment was removed from the water-repellent plots than from the wetting agent-treated, low-repellency plots after precipitation. Scientists also found that the impacts of SWR on erosion depend greatly on the degree of preferential flow of a given hydrophobic matrix (Shakesby et al., 2000). Booker et al. (1993) reported that surface flow was only promoted without presence of by-passing routs, such as cracks, in the water-repellent layer. In contrast, extreme soil loss via land-slides was observed by Booker et al. (1993) on sloped-land where preferential flow enhanced the transfer of water to the subsoil horizons and consequentially caused instability.

Although SWR increased soil erosion was usually observed in most related studies, a protective effect of SWR on erosion was also reported, mainly due to the development of a stable aggregate system (Wallis and Horne, 1992). DeBano (1981)

found that hydrophobic organic materials enhanced aggregate stability by reducing mechanical interference to the aggregate structure. Others also reported improved water stability of water-repellent soil aggregates (Rawitz and Hazan, 1978; Giovannini and Lucchesi, 1983; Capriel et al., 1995).

It has been commonly acknowledged that SWR is prone to associate with coarser soil particles, particularly sandy soils (DeBano, 1991; McGhie and Posner, 1980; Roberts and Carbon, 1971; Wilkinson and Miller, 1978). Coarser particles, such as sand, are more susceptible to develop hydrophobicity in the presence of HOCs due to their significantly smaller ( $>10^5$  times) specific surface area (area/mass) compared with peat and clay (Blackwell, 1993; DeBano, 1971; Giovannini and Lucchesi, 1983; Rowell, 1994). Some studies even reported a positive correlation between particle size and SWR within a soil sample (Crockford et al., 1991), while others reported that SWR is more likely to develop in soils with  $< 10\%$  clay content (DeBano, 1991). Additionally, Hallett et al. (2001) stated that the significantly smaller specific surface area but higher distribution of macropores in sandy soils also provided a preferred habitat for fungal growth rather than bacteria, which may facilitate the development of SWR.

Since the majority of the golf greens are constructed with a sand-based medium, more and more studies were published to address the issue with the wettability of golf greens as related to SWR and localized dry spots (LDS) in Australia, Great Britain, New Zealand, and the United States (Charters, 1980; Hudson et al., 1994; Karnok et al., 1993; Shiels, 1982; Taylor and Blake, 1982; Tucker et al., 1990; Wallis et al., 1989; York and Baldwin, 1992). SWR is also a common issue on pasture grassland in different regions such as Australia (Crockford et al., 1991), Canada (Barrett and Slaymaker, 1989), and the

Netherlands (Dekker and Ritsema, 1994). Although the mechanisms have not been clarified, Schantz and Piemeisel (1917) suspected that the 'fairy rings' forming fungus Basidiomycota may release hydrophobic compounds such as b-diketones (Horn et al., 1963; Kolattukudy et al., 1976; Tulloch, 1976) when decomposing litter and lignins in soils (Scheffer and Schachtschabel, 1989), and thus increase SWR.

### **SWR management strategies**

In order to ameliorate the SWR issue, management strategies were developed, mainly based on: physical, biological, and chemical approaches.

#### ***Physical approaches***

Physical treatments involve mechanical interference of the water repellent soil by: 1) Cultivation, which causes the abrasion of soil particles, thus aids in removal of hydrophobic coatings (Buczko et al., 2006). However, the effect is only temporary and cultivation may cause secondary problems such as erosion in pasture land and elevated greenhouse gas emissions; 2) Aeration, which is commonly used on turf land, with the goal of removing/breakdown of surface thatch/excessive SOM (Beard, 1973; Wallis and Horne, 1992); 3) Maintenance of topsoil moisture by frequent but proper amount of irrigation, based on scientific research results (Cisar et al., 2000; Wallis et al., 1990).

#### ***Biological approaches***

Four strategies were utilized in this category: 1) Proper phenotype selection for drought and water-repellent plant species that will naturally adapt to target soils (Blackwell, 2000); 2) Bioremediation, which utilizes actinobacteria as the consuming

agent of complex HOC such as waxes, thus reducing overall SWR (Dunkelberg et al., 2006; McKenna et al., 2002; Roper, 2004; Williams et al., 1989); 3) Earthworms, which enhances physical mixing of hydrophobic topsoil with wettable subsoil, promotes microbial decomposition by providing already-processed organic matter, and increased water infiltration by earthworm burrows; 4. Stimulation of microbial breakdown of water repellency through management practices such as aeration, compost, lime, and fertilizer applications (Michelson and Franco, 1994; Roper, 2005).

### ***Chemical approaches***

The most effective and popular approaches are chemical treatments, including: 1) addition of small particle minerals mainly clay; 2) soil pH adjustment by liming; and 3) application of wetting agents/surfactants.

### ***Soil claying***

Soil claying is a treatment that involves adding large amounts of clay in the upper water repellent layer by cultivation methods, such as deep plowing, into a clayey subsoil or top dressing with clay to reduce SWR (Blackwell, 2000; Tschapek, 1984), especially for sandy soils (Cann, 2000; Dlapa et al., 2004; Lichner et al., 2002; Li et al., 2008; Ma'shum et al., 1989; McKissock et al., 2000; Roper, 2005; Ward and Oades, 1993). Numerous experiments have been conducted to investigate the effect of clay mineralogy and exchangeable cations on water-repellent soils. These studies have confirmed the significant influence of clay mineralogy on remediating SWR, where clay particles with better ability to disperse during rewetting were more effective at reducing SWR (Ma'shum et al., 1989; McKissock et al., 2000). Additionally, the dispersion of clay

particles is affected by exchangeable cations in soil solution (Lichner et al., 2002; Ward and Oades, 1993). Generally, the tendency to flocculate increases with increasing cationic charge (Lichner et al., 2002; Ward and Oades, 1993). Currently, soil claying is mainly used in water-repellent sandy soil as an indirect remediation technique because this approach physically diminishes the SWR instead of directly removing or breaking down HOCs (Doerr et al., 2006). However, the secondary effects from soil claying may bring long-term benefits on aspects such as increased soil fertility and microbiological activity (Blackwell, 2000).

#### *Liming/high pH treatment*

The purpose of liming (lime amendment) in the particular case of remediating SWR is to raise the soil pH to microbiologically favorable neutral levels, especially in acidic soils (Kennedy et al., 2004; Lupwayi et al., 2009). More than a 10-fold increase of wax-degrading bacteria populations in lime amended soils was reported by Roper (2005). Sequentially, the enhanced microorganism diversity and community stimulates HOC decomposition. High pH treatment on water repellent sand-based golf greens was tested by Karnok et al. (1993) who successfully reduced SWR by saturating the topsoil with 0.1M NaOH, followed by flushing the chemical out of the system with a pore volume of water. However, the potential phytotoxicity of NaOH remains a concern. Other potential issues with liming or high pH treatments include potentially altered beneficial microbial communities (Pawlett et al., 2009), excessive loss of organic matter, and increased greenhouse gas emissions.

#### *Application of wetting agents/surfactants*

Surfactants are amphiphilic molecules with double-affinity: a polar-nonpolar coexistence which is represented by the two Greek language roots ‘amphi’ (‘double’, ‘around’, or ‘both ends’) and ‘philos’ (affinity, relationship) in the word ‘amphiphile’ (Winsor, 1954). One side of the molecule has a polar characteristic which usually contains variable atoms that form versatile organic functional groups. On the other side is a nonpolar tail generally consisting of alkyl chains as well as rings and multi-bonded structures. Consequently, the polar side will have a high affinity for any polar phases (e.g. water) usually through dipole interactions, ionic bonding, or hydrogen bonding. The hydrophobic portion of the amphiphile, often called the hydrophobe, has strong affinity for nonpolar phases and interacts with nonpolar phases via physical forces such as hydrophobic and van der Waals interactions. While we know that ‘surfactants’, short for surface-active-agents, activate the ‘surface’ between a condensed phase (e.g. solid) and gas phase or the ‘interface’ between two condensed phases, the polar-nonpolar dual affinity needs to reduce the surface/interface tension (Schwartz and Perry, 1978). Although surfactants are often grouped according to their use such as detergents, cosmetics, pharmaceuticals, paints, foods, and petroleum production additives, it is more accepted and scientifically correct to classify them based on variable natures (charges after dissociation in water and molecular structures) of their polar heads/hydrophilic heads. The two most mentioned groups are ionic and nonionic surfactants.

Nonionic surfactants have been used as the primary wetting agent compounds. As the name indicates, nonionic surfactants do not form ions in aqueous solution, because their hydrophilic heads such as alcohol, ether, ester, or amide functional groups are integrated with the polar tail (Schick, 1987). Nonionic surfactants are often used as

detergents, wetting agents, emulsifiers for pharmaceuticals, cosmetics and food products due to their low toxicity. When used as soil wetting agents, the long chain polymer structures of nonionic surfactants can be easily manipulated for desired molecular weights, hydrophilic-lipophilic ratio, and solubility. Numerous studies have been published since the 1960s on topics related to evaluating the effects of surfactants on turfgrass-based sandy soils. Multiple studies aimed at comparing the efficacy of commonly used wetting agents have been conducted, but inconsistent results were often observed even under similar soil type or within the same surfactant groups (Henle et al., 2007; Leinauer et al., 2007; Soldat et al., 2010). The performance was dramatically influenced by various formulation blends, application rates, and environmental conditions (Cisar et al., 2000; Henle et al., 2007; Kostka et al., 2007).

There are mainly five chemical groupings of nonionic wetting agents on the market.

1. Polyoxyethylene (POE) and alkylphenol ethoxylate (APE) formulations.  
A POE or APE formulation is the original wetting agent chemistry that was first developed and introduced as Aqua-Gro in 1954 (Zontek and Kostka, 2012).  
These types of wetting agents were developed to enhance water movement (infiltration) and maintain even water distribution. Commercial POEs wetting agents include: APSA-80, E-ZWet, FloThru, Injector, Lesco Wet, Mizer, One Putt, PenMaxx, Surfside, Water-in, and Wet-Sol (Zontek and Kostka, 2012).
2. Block co-polymer formulations.  
With the development of material science, manufacturers can incorporate multiple homopolymers into build blocked coexisting-polymers via copolymerization techniques. Usually, a co-polymer unit consists of two or three distinct blocks and these chemicals are called di-block or tri-block copolymers,

respectively (Davis and Matyjaszewski, 2002). This multiple-functional-group integrated structure of block co-polymer wetting agents enables them to improve SWR mediation efficiency. Commercially, two main chemical structures are used: the normal (straight) orientation with POE–polyoxypropylene (POP)–POE structure, and the reversed blocking orientation with POP-POE-POP structure (Ortona et al., 2006). Straight block co-polymers facilitate water movement in the soil while reverse block co-polymers help with soil water retention. Examples of straight block co-polymer formulated wetting agents include: Brilliance, Capacity, Cascade Plus, Conduit 90, Hydro-Wet, LescoFlo Ultra, Remain, and Sixteen90; examples of reverse block co-polymer wetting agents include: Primer Select, Magnus, ReLoad, Rely II, Respond 3, Retain, TriCure AD, and TriCure Micro. Manufacturers also blend the two types of polymers for balanced water infiltration and water retention, example products include: Aqueduct, Resurge, and ReWet (Zontek and Kostka, 2012).

### 3. Alkyl polyglucoside (APG) formulations

Wetting agents made of APG are derived from sugars and fatty alcohols (Hill et al., 2008). While the raw materials are usually starch and fat, the sugar portion of the molecules contribute to the hydrophilic end and fatty acid alkyl groups form the hydrophobic end in final wetting agent products (Iglauer et al., 2010). This chemistry was first introduced in 2000 and has shown synergistic wetting/infiltration effect when blend with straight block co-polymers (Zontek and Kostka, 2012). Example wetting agents with a blend of alkyl polyglucoside and straight block co-polymers include: Dispatch Injectable, Dispatch Sprayable, and Tournament-Ready.

4. Modified methyl capped block co-polymers  
Structurally, this group of wetting agents has modified terminal groups where the alcohol hydroxyl functional groups (-OH) are replaced by methyl caps (-CH<sub>3</sub>) (Kostka et al., 2008). Generally, hydroxyl groups are hydrophilic and methyl groups are hydrophobic, leading to slight hydrophobicity which helps to avoid excessive infiltration and improve the wetting pattern (Kostka et al., 2008; Zontek and Kostka, 2012). A patent of this wetting agent group in the U.S. and worldwide was initiated in 2005 (Kostka and Schuermann, 2005), although this chemistry was introduced into turf industry in 2004 and sold under the brand name: Revolution.

5. Organic solvent and surfactant complexes.

This special group of wetting agents has a highly-branched structure with humic-substance-like high molecular weight and multiple interactive sites. Long term SWR control is expected, as the complex branching structure is more persistent under microbial degradation while the breakdown molecules can still perform as normal simple linear wetting agents that mitigate SWR (Zontek and Kostka, 2012). This group of wetting agents was developed and patented by Milliken & Co. in 2005 and manufactured by Aqua-Aid in 2003 with the goal of removing/breaking hydrophobic humic substances in top soil layer (Moore et al., 2006). Products are mainly under the Aqua-Aid product line as OARS and PBS-150.

Application of surfactants was initially introduced to agriculture in the early-1950s (De Boodt, 1972), and has been the most efficient treatment for SWR control. Wetting agents were originally patented as AquaGro® in 1954 which was manufactured by

blending non-ionic surfactants such as alkylphenol ethoxylate (APE). More recently, formulations with ethylene oxide and propylene oxide (EO/PO) block copolymers were utilized (Alexandridis and Hatton, 1995; Bates and Fredrickson, 1990; Green et al., 1997; Piirma, 1992). The purpose of applying wetting agents/surfactants was to increase soil water movement (infiltration), promote homogeneous soil moisture, and if possible, prevent the development of SWR.

While effectively reducing SWR in sandy soils, wetting agents tend to have short-term residual effects, and repeated applications are often required regularly throughout the warmer seasons. Wetting agents are also costly, thus it is not an economic solution for agricultural scenarios such as crop production and pasture land. One of the major concerns is the potential impact of surfactants on plant physiology, such as plant cell growth (Haapala, 1970), seed germination and development (Burrige and Jorgensen, 1971; Miyamoto and Bird, 1978), and root growth (Valoras et al., 1974). Other interesting but unclear aspects related to the consequences of soil surfactant application include: the impact to soil structure (Hallett, 2007; Mustafa and Letey, 1969; von Lutzow et al., 2006); soil moisture/water potential balancing (Dekker et al.; 2005); distribution patterns of agrochemicals (Larsbo et al., 2008; Nektarios, 2002; Sharma et al., 1985); and soil microbial communities (Müllera and Deurerb, 2011). As a result, it is important to investigate the potential benefits and negative impacts when using surfactants in agricultural scenarios with comprehensive consideration of not only economic profits but also ecological impacts.

## **Objectives**

Despite the long history of using wetting agents on turf, detailed research documenting the influence of wetting agents on soil hydrology (physics) and investigation of chemical/physical activity mechanisms at the surfactant-hydrophobic sand interface is limited. The amphiphilic property of wetting agents was considered as the origin of their mode of action where the sorption of surfactant ingredients onto the sand surface is expected. Further, wetting agents/surfactants have been considered as potential solvents for extraction of HOCs from soil; thus, relatively newer products were developed with the goal of removing SWR caused by HOCs.

This dissertation study was conducted to investigate: 1) influences of selected wetting agents on water infiltration into water-repellent sand, in correlation with liquid surface tension and liquid-solid contact angle properties; 2) effects of selected wetting agents on hydrophobic organic coatings and underlying working mechanisms, utilizing organic carbon analysis and electron microscopy techniques; and 3) impacts of repeated soil surfactant applications to the soil microbial community/diversity under field conditions, utilizing phospholipid fatty acids (PLFA) analysis.

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## Chapter II: Part One

### Wetting Agent Influence on Water Infiltration into Hydrophobic Sand: I.

#### Rewettability

Enzhan Song<sup>1</sup>, Keith W. Goyne<sup>2</sup>, Robert J. Kremer<sup>2</sup>, Stephen H. Anderson<sup>2</sup>, Xi Xiong<sup>1\*</sup>

<sup>1</sup>Division of Plant Sciences, University of Missouri, Columbia, MO 65211, USA

<sup>2</sup>School of Natural Resources, University of Missouri, Columbia, MO 65211, USA

#### Abstract

Soil water repellency causes non-uniform water infiltration at slow flow rates, which leads to localized dry spot (LDS) on golf course putting greens. Wetting agents are the primary tool used to reduce soil water repellency on golf courses. Field experiments evaluating the efficacy of wetting agents often result in inconsistent conclusions due to variable environmental conditions, management intensity, and level of hydrophobicity. This study used octadecylamine treated sand, which exhibits stable and consistent water repellency, to test the influence of six commercially available wetting agents on water infiltration and sand rewettability. Replicated and repeated experiments were conducted using an infiltration tube system with a 4.4-cm ponding depth ( $h_0$ ). Results showed that Cascade Plus, Tournament-Ready, and Hydro-Wet solutions exhibited significantly faster infiltration with steady flow rates at 35 mm min<sup>-1</sup> or more, followed by Revolution and LescoFlo Ultra with a 25 mm min<sup>-1</sup> steady flow rate. All treatments enhanced infiltration, but rewettability varied among tested wetting agents following drying cycles at 55 °C until treated sand columns reached a constant weight. After three dry–wet cycles, LescoFlo Ultra treated sand exhibited the best rewettability with a steady flow rate at 34 mm min<sup>-1</sup>. In contrast, treatment with Surfside 37 resulted in limited rewettability; water

did not infiltrate after the second dry–wet cycle. Results suggest that there are significant differences in infiltration and rewettability among the wetting agents tested in this study. It is advised that specific management needs deserve consideration before selecting the appropriate wetting agent.

## **Introduction**

Soil water repellency is a widespread problem affecting pastures, agronomic fields, forests and other natural areas especially where sandy soil is abundant (Dekker et al., 2005a; Larsbo et al., 2008). Within the turf community, water-repellent soil is known to cause localized dry spot (LDS) on sand-based putting greens on golf courses (Wilkinson and Miller, 1978). Regardless of management intensity, water repellency will eventually develop, and LDS may be observed in sand-based greens as few as six months after construction (Tucker et al., 1990). Without wetting agent treatment, water bypasses hydrophobic rootzones and ultimately leads to the death of turfgrass plants in the affected area. Evidence suggests that the coating of hydrophobic organic compounds on soil particles is the main cause of soil water repellency (Doerr et al., 2000; Miller and Wilkinson, 1977; Roberts and Carbon, 1972). This phenomenon is more common on sand-based greens due to the small specific surface area of sand particles (Karnok and Tucker, 1989; Larsbo et al., 2008).

A water-repellent soil cannot wet spontaneously when in contact with water, unless a positive hydraulic pressure is applied to force liquid into the soil (Bauters et al., 2000; Wang et al., 1998). Infiltration into water-repellent soil is often accompanied by preferential flow, which is driven by an unstable wetting front and causes non-uniform

distribution of water within the rootzone (Nieber, 1996; Parlange and Hill, 1976). A relatively high positive hydraulic pressure, approximately three times greater than the water entry pressure head ( $h_w$ ), must be applied to increase the hydraulic conductivity ( $K$ ) of water-repellent soils to a level similar to the corresponding wettable soil (Feng et al., 2001; Wang et al., 2000). This solution, however, is typically impractical for routine management of a green.

An alternative solution to remedy LDS involves using wetting agents (Karnok and Tucker, 1989; Kostka, 2000). Approximately 98% of golf course superintendents in the U. S. have experience using wetting agents (Karnok, 2006). Wetting agents are amphiphilic compounds and within soils, the hydrophobic (non-polar) portions of the compounds adhere to hydrophobic sand surfaces, while the hydrophilic (polar) portion of the compound interacts with water molecules. By attaching to their hydrophobic surfaces, wetting agents alter soil hydrophobicity and can potentially transform water-repellent soil into a more wettable growing media (Cisar et al., 2000; Dekker et al., 2005b; Karnok et al., 2004; Kostka, 2000). Subsequently, wetting agent applications typically improve water infiltration into water-repellent soil.

Despite the widespread use of wetting agents, detailed research documenting the influence of wetting agents on water infiltration into water-repellent, sand-based greens is limited (Throssell, 2005). One of the challenges that has limited such research is variation in the degree of hydrophobicity under field conditions (Throssell, 2005). Other factors that complicate this issue include the time-consuming procedures for infiltration measurements, such as use of the double ring infiltrometer technique (Gregory et al., 2005; Lai and Ren, 2007). Additionally, temporal changes in water repellency can create

a confounding effect, as the degree of repellency for some soils can be changed after contact with water over time (Feng et al., 2001). Therefore, the objectives of this study were to utilize consistently water-repellent sand to evaluate water infiltration and sand rewettability as influenced by selected wetting agents.

## **Materials and Methods**

Water-repellent sand was developed following procedures described by Bauters et al. (1998) and Bradford and Leij (1996). Washed silica sand that meets the United States Golf Association (USGA) specifications for putting green construction (USGA, 2004) was used in this study. Particle distribution of the sand was 5% very coarse sand, 90% combination of coarse and medium sand, and 3.5% fine sand. Total porosity was determined to be 40% with 25% air-filled pores at a bulk density ( $D_b$ ) of  $1.7 \text{ g cm}^{-3}$  (Nimmo, 2004). A mass of 120 kg of sand was mixed with 90 g octadecylamine (N,N-Dimethyl-n-octadecylamine) in 60 L tap water using a concrete mixer. After mixing for 24 h, the sand was dried in an oven at  $75 \text{ }^\circ\text{C}$  for 24 h. The sand was then rinsed three times with tap water to remove excessive octadecylamine, and dried again at  $75 \text{ }^\circ\text{C}$  for an additional 24 h. The treated sand was thoroughly mixed and stored for the experiments.

Hydrophobicity of the treated sand was determined using the water droplet penetration test (WDPT) (Bisdom et al., 1993) and the molarity of ethanol droplet test (MED) (King, 1981; Watson and Letey, 1970) after sand was packed to a  $D_b$  of  $1.7 \text{ g cm}^{-3}$ . The treated sand exhibited a stable water repellency, i.e., the degree of repellency did not change after contact with water (Carrillo, et al., 2000); tap water droplets never dissipated and eventually evaporated. The MED value of the treated sand was 7.2, which

surpasses the threshold value of severe hydrophobicity ( $MED = 4.0$ ) (Karnok and Tucker, 2001).

The treated sand was also measured for liquid-solid contact angle ( $\theta$ ) and  $h_w$ , because both factors affect infiltration. The  $\theta$  of tap water was  $101^\circ$ , which was determined by using an Attension Theta Lite tensiometer (Biolin Scientific, Inc., Linthicum Heights, MD). The  $h_w$  was determined to be 8.1 cm using the water-ponding method developed by Wang et al. (1998). All experiments conducted for this study utilized the same lot of water-repellent sand.

For the infiltration measurements, a system was built using Harvel Clear PVC tubes (Georg Fischer Harvel LLC, Easton, PA) with a 5.08 cm inner diameter and 0.48 cm wall thickness. Tubes were cut to lengths of 20 cm or 50 cm for use as sand columns and for holding treatment solutions, respectively. A fine fabric screen was capped at the bottom of the 20 cm tubes to retain the sand and permit air exchange. A no-hub coupling (5.08 cm inner diameter and 10 cm long) (Fernco Inc., Davison, MI) was used to connect the sand column to the bottom of the liquid column. To prevent preferential flow at the contact of sand and column walls, the interior of the tubes was coated with Teflon Non-Stick Dry-Film Lubricant (DuPont, Wilmington, DE). Treated sand was slowly added into columns in three separate events to fill approximately one third volume of the column for each event. The column was gently tapped on a hard surface while pouring the sand to achieve a  $D_b$  of  $1.7 \text{ g cm}^{-3}$ . A consistent ponding depth ( $h_o$ ) was maintained by placing a Mariotte bottle on a scale at an elevated height with solutions transported into the infiltration tube by syphon. The change in mass of solution in the Mariotte bottle ( $\Delta v$ )

over a time period ( $\Delta t$ ) was recorded and used to calculate the infiltration rate ( $i$ ):

$$i = \frac{\Delta v}{r^2 * \pi * \Delta t} \quad [1]$$

where  $r$  is the inner radius of the tube. A  $h_o$  of 4.4 cm, which was established after preliminary studies, was maintained during all experiments. The  $\Delta v$  was recorded every min ( $\Delta t$ ) for 30 min for each treatment. The  $K$  was calculated by dividing the steady flow rate by the hydraulic head gradient across the sand column:

$$K = \frac{i_c * L}{\Delta h} \quad [2]$$

where  $i_c$  is the steady infiltration rate, and  $\Delta h/L$  is the hydraulic gradient across the sand column (Reynolds and Elerick, 2002). Seepage time ( $T_s$ ) was recorded as the time required for water to first exit the bottom of the sand column.

The six wetting agents included in this study were Cascade Plus (10% alcohol ethoxylates, 90% polyethylene, and polypropylene glycols), Hydro-Wet (87.5% blend of poloxanlene, 2-butoxyethanol), LescoFlo Ultra (90% polyether polyol and 10% glycol ether), Revolution (100% modified alkylated polyol), Surfside 37 [37% nonylphenoxypoly (ethyleneoxy) ethanol, 18 % polyoxyethylene esters of cyclic acid, and 14% polyethylene glycol], and Tournament-Ready (a blend of nonionic carbohydrate surfactants, polyoxyethylene-polyoxypropylene glycol, and polydimethylsiloxane). Infiltration of the six wetting agent solutions was measured following application at rates equivalent to ¼ of the corresponding label rates (Table 2.1). The ¼ label rates were chosen based on a series of preliminary studies, as infiltration is influenced by factors such as  $h_o$  and wetting agent concentration, to ensure a relatively slow infiltration rate that could be recorded for all tested wetting agents. Infiltration was also conducted using water-only treatment at the same  $h_o$  of 4.4 cm. However, water did not infiltrate into the

hydrophobic sand, because an  $h_o$  of 8.1 cm was required for infiltration, which was described above. Thus, no infiltration data were collected for water-only untreated control.

After measuring infiltration with the wetting agent solutions, sand columns were carefully disassembled and placed in an oven at 55°C until a constant weight was reached. The dry, wetting-agent-treated sand columns were reattached to the infiltration system without disturbing the sand, and tap water was applied with the same  $h_o$  (4.4 cm) to investigate re-wettability. This process was repeated twice for a total of three dry-wet cycles for each wetting-agent-treated sand column. All experiments were conducted in the laboratory at 22 °C.

The experimental design for this study was a completely randomized design with three replications, and the entire study was performed twice. Analysis of variance was conducted using the Proc Mixed procedure of SAS 9.2 (SAS Institute, Cary, NC). There were no significant treatment by run interactions for any measurement; thus, data were pooled over the two studies and significant mean separations were carried out based on Fisher's Protected LSD at  $P = 0.05$ .

## **Results and Discussion**

### ***Wetting agent effects on infiltration***

Infiltration of the six wetting agent solutions (Table 2.1) into the 20 cm hydrophobic sand columns under a constant  $h_o$  of 4.4 cm were calculated and are presented as a function of time in Fig. 2.1. The infiltration pattern of all wetting agent solutions showed a rapid increase before reaching a steady flow rate and after the initiation of seepage from the column. This trend is different from a wettable soil in

which the infiltration rate typically decreases over time (Wang et al., 2000), but is consistent with infiltration patterns observed in water-repellent soils (Feng et al., 2001; 2002; Wang et al., 2000). It is unlikely that the increase in infiltration rate over time is due to the release of organic coatings from the sand particles by the wetting agents (Letey et al., 1962), because the hydrophobic sand used in this experiment exhibited stable water repellency after contact with water (Carrillo et al., 2000). Our results support the explanation proposed by Feng et al. (2001), who concluded that as solution infiltrates into the water-repellent soil, the hydraulic head increases as the depth of wetting front increases, which results in an increase in soil water content (Carrillo et al., 2000), and consequently an increase in infiltration.

Despite a similar pattern, infiltration of the six tested wetting agent solutions showed distinct rates (Fig 2.1). Cascade Plus, Tournament-Ready, and Hydro-Wet infiltrated quickly and reached a steady flow rate of  $35 \text{ mm min}^{-1}$  or greater within nine min after ponding. Revolution showed an intermediate infiltration rate and columns treated with this product reached a steady infiltration rate of  $25 \text{ mm min}^{-1}$  within 15 min of ponding. Surfside 37 showed the slowest infiltration rate ( $17 \text{ mm min}^{-1}$ ) and did not reach a steady flow rate until 20 min after ponding. Previous research found that infiltration pattern and rate of water-repellent soils are correlated with the ratio of  $h_o$  to required liquid entry pressure head ( $h_p$ ); increasing the  $h_o/h_p$  ratio increases infiltration rate (Feng et al., 2001). Because  $h_o$  was maintained at a consistent level for all experiments, variation in infiltration rate is likely due to the modification in degree of water repellency caused by wetting agent adsorption to sand particles (Feng, et al., 2002). As the degree of water repellency affected the required  $h_p$ , adsorption of the wetting

agents to the sand particles subsequently changed the  $h_p$  necessary for the solutions infiltrating into the water-repellent sand (Carrillo et al., 2000).

Different from other wetting agents, the infiltration pattern of LescoFlo Ultra exhibited an increase followed by a decrease in flow rate before reaching a steady flow rate similar to Revolution. The initial increase in infiltration is typical of infiltration patterns for water-repellent soils, but the following decrease before reaching a steady flow rate is more typical of a wettable soil. Even for water-repellent soils, Feng et al. (2001) showed that the infiltration pattern could transform from increasing through time to decreasing through time, which is typical of a wettable soil when the ratio of  $h_0/h_p$  is greater than the critical value of 2.6. It is likely that the initial adsorption of LescoFlo Ultra resulted in a greater reduction in water repellency, which produced a more wettable sand.

After a certain period of ponding, wetting agent solutions started to seep out of the sand columns. Significant differences in  $T_s$  were observed among the wetting agents evaluated (Table 2.1). Wetting agents that infiltrated quickly, such as Cascade Plus, seeped out in less than 50 sec after ponding, compared with wetting agents that infiltrated slower, such as Surfside 37, which took approximately twice as long for initial seepage.

Hydraulic conductivity was calculated based on the steady infiltration rate (Table 2.1). Similar to the results of  $T_s$ , significant differences were found in  $K$  among the wetting agents evaluated. Wetting agents with shorter  $T_s$  resulted in higher  $K$ , such as Cascade Plus, which showed a two times greater  $K$  value compared to Surfside 37. Although  $K$  values of the evaluated wetting agents ranged from 14 to 30 mm min<sup>-1</sup>, they

all meet the USGA suggested minimum saturated hydraulic conductivity ( $K_{sat}$ ) of 2.5 mm  $\text{min}^{-1}$  for a putting green rootzone (USGA, 2004).

### ***Wetting agent effects on re-wettability***

After three dry-wet cycles, water infiltration rates at the same  $h_o$  (4.4 cm) into wetting-agent-treated sand columns are presented as a function of time after 1, 2, and 3 dry-wet cycles in Figures 2.2. a, b, and c, respectively. Similar to the infiltration of wetting agent solutions (Fig. 2.1), water infiltration into the water-repellent sand columns after dry-wet cycles showed an initial rapid increase before reaching a relatively steady flow rate. This result is different from that of Feng et al. (2002) who reported that water infiltration into wetting-agent-treated sand columns decreased over time, which is typical for wettable soils. However, the  $h_o$  was 20 cm in the study conducted by Feng et al. (2001), which was four times greater than the 4.4 cm  $h_o$  used in this study.

The six wetting agents evaluated showed distinct differences in flow after rewetting the wetting-agent-treated sand columns. LescoFlo Ultra and Cascade Plus were the only two wetting agents that maintained re-wettability after three dry-wet cycles (Fig. 2.2c). Tournament-Ready and Revolution treated sand columns showed a progressive decline in steady infiltration rate after the first two dry-wet cycles, and water did not infiltrate after the third drying event (Fig. 2.2b and c). The least degree of re-wettability resulted from Hydro-Wet and Surfside 37 treated sand columns, where minimal infiltration was observed after only one dry-wet cycle (Fig. 2.2a).

Compared to the infiltration of the wetting agent solutions (Fig. 2.1), the rate of water infiltration into LescoFlo Ultra treated columns showed a 45% increase after the first drying event (Fig 2.2a). This result is in agreement with Feng et al. (2002), who

reported that water-repellent sand treated with some wetting agents exhibited an increase in rewet flow rate compared with the original infiltration of wetting agent solutions.

LescoFlo Ultra treated sand columns maintained a  $34 \text{ mm min}^{-1}$  steady flow rate, even after three dry-wet cycles (Fig. 2.2c). Cascade Plus treated sand maintained a steady flow rate of  $25 \text{ mm min}^{-1}$  after the final dry-wet cycle.

Seepage time results showed a similar trend (Table 2.2). Water did not seep out from Hydro-Wet and Surfside 37 treated columns after the second drying event, or from Revolution and Tournament-Ready treated columns after the third drying event.

Compared to the  $T_s$  of wetting agent solutions prior to drying, longer times (67 to 635 sec) were needed for water to seep out of wetting-agent-treated columns after the first drying event. For sand columns previously treated with Cascade Plus or LescoFlo Ultra, the  $T_s$  increased progressively and was approximately two to four times greater after three dry-wet cycles compared to the  $T_s$  after one drying event.

Similarly, sand columns treated with Cascade Plus or LescoFlo Ultra maintained a  $K$  of  $21 \text{ mm min}^{-1}$  or greater, even after three dry-wet cycles (Table 2.2). Hydraulic conductivity was not calculated for Surfside 37 and Hydro-Wet treated sand columns after one dry-wet cycle, or for Revolution and Tournament-Ready treated sand columns after two dry-wet cycles, because water could not penetrate these treated columns. Preferential flow ( $5 \text{ mm min}^{-1}$  or less) (Fig. 2.2b) was observed through the transparent PVC tube in columns treated with these wetting agents, which led to a slow increase in infiltration even after 2 h of ponding (Fig. 2.2b). This result supports the findings of Carrillo et al. (2000), Feng et al. (2001), and Wang et al. (2000), who indicated that the

occurrence of preferential flow in water-repellent soils is associated with slow infiltration and an increase in soil water content over time.

Collectively, our results demonstrate that more wettable soil conditions can be obtained by using certain wetting agents, such as Cascade Plus and LescoFlo Ultra. The label of LescoFlo Ultra suggests a season-long residual effect, compared with most other wetting agents, which require repeat applications at a maximum 30 d interval. Our results also agree with field data reported by Cisar et al. (2000) who showed that one application of Cascade Plus and LescoFlo Ultra in May resulted in less than 10% LDS in August, compared to 93% LDS in untreated plots. Another study conducted by Karnok and Tucker (2008) found that with reduced irrigation, plots treated with two applications of Cascade Plus in July maintained a steady soil moisture level (15%) three months after the applications, while Surfside 37 treated plots only maintained a steady moisture level for three weeks.

## **Conclusions**

All tested wetting agents improved infiltration into water-repellent USGA grade sand, compared with water-only applications which did not infiltrate into the water-repellent sand at 4.4 cm  $h_o$  in this experiment. However, significant differences in infiltration pattern, rate, and effects on re-wettability occurred among the six wetting agents. Treatments with LescoFlo Ultra and Cascade Plus maintained stable re-wettability of water-repellent sand after three dry-wet cycles. In comparison, Surfside 37 exhibited a minimal residual effect; water did not seep out of the sand columns after a single drying event. Although differences in infiltration and re-wettability are evident among tested wetting agents, it is important to note that besides facilitating infiltration,

golf course superintendents also use wetting agents for a wide range of purposes, such as improving water retention, promoting uniform water distribution within the rootzone, and reducing dew and frost formation. An ideal wetting agent product would maintain a balance between water retention and infiltration. Future research is needed to elucidate the complex effects of wetting agents on turfgrass plant growth in water-repellent soil.

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**Table 2.1.** Seepage time ( $T_s$ )<sup>†</sup> and hydraulic conductivity ( $K$ ) influenced by various wetting agents at 4.4 cm ponding depth infiltrated into 20-cm water-repellent sand columns<sup>‡</sup>.

Wetting agent	Concentration <sup>§</sup>	$T_s$	$K$
	g L <sup>-1</sup>	sec	mm min <sup>-1</sup>
Cascade Plus	7.73	46e <sup>¶</sup>	30a
Hydro-Wet	3.06	90b	29ab
LescoFlo Ultra	7.73	57d	20c
Revolution	5.74	80c	20c
Surfside 37	6.19	137a	14d
Tournament-Ready	7.73	53d	28b

<sup>†</sup> Seepage time = required time for the initial water to exit the bottom of the sand column.

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

<sup>§</sup> The wetting agent concentrations are equivalent to 1/4 of label rates for each product.

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

**Table 2.2.** Seepage time ( $T_s$ )<sup>†</sup> and hydraulic conductivity ( $K$ ) of water at 4.4 cm ponding depth infiltrated into 20-cm water repellent sand columns previously treated with wetting agents and dried at 55 °C for 1, 2, and 3 dry-wet cycles<sup>‡</sup>.

Treatment	Concentration <sup>§</sup>	$T_s$			$K$		
		1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	3 <sup>rd</sup> cycle	1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle	3 <sup>rd</sup> cycle
	g L <sup>-1</sup>	-----	sec	-----	-----	mm min <sup>-1</sup>	-----
Cascade Plus	7.73	69c <sup>¶</sup>	153c	292a	30a	26b	21b
Hydro-Wet	3.06	441b	- <sup>#</sup>	-	-	-	-
LescoFlo Ultra	7.73	67c	96d	111b	30a	33a	28a
Revolution	5.74	89c	713b	-	20b	-	-
Surfside 37	6.19	653a	-	-	-	-	-
Tournament-Ready	7.73	81c	805a	-	22b	-	-

<sup>†</sup> Seepage time = required time for the initial water to exit the bottom of the sand column.

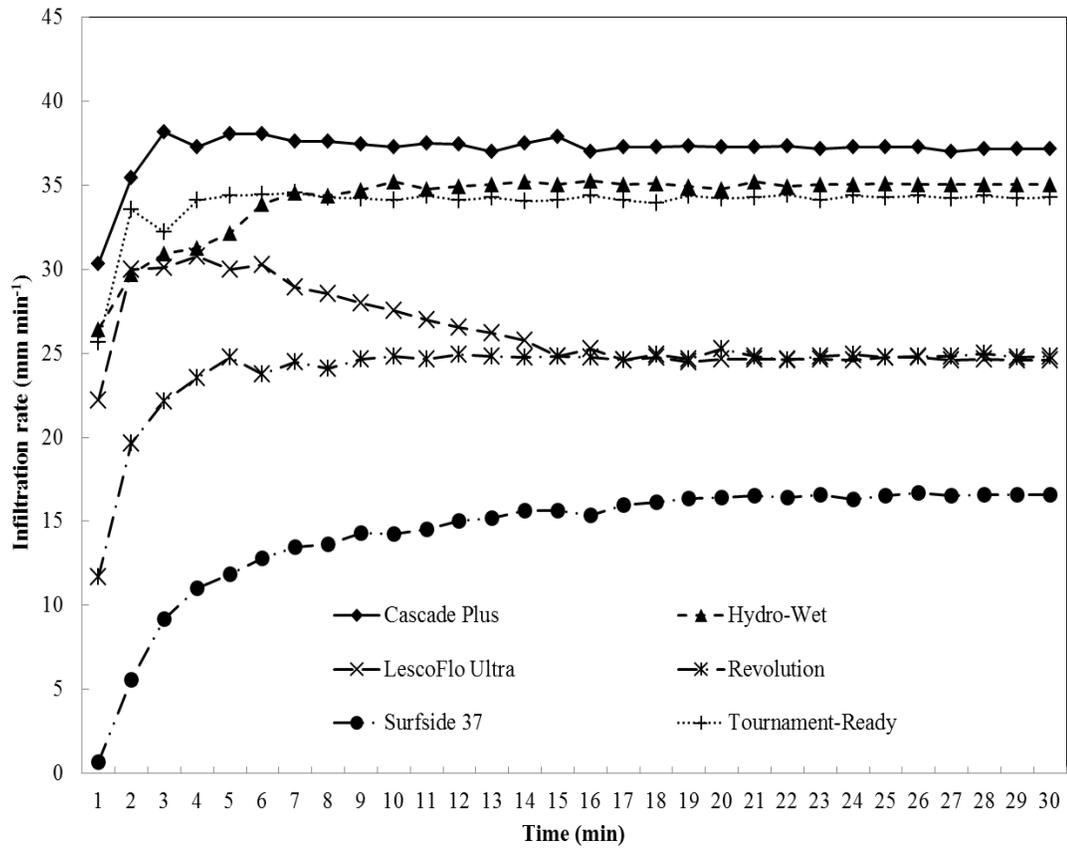
<sup>‡</sup> Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at 4.4 cm ponding depth, thus no data were collected.

<sup>§</sup> The wetting agent concentrations are equivalent to ¼ of label rates for each product.

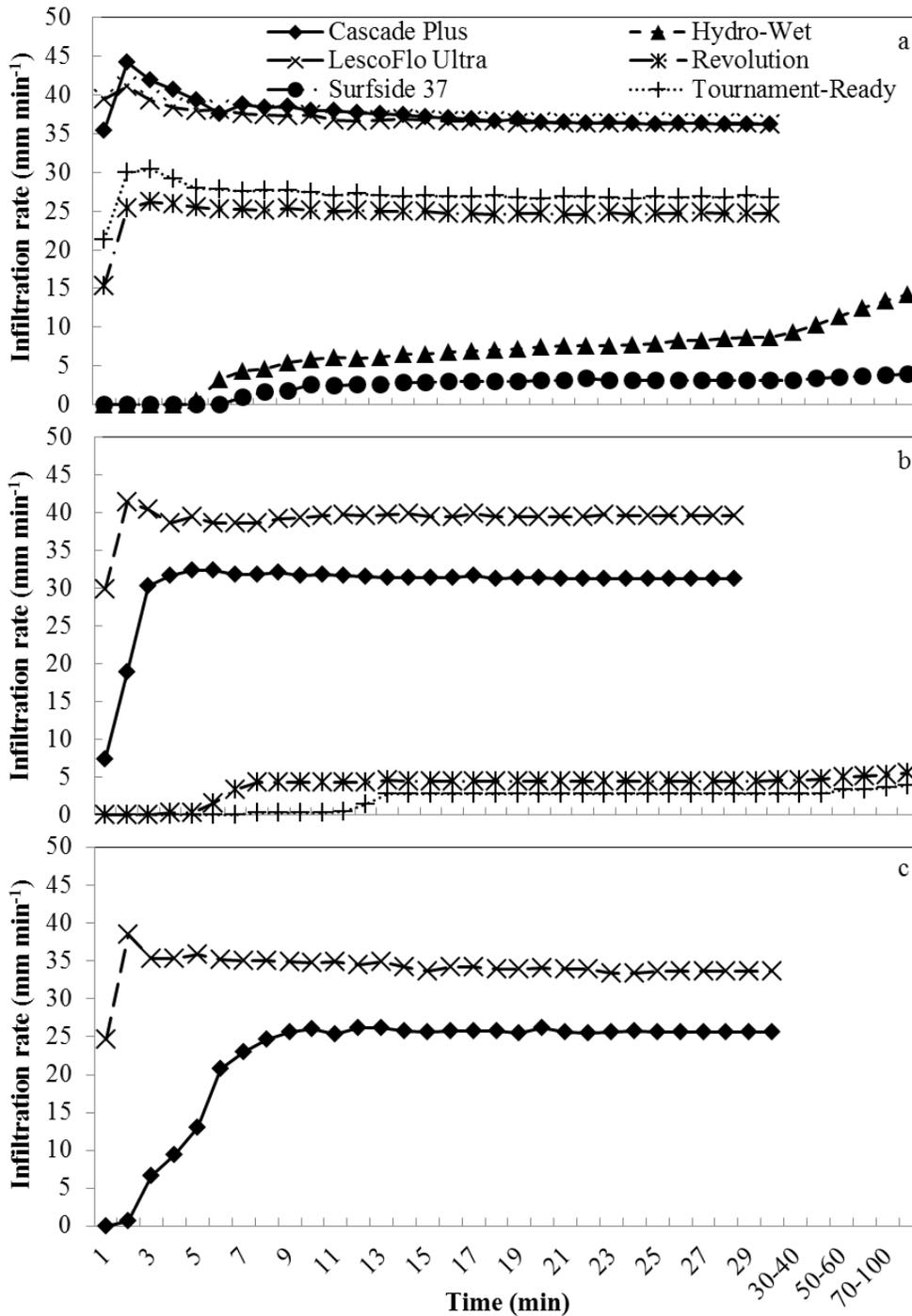
<sup>¶</sup> Means followed by different letters in each column indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ .

<sup>#</sup> 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.** Infiltration as a function of time influenced by six wetting agents, Cascade Plus, Hydro-Wet, LescoFlo Ultra, Revolution, Surfside 37, and Tournament-Ready, measured under a constant ponding depth of 4.4 cm. Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at 4.4 cm ponding depth, thus no data were collected.



**Figure 2.2.** Water infiltration as a function of time into sand columns previously treated with various wetting agents under a constant ponding depth of 4.4 cm after the 1<sup>st</sup> (a), the 2<sup>nd</sup> (b), and the 3<sup>rd</sup> dry-wet cycle (c). Untreated control with water-only treatment did not infiltrate into the hydrophobic sand at 4.4 cm ponding depth, thus no data were collected.



## Chapter II: Part Two

### Wetting Agent Influence on Water Infiltration into Hydrophobic Sand: II. Physical Properties

Enzhan Song<sup>1</sup>, Keith W. Goyne<sup>2</sup>, Robert J. Kremer<sup>2</sup>, Stephen H. Anderson<sup>2</sup>, Xi Xiong<sup>1\*</sup>

<sup>1</sup>Division of Plant Sciences, University of Missouri, Columbia, MO 65211, USA

<sup>2</sup>School of Natural Resources, University of Missouri, Columbia, MO 65211, USA

#### Abstract

Wetting agents are commonly used to remedy localized dry spot (LDS) caused by soil water repellency on golf course putting greens. Information gleaned from field experiments assessing wetting agent effects on infiltration can be difficult to interpret due to temporal and spatial variations. To avoid this challenge, a laboratory study was conducted to evaluate the influence of six commercial wetting agents at four concentrations (500, 1000, 3000, and 5000 mg L<sup>-1</sup>) on surfactant physical properties and to establish relationships between physical properties and water infiltration into a water-repellent United States Golf Association (USGA) grade sand. As wetting agent concentration increased, notable decreases in surface tension ( $\gamma$ ), liquid-solid contact angle ( $\theta$ ), and liquid entry pressure head ( $h_p$ ) were measured. These decreases were negatively correlated with the hydraulic conductivity ( $K$ ) of water-repellent sands treated with the wetting agents. Improved infiltration as a function of wetting agent concentration was explained by reduced hydrophobicity following wetting agent application. Cascade Plus and LescoFlo Ultra at concentrations of  $\geq 3000$  and  $1000$  mg L<sup>-1</sup>, respectively, transformed the water-repellent sand to a wettable media, as evidenced by negative  $h_p$  values. A multiple regression model ( $R^2=0.82$ ) found that  $K$  of wetting agent

treated soil can be explicated by variables  $\gamma$ ,  $h_p$ , and wetting agent concentration. Our results showed that all tested wetting agents improved water infiltration but the effectiveness was compound dependent. Therefore, it is essential to select appropriate wetting agents and application rates when seeking to improve water infiltration into hydrophobic sands.

## **Introduction**

Soil water repellency is known to cause localized dry spots (LDS) on golf course greens (Karnok and Tucker, 1989; Wilkinson and Miller, 1978). Water movement into water-repellent soil is affected by an unstable wetting front and preferential flow, which results in uneven water distribution in the soil profile. Preferential flow is particularly problematic in sand-based United States Golf Association (USGA) putting greens (Nektarios et al., 1999; Wang et al., 2000b), not only due to the structureless nature of sand media (Nektarios et al., 2002), but also the small specific surface area of sand particles that is more prone to water repellency development (Karnok and Tucker, 1989; Larsbo et al., 2008). It has been hypothesized that the development of water repellency results from the coating of sand grain surfaces by layers of organic matter (Roberts and Carbon, 1972). The mechanisms driving organic coating accumulation are not fully understood, but have been attributed to soil microbial activities and in some cases, plant species (Czarnes et al., 2000; Doerr et al., 2000; Miller and Wilkinson, 1977). No matter the frequency, supplemental water irrigation alone cannot reduce soil water repellency or prevent LDS (Wallis et al., 1989; 1990).

Applying wetting agents is the primary management strategy used to improve water infiltration into water-repellent soils (Cisar et al., 2000; Karnok, 2006; Kostka, 2000). Although wetting agents have been widely adopted by golf course superintendents, research-based information explicitly assessing effects of wetting agent on infiltration under field conditions is limited. Initiated in 2003, a two-year field study co-funded by the Golf Course Superintendents Association of America (GCSAA) and USGA, was carried out in nine states (Throssell, 2005a; 2005b). The primary objective of this study was to provide superintendents unbiased information regarding the selection and use of 10 selected wetting agents. However, results from this study could only be summarized by state due to the variations in the environment, cultural management practices, and degree of hydrophobicity among sites. For example, applying Aqueduct (Aquatrols, Paulsboro, NJ) to putting greens in TX resulted in a water droplet penetration test (WDPT) value equal to the untreated control (50 s). In contrast, use of Aqueduct in FL yielded significantly lower WDPT (< 10 s) than the control in two years of study (Throssell, 2005b). Temperature at the FL research site increased linearly from 26 to 32 °C between February and August, and peak precipitation occurred during June and July. In TX, temperatures were consistently in the 30's °C between May and August, and precipitation events occurred only in June (Throssell, 2005a). Therefore, environmental variations among the study sites make it very challenging to draw definitive conclusions from this large-scale wetting agent study (Karnok, 2006).

Wetting agent effects on water infiltration into water-repellent soil can also be investigated in the laboratory where more consistent experimental conditions can be maintained. This includes constructing soil columns/chambers for direct measurement of

infiltration rates (DeBano, 1971; Nektarios et al., 2002). Laboratory studies have been conducted to investigate the impact of soil water repellency on water infiltration, wetting front instability, preferential flow, and their relationships with ponding depth ( $h_o$ ) or water entry pressure ( $h_w$ ) (Carrillo et al., 2000; Feng et al., 2001; Nektarios et al., 1999; Ritsema et al., 1993; Wang et al., 2000b). However, detailed research focused on elucidation of wetting agent properties and their influences on infiltration in hydrophobic sands is limited.

Explained by the liquid-solid contact angle ( $\theta$ ) concept, a water-repellent soil is defined as having an initial value of  $\theta > 90^\circ$  (Emerson and Bond, 1963). Under such conditions, the soil does not spontaneously wet without a positive pressure head (Carrillo et al., 1999). Addition of wetting agents reduces the liquid surface tension ( $\gamma$ ) of the infiltrating solution and, therefore, the hydrophobicity of the water-repellent soil (DeBano, 2000; Feng et al., 2002; Pelishek et al., 1962). Consequently, wetting agent applications reduce the required liquid entry pressure head ( $h_p$ ) of water-repellent soil, as  $h_p$  for a solution is positively correlated to the level of water repellency of the soil (Wang et al., 2000a). Therefore,  $\gamma$  and  $h_p$  of a wetting agent solution can be used to predict infiltration rate into a water-repellent soil.

Currently, no method is available for directly measuring the  $\theta$  of a wetting agent solution, because the initial contact of wetting agent solutions changes the hydrophobicity of water-repellent soil (Carrillo et al., 1999). However, Zisman (1964) discovered a linear relationship between  $\theta$  and  $\gamma$  of a solution, which was further studied to develop into an equation used to predict  $\theta$  from the  $90^\circ$  surface tension ( $\gamma_{ND}$ ) and  $\gamma$  (Girifalco and Good, 1957; Ritsema et al., 1993; Watson and Letey, 1970). The  $\gamma_{ND}$  is the  $\gamma$  of a liquid,

typically an ethanol solution, with  $90^\circ$   $\theta$  on a given soil (Watson and Letey, 1970). The objective of this study was to evaluate  $\gamma$ ,  $\theta$ , and  $h_p$  of various wetting agents to assess their influence on infiltration into water-repellent USGA grade sand.

### **Materials and Methods**

Six wetting agents, including Cascade Plus (10% alcohol ethoxylates, 90% polyethylene, and polypropylene glycols), Hydro-Wet (87.5% poloxanlene, 2-butoxyethanol), LescoFlo Ultra (90% polyether polyol and 10% glycol ether), Revolution (100% modified alkylated polyol), Surfside 37 (37% nonylphenoxypoly (ethyleneoxy) ethanol, 18 % polyoxyethylene esters of cyclic acid, and 14% polyethylene glycol), and Tournament-Ready (100% blend of nonionic carbohydrate surfactants, polyoxyethylene-polyoxypropylene glycol, and polydimethylsiloxane), were evaluated in this study.

Wetting agent solutions at four concentrations (500, 1000, 3000, and 5000 mg L<sup>-1</sup>) were prepared with tap water. The  $\gamma$  of these solutions, plus tap water as a control, were measured by an Attension Theta Lite tensiometer (Biolin Scientific, Inc., Linthicum Heights, MD), and  $\theta$  was calculated using the following equation (Carrillo et al., 1999):

$$\cos\theta = [(\gamma_{ND}/\gamma)^{1/2} - 1] \quad [1]$$

where  $\gamma$  is the liquid surface tension of wetting agent solutions or water, and  $\gamma_{ND}$  is the  $90^\circ$  surface tension of the water-repellent sand.

Washed silica sand that meets the USGA recommendations for putting green construction (USGA, 2004) was used in this study. The particle distribution of the sand measured 5% very coarse sand, 90% combination of coarse and medium sand, and 3.5% fine sand. After packing the sand to a bulk density ( $D_b$ ) of 1.7 g cm<sup>-3</sup>, the total porosity was determined to be 40% with 25% air-filled pores (Nimmo, 2004). Water repellency

was induced by mixing 120 kg sand with 90 g octadecylamine (1-Aminooctadecane; Sigma-Aldrich Co., St. Louis, MO) in 60 L tap water for 24 h using a concrete mixer before drying the treated sand in an oven at 75°C for 24 h. The treated sand was rinsed three times with tap water to remove excessive octadecylamine, and dried again at 75°C for an additional 24 h (Bauters et al., 1998; Braford and Leij, 1996). Hydrophobicity of the treated sand was measured using the WDPT (Bisdorn et al., 1993) and molarity of ethanol droplet test (MED) (King, 1981; Watson and Letey, 1970) after packing the sand to a  $D_b$  of 1.7 g cm<sup>-3</sup>. The  $\gamma_{ND}$  of the water-repellent sand was determined by measuring the  $\gamma$  of aqueous ethanol solution with the lowest ethanol concentration able to penetrate into the treated sand in < 5 sec as defined by Watson and Letey (1970).

The  $h_w$  was determined using the water-ponding method developed by Wang et al. (1998). After packing the treated sand in a 50 cm PVC column to a  $D_b$  of 1.7 g cm<sup>-3</sup>, water was slowly added and the  $h_o$  that initiated water infiltration was recorded as  $h_w$ . After determination of  $h_w$ , the  $h_p$  of different wetting agent solutions was calculated using the equation (Feng et al., 2002):

$$h_p = -2\gamma\cos\theta/\rho gr \quad [2]$$

where  $\gamma$  is the liquid surface tension,  $\theta$  is the liquid-solid contact angle,  $r$  is the capillary radius,  $\rho$  is the liquid density, and  $g$  is the gravitational constant.

Infiltration of water-repellent sand columns applied with various wetting agents at different concentrations was measured using an infiltration system constructed of Harvel Clear PVC tubes (Georg Fischer Harvel LLC, Easton, PA) with a 5.08 cm inner diameter and 0.48 cm wall thickness. A 50 cm long solution column was connected to a 20 cm long sand column by a no-hub coupling (5.08 cm inner diameter and 10 cm long) (Fernco

Inc., Davison, MI). The interior surface of each sand column was coated with Teflon non-stick dry-film lubricant (DuPont, Wilmington, DE) to prevent preferential flow (Feng et al., 2001). A consistent  $h_o$  at 6.6 cm, which was determined through preliminary studies, was maintained by using a Mariotte bottle. The mass change of solution within the bottle ( $\Delta v$ ) was recorded every min ( $\Delta t$ ) for 30 min to determine the infiltration rate ( $i$ ). Hydraulic conductivity ( $K$ ) was calculated by dividing the steady flow rate by the hydraulic head gradient across the sand column based on the constant head measuring theory (Reynolds and Elerick, 2002). The time necessary for the solution to exit the bottom of the sand column was recorded as seepage time ( $T_s$ ). All of the studies described above were conducted in the laboratory at room temperature (22 °C).

The experimental design was a completely randomized design with three replications and the experiment was performed twice. Analysis of variance was conducted by using the Proc Mixed procedure of SAS 9.2 (SAS Institute, Cary, NC). There were no treatment by experiment interactions for all measurements; thus, data were pooled over the two experiments and significant mean separations were carried out by Fisher's Protected LSD at  $P = 0.05$ . Pearson's correlation was performed to determine the correlations between  $K$  and  $\gamma$ ,  $\theta$ , and  $h_p$  of the solutions. Multiple regression analysis with stepwise selection criterion was used to develop a model capable of predicting  $K$  of wetting agent solutions based on their physical properties: i.e., concentration,  $\gamma$ ,  $\theta$ , and  $h_p$ .

## **Results and Discussion**

### ***Water repellency of treated sand***

The treated, water-repellent sand exhibited extreme hydrophobicity with an infinite WDPT and a MED of 7.2M (Doerr, 1998; Karnok and Tucker, 2001). The  $\gamma_{ND}$  of

the water-repellent sand was  $31.3 \text{ mN m}^{-1}$ , indicating that a solution with  $\gamma < 31.3 \text{ mN m}^{-1}$  can wet the treated sand spontaneously (Miyamoto and Letey, 1971; Watson and Letey, 1970). The  $h_w$  that initiated water infiltration into the hydrophobic sand at a  $D_b$  of  $1.7 \text{ g cm}^{-3}$  was determined to be  $8.1 \text{ cm}$ . The saturated hydraulic conductivity ( $K_{sat}$ ) of the corresponding wettable sand (USGA grade sand without octadecylamine treatment) was measured as  $19 \text{ mm min}^{-1}$ . This value meets the USGA suggested minimal  $K_{sat}$  of  $2.5 \text{ mm min}^{-1}$  for a putting green root zone (USGA, 2004).

### ***Surface tension, liquid-solid contact angle, and liquid entry pressure head***

Significant differences were found for  $\gamma$  and  $\theta$  among the wetting agents at various concentrations (Table 2.3). The overall trend was a decrease in  $\gamma$  with increasing wetting agent concentration. However, with the exception of Hydro-Wet, there was no additional reduction of  $\gamma$  when a concentration of  $5000 \text{ mg L}^{-1}$  was applied. Our results agree, in part, with Feng et al. (2002), who found that the  $\gamma$  of two surfactants reached a plateau ( $35 \text{ mN m}^{-1}$ ) at concentrations  $> 25 \text{ mg L}^{-1}$ . In contrast, the wetting agents tested in our study exhibited a wide range of  $\gamma$  values ( $30.1$  to  $44.8 \text{ mN m}^{-1}$ ) at  $5000 \text{ mg L}^{-1}$  and  $\gamma$  values among the surfactants are significantly different ( $p < 0.05$ ) at the greatest concentration investigated. Feng et al. (2002) concluded, based on a lack of  $\gamma$  differences between the two surfactants at concentrations ranging from  $25$  to  $1000 \text{ mg L}^{-1}$ , that  $\gamma$  of a surfactant at different concentrations had little value in predicting infiltration rates. Our results disagree with this conclusion, which is elaborated upon below.

Regardless of concentration, Surfside 37 exhibited the greatest  $\gamma$  among wetting agents tested with values  $\geq 44.8 \text{ mN m}^{-1}$ , which was comparable to the  $\gamma$  of tap water which was determined to be  $47.9 \text{ mN m}^{-1}$ . The  $\gamma$  values associated with Surfside 37 are all

greater than the measured  $\gamma_{ND}$  (31.3 mN m<sup>-1</sup>). This indicates that a positive pressure head is necessary to force Surfside 37 solutions to infiltrate into hydrophobic sand at the concentrations tested (Carrillo et al., 1999). In comparison, Cascade Plus and LescoFlo Ultra applied at concentrations  $\geq 3000$  and  $1000$  mg L<sup>-1</sup>, respectively, displayed  $\gamma$  values  $< \gamma_{ND}$ . These results indicate that the two wetting agents can spontaneously wet the water-repellent sand in absence of a positive  $h_o$  when applied at greater concentrations (Carrillo et al., 1999; Miyamoto and Letey, 1971; Watson and Letey, 1970). Other wetting agents that showed  $\gamma$  values  $> \gamma_{ND}$  even at  $5000$  mg L<sup>-1</sup> are likely to produce preferential flow without a positive  $h_o$  (Feng et al., 2001).

A similar trend was observed in the  $\theta$  results (Table 2.3). Greater concentrations of wetting agents exhibited smaller  $\theta$  values when compared with results obtained at reduced surfactant concentrations (Table 2.3). Except Surfside 37 at  $500$  mg L<sup>-1</sup>, all tested wetting agents showed a lower  $\theta$  value than tap water, which was determined as  $101^\circ$ . Wetting agents showing  $\gamma$  values  $< \gamma_{ND}$ , such as Cascade Plus and LescoFlo Ultra at concentrations  $\geq 3000$  and  $1000$  mg L<sup>-1</sup>, respectively, also resulted in  $\theta \leq 90^\circ$ . This result corroborates results from  $\gamma$  measurements, which indicates that these two wetting agents can spontaneously wet the hydrophobic sand at higher concentrations (Letey et al., 2000).

However, for LescoFlo Ultra, increasing concentration from  $1000$  to  $5000$  mg L<sup>-1</sup> yielded no further improvement in  $\gamma$  or  $\theta$ . Similar results were reported by Bernett and Zisman (1959), who found that the relationship between  $\gamma$  and surfactant concentration resulted in a knee-shaped curve with different slopes for various surfactants. Initially,  $\gamma$  dramatically decreased as the concentration increased, but a plateau was reached at various concentrations depending on properties of the surfactants studied. Development

of such a relationship may be attributed to the formation of self-associated micelles in the liquid phase. Once the saturation point or critical micelle concentration (CMC) was reached, additional surfactants added to solution are associated with the micelles instead of the water phase; thus, reaching CMC diminishes any further surfactant influence on solution properties (e.g.,  $\gamma$  and  $\theta$ ) (Domínguez et al., 1997; Leibler et al., 1983; Lin et al., 1999). The manufacturer suggested rate for LescoFlo Ultra is equivalent to a concentration range from 30,920 to 61,840 mg L<sup>-1</sup>, which is more than 6 times greater than the highest concentration used in this study. Our results indicate that the manufacturer suggested application rate for LescoFlo Ultra may be much greater than needed to influence  $\gamma$ ,  $\theta$ , and subsequently infiltration, which is discussed below.

Water-repellent soil requires a positive  $h_o$  to force water into the soil profile (Wang et al., 2000a). In our study, hydrophobic sand packed to a  $D_b$  of 1.7 g cm<sup>-3</sup> required an 8.1 cm pressure head to initiate water infiltration. Application of wetting agents to the water-repellent soil alters hydrophobicity and reduces the required  $h_p$  (Table 2.4). With the exception of Surfside 37 at 500 mg L<sup>-1</sup>, all wetting agents solutions tested in this study showed a reduced  $h_p$  compared with the required pressure head for initial water infiltration into the hydrophobic sand.

The magnitude of required entry pressure for hydrophobic soil is affected by soil properties, including soil moisture (Wang et al., 2000a). In our study, significant differences were observed for the required  $h_p$  among the sand columns treated with wetting agent solutions, reflecting a change in water repellency, or wettability, resulting from wetting agent application. Similar to trends observed within the  $\gamma$  and  $\theta$  results, increased wetting agent concentration led to decreases in  $h_p$ . This is likely due to the

increased wetting agent adsorption to the sand particles at greater concentrations of the wetting agents in solution (Feng et al., 2002; Valoras et al., 1969).

When Cascade Plus or LescoFlo Ultra were tested at concentrations  $\geq 3000$  and  $1000 \text{ mg L}^{-1}$ , respectively, they exhibited a negative  $h_p$  (Table 2.4), which is typically associated with a wettable soil (Wang et al., 2000a). Wang et al. (2000a) reported that the  $h_p$  of a wettable sand ranged from -11 to -25 cm, while water-repellent sand with a WDPT value  $> 3600 \text{ s}$  required a 12 cm positive  $h_p$ . Results from our study indicate that Cascade Plus or LescoFlo Ultra at greater concentrations transformed the water-repellent sand into a more wettable media. In contrast, Tournament-Ready ( $500 \text{ mg L}^{-1}$ ) and Surfside 37 ( $500$  and  $1000 \text{ mg L}^{-1}$ ) resulted in an  $h_p$  value greater than the consistent  $h_o$  (6.6 cm) maintained in the study. Occurrence of infiltration under such conditions, as shown in Fig. 2.3., is likely attributed to preferential flow (Feng et al., 2001).

#### ***Seepage time and hydraulic conductivity***

Seepage time varied significantly among the wetting agent treatments studied and ranged from 46 to 250 sec (Table 2.5). As concentration increased, shorter  $T_s$  were observed for the wetting agents examined. At  $5000 \text{ mg L}^{-1}$ , there was no significant difference in  $T_s$  (49 to 59 sec) for all wetting agents tested with the exception of Surfside 37, which took 84 sec. Compared with other wetting agents, greater  $T_s$  were generally needed for water to seep out of the sand columns treated with Surfside 37 at three of the four concentrations tested. The most rapid  $T_s$  were observed for sand treated with Cascade Plus at all concentrations evaluated, with  $T_s$  ranging from 46 to 94 sec.

Hydraulic conductivity was calculated based on the steady flow rate (Table 2.5). An earlier study reported that a  $h_o$  approximately 2.6 times greater than  $h_p$  is required to

accelerate the  $K$  of a water-repellent soil to a rate similar to the  $K_{sat}$  of a corresponding wettable soil (Feng et al., 2001). When the  $h_o/h_p$  is  $< 2.6$ , water infiltration into the water-repellent soil might occur as preferential flow and, subsequently, soil water distribution becomes non-uniform (Bens et al., 2005; Wang et al., 2000b). In our study, the  $K_{sat}$  of non-treated, wettable sand was determined to be  $19 \text{ mm min}^{-1}$ . This means that to obtain the same  $K$ , a 2.6 times greater  $h_o$  is required. The required  $h_w$  into the water-repellent sand was determined to be 8.1 cm. It is unrealistic, under field conditions, to generate a 21 cm  $h_o$  of water via irrigation.

However, the use of wetting agents reduces soil water repellency and improves infiltration without manipulating  $h_o$ . Although only a 6.6 cm  $h_o$  was maintained in our study, all wetting agent solutions tested showed a  $K \geq 20 \text{ mm min}^{-1}$ , except Surfside 37 at concentrations  $\leq 1000 \text{ mg L}^{-1}$  (Table 2.5). All other wetting agent solutions and Surfside 37 at concentrations  $> 1000 \text{ mg L}^{-1}$  reduced the water repellency of the sand over time, thereby increasing soil water content and saturating the water-repellent sand. Based on the  $h_p$  values determined for each wetting agent solution (Table 2.4), the  $h_o/h_p$  ratio of wetting agent solutions resulting in a  $K$  greater than  $K_{sat}$  of the non-treated wettable sand ranged from 0.89 to 11. This indicates that, unlike water, which requires a 2.6 or greater  $h_o/h_p$  ratio to saturate the water-repellent soil, addition of wetting agents altered soil hydrophobicity and reduced the required  $h_p$  (Feng et al., 2001; 2002). The negative values of  $h_p$  from Cascade Plus and LescoFlo Ultra at greater concentrations (Table 2.4) further validated soil transformation to a wettable media resulting from wetting agent application. These results show that changes in infiltration are highly variable among the tested

wetting agents, likely due to their chemical properties and ability to modify surface chemistry of the water-repellent sand (Zontek and Kostka, 2012).

### ***Infiltration***

Infiltration into the water-repellent sand under a constant  $h_o$  of 6.6 cm varied among the six wetting agents and concentrations studied (Fig. 2.3). In general, more concentrated wetting agent solutions led to faster steady flow rates. Unlike LescoFlo Ultra and Surfside 37, the other wetting agents, Cascade Plus, Hydro-Wet, Revolution, and Tournament-Ready at 3000 and 5000 mg L<sup>-1</sup> resulted in 40 mm min<sup>-1</sup> or greater steady flow rates. Surfside 37 exhibited a slower flow rate at 20 mm min<sup>-1</sup> or less. This result corroborates the increased  $T_s$  and reduced  $K$  results described previously (Table 2.5).

Despite the influence of concentration, most wetting agents showed an initial increase in infiltration before reaching a steady flow rate. This is typical of infiltration patterns for water-repellent soil (Feng et al., 2001; 2002; Wang et al., 2000b). Previous studies have found that increased infiltration is highly correlated to increased soil water content, due to the wetting front buildup (Carrillo et al., 2000; Feng et al., 2001). Continuously increasing flow rate without reaching a steady rate, such as demonstrated by Surfside 37 at the 500 mg L<sup>-1</sup> concentration, indicates that the wetting front was unstable during wetting and preferential flow occurred (Carrillo et al., 2000; Nektarios et al., 2002; Wang et al., 2000b).

A different infiltration pattern was observed for LescoFlo Ultra at concentrations of 3000 and 5000 mg L<sup>-1</sup> (Fig. 2.3c). The flow rates associated with LescoFlo Ultra at the two greatest concentrations studied reached a maximum of 36 and 40 mm min<sup>-1</sup> at 6 and

3 min, respectively. The rates then decreased to a steady rate of 29 mm min<sup>-1</sup>. A similar trend was observed for Cascade Plus and Revolution at a concentration of 5000 mg L<sup>-1</sup> (Fig. 2.3a and d). Such infiltration patterns are typical of wettable soil, as characterized by an initial peak in infiltration followed by a small decrease and then a steady flow rate (Feng et al., 2001; Wang et al., 2000b). These results suggest that the adsorption of Cascade Plus, LescoFlo Ultra, and Revolution at higher concentrations transform water-repellent soil into a more wettable media. It is important to note that the labeled rates of these wetting agents are equivalent to a concentration at least four times greater than the highest concentrations tested in this study.

Applying wetting agents to a wettable soil either has no effect or a negative effect on infiltration (Feng et al., 2002; Pelishek et al., 1962). A field-based study reported by Sullivan et al. (2009) found that addition of surfactant actually decreased infiltration, increased runoff, and increased the potential for water loss. In our study, certain wetting agents, such as LescoFlo Ultra at 5000 mg L<sup>-1</sup>, exhibited an infiltration pattern typical of a wettable soil, and resulted in a slower steady flow rate than the solution at 1000 mg L<sup>-1</sup>. Collectively, this indicates that under field conditions, repeated application of wetting agents such as LescoFlo Ultra at the label rate, which is at or above 30,920 mg L<sup>-1</sup>, could be either beneficial or negative, depending on the magnitude of changes in soil hydrophobicity.

#### ***Correlation and regression of hydraulic conductivity with wetting agent properties***

Significant correlations ( $P < 0.05$ ) were found between  $K$  and  $\gamma$ ,  $\theta$ , and  $h_p$  of various wetting agents (Table 2.6). Although the wetting agents used in this study showed different levels of effectiveness, lower solution  $\gamma$ ,  $\theta$ , and  $h_p$  led to increased  $K$ .

Among the wetting agents tested, LescFlo Ultra exhibited weaker correlations compared with other wetting agents (Table 2.6). This result supports the infiltration results described earlier, and indicates that the label suggested rates might be greater than optimal for water infiltration. For this reason, LescFlo Ultra was not included in the following regression analysis.

Stepwise multiple regression analysis using four variables, i.e., concentration (conc),  $\gamma$ ,  $\theta$ , and  $h_p$ , indicate that  $K$  can be modeled using these parameters ( $R^2=0.82$ ). The analysis removed  $\theta$  from the final model ( $K = -21.8 + 0.79 \gamma - 1.80 h_p + 0.00016 \text{ conc}$ ), and the three variables were significant at the 0.01 or 0.001 level. These results differ from Feng et al. (2002), who concluded that the concentration effect on  $\gamma$  has little value in predicting the infiltration rate of a wetting agent. This is because the two surfactants in Feng et al. (2002) study reached a plateau in  $\gamma$  at a relatively low concentration (25 mg L<sup>-1</sup>).

## **Conclusions**

This study evaluated six commercially available wetting agents for their impact on water properties and water infiltration into a water-repellent USGA grade sand. Except for LescFlo Ultra, effects of concentration were observed for most wetting agents, where an increase in concentration led to a decrease in  $\gamma$ ,  $\theta$ , required  $h_p$ , and consequently the steady flow rate into water-repellent sand. Hydraulic conductivity of various wetting agents was negatively correlated to wetting agent properties, including  $\gamma$ ,  $\theta$ , and required  $h_p$ . Stepwise multiple regression analysis showed that the  $K$  of wetting agent solutions can be predicted by their various physical properties. Although this study was conducted in the laboratory, the same principles can be applied to field conditions,

where infiltration effects from wetting agents can be difficult to assess due to spatial and temporal variations. However, it is worth noting that findings from this laboratory-based study do not take into account field putting green conditions, such as presence of plant organic matter, thatch thickness, age of green, and other management considerations, which likely affect the rates of wetting agents that are effective. Overall, our results suggest that selecting a proper wetting agent and recommending an appropriate concentration requires in-depth analysis of soil and wetting agent properties.

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**Table 2.3.** Liquid surface tension ( $\gamma$ ) and liquid-solid contact angle ( $\theta$ ) of different wetting agents at concentrations of 500, 1000, 3000 and 5000 mg L<sup>-1</sup>.

Treatment	$\gamma$				$\theta^\dagger$			
	500 mg L <sup>-1</sup>	1000 mg L <sup>-1</sup>	3000 mg L <sup>-1</sup>	5000 mg L <sup>-1</sup>	500 mg L <sup>-1</sup>	1000 mg L <sup>-1</sup>	3000 mg L <sup>-1</sup>	5000 mg L <sup>-1</sup>
	----- mN m <sup>-1</sup> -----				----- °-----			
Cascade Plus	39.7dA‡	35.7eB	30.6eC	30.1fC	96.5dA	93.7dB	89.4eC	88.8fC
Hydro-Wet	43.4cA	41.7dB	40.3cC	39.2cD	98.7cA	97.7cB	96.9cC	96.2cD
LescoFlo Ultra	32.6eA	30.8fB	31.1eB	30.9eB	91.2eA	89.5eB	89.8eB	89.6eB
Revolution	44.7cA	42.9cB	41.4bC	40.6bC	99.4cA	98.4bB	97.5bC	97.0bD
Surfside 37	51.5aA	47.3aB	44.9aC	44.8aC	102.8aA	100.8aB	99.5aC	99.4aC
Tournament- Ready	46.6bA	43.9bB	38.1dC	32.1dC	100.4bA	99.0bB	95.4dC	90.7dD

† The liquid-solid contact angle ( $\theta$ ) was calculated using the equation:  $\cos\theta = [(\gamma_{ND}/\gamma)^{1/2} - 1]$ , where  $\gamma$  is the surface tension of wetting agent solutions at different concentration, and  $\gamma_{ND}$  is the 90° surface tension of the water-repellent sand.

‡ Means followed by different lowercase letters in each column indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ ; means followed by different uppercase letters in each row for each parameter indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ .

**Table 2.4.** Liquid entry pressure head ( $h_p$ ) into the hydrophobic sand as influenced by different wetting agents at concentrations of 500, 1000, 3000 and 5000 mg L<sup>-1</sup>.

Treatment	$h_p^\dagger$			
	500 mg L <sup>-1</sup>	1000 mg L <sup>-1</sup>	3000 mg L <sup>-1</sup>	5000 mg L <sup>-1</sup>
	----- cm -----			
Cascade Plus	3.9eA	2.0eB	-0.3eC	-0.5eC
Hydro-Wet	5.8dA	4.9dB	4.2cC	3.7cD
LescoFlo Ultra	0.6fA	-0.2fB	-0.1eB	-0.2eB
Revolution	6.4cA	5.5cB	4.8bC	4.4bC
Surfside 37	10.0aA	7.8aB	6.5aC	6.5aC
Tournament-Ready	7.4bA	6.0bB	3.2dC	0.3dD

† The liquid entry pressure heads ( $h_p$ ) were calculated using the equation:  $h_p = -$

$2\gamma\cos\theta/\rho gr$ , where  $\gamma$  is the liquid surface tension,  $\theta$  is the liquid-solid contact angle,  $r$  is the capillary radius,  $\rho$  is the liquid density, and  $g$  is the gravitational constant.

‡ Means followed by different lowercase letters in each column indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ ; means followed by different uppercase letters in each row indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ .

**Table 2.5.** Seepage time ( $T_s$ ) and hydraulic conductivity ( $K$ ) of different wetting agents at concentrations of 500, 1000, 3000 and 5000 mg L<sup>-1</sup> after infiltrating into 20 cm sand columns under a 6.6 cm ponding depth.

Treatment	$T_s$				$K$			
	500	1000	3000	5000	500	1000	3000	5000
	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>				
	----- sec -----				----- mm min <sup>-1</sup> -----			
Cascade Plus	94eA <sup>†</sup>	69cB	46dC	49bC	27aB	26aB	36aA	35aA
Hydro-Wet	198cA	136aB	75bC	59bD	23bC	22bC	30bB	34aA
LescoFlo Ultra	106dA	74cB	76bB	59bC	20cB	25aA	22cB	22bB
Revolution	106dA	73cB	59cC	50bC	20cD	23bC	30bB	34aA
Surfside 37	250aA	124bB	95aC	84aD	NA <sup>‡</sup>	15cB	21cA	23bA
Tournament-Ready	217bA	133abB	54cdC	50bC	23bC	27aB	36aA	35aA

<sup>†</sup> Means followed by different lowercase letters in each column indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ ; means followed by different uppercase letters in each row for each parameter indicate significant differences based on Fisher's Protected LSD at  $P = 0.05$ .

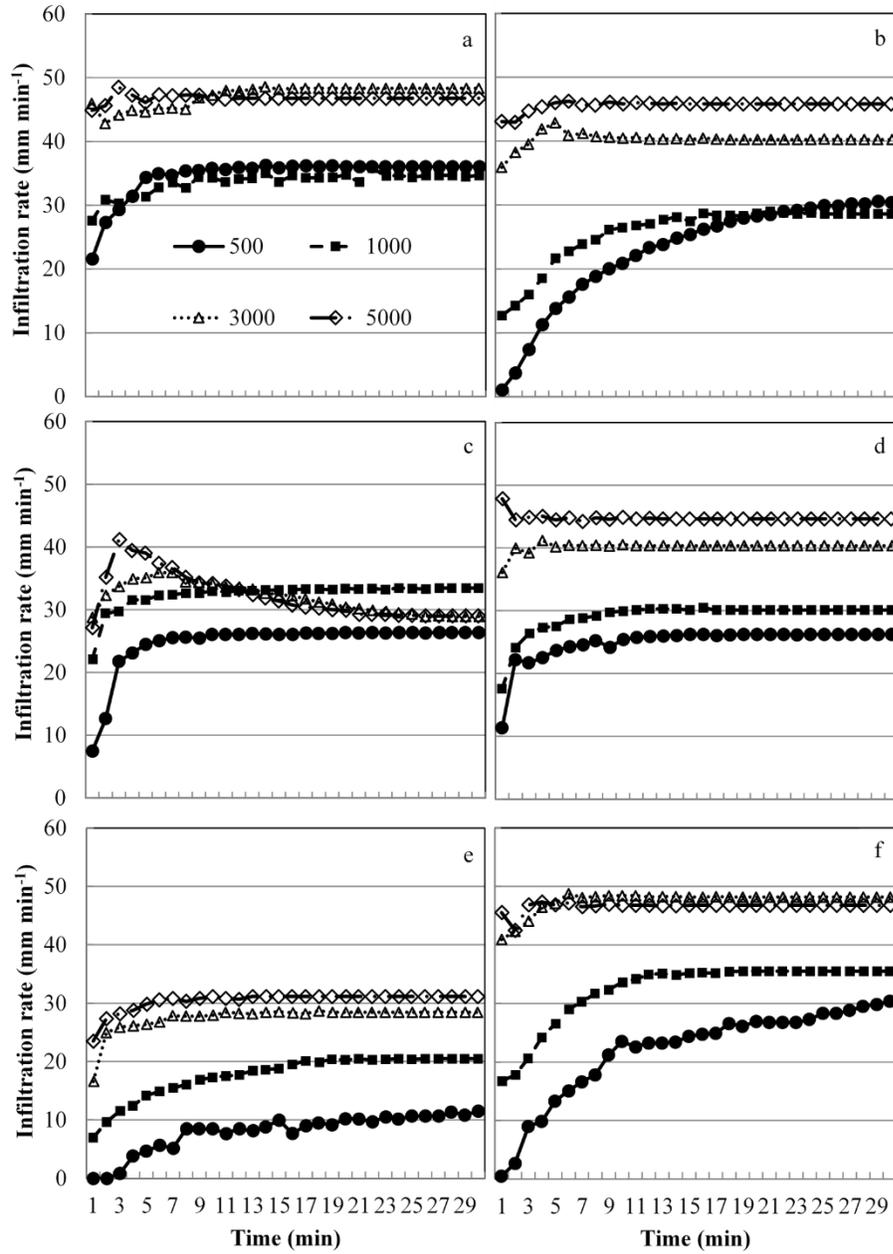
<sup>‡</sup> NA=not available;  $K$  was not calculated for Surfside 37 at 500 mg L<sup>-1</sup>, as it did not reach a steady flow rate after 60 min of ponding.

**Table 2.6.** Pearson’s correlation coefficients between hydraulic conductivity ( $K$ ) and liquid surface tension ( $\gamma$ ), liquid-solid contact angle ( $\theta$ ), and liquid entry pressure head ( $h_p$ ) influenced by various wetting agents at concentrations of 500, 1000, 3000 and 5000 mg L<sup>-1</sup>.

Treatment	$K$ vs. $\gamma$	$K$ vs. $\theta$	$K$ vs. $h_p$
Cascade Plus	-0.76**	-0.79**	-0.75**
Hydro-Wet	-0.76**	-0.77**	-0.76**
LescoFlo Ultra	-0.68*	-0.69*	-0.67*
Revolution	-0.92***	-0.92***	-0.91***
Surfside 37	-0.92***	-0.92***	-0.91***
Tournament-Ready	-0.89***	-0.86***	-0.90***

\*, \*\*, \*\*\* Significant at 0.05, 0.01, and 0.001 probability level, respectively.

**Figure 2.3.** Infiltration rates into 20 cm sand columns as a function of time for six wetting agents at concentrations of 500, 1000, 3000, or 5000 mg L<sup>-1</sup> and a 6.6 cm ponding depth. a = Cascade Plus; b = Hydro-Wet; c = LescoFlo Ultra; d = Revolution; e = Surfside 37; and f = Tournament-Ready.



## Chapter III: Part One

### Effect of wetting agents on removing hydrophobic organic matter from water-repellent sand particles

Enzhan Song<sup>1</sup>, Keith W. Goyne<sup>2</sup>, Robert J. Kremer<sup>2</sup>, Stephen H. Anderson<sup>2</sup>, Xi Xiong<sup>1\*</sup>

<sup>1</sup>Division of Plant Sciences, University of Missouri, Columbia, MO 65211, USA

<sup>2</sup>School of Natural Resources, University of Missouri, Columbia, MO 65211, USA

#### Abstract

Wetting agents or soil surfactants have been used as the primary means for mitigating soil water repellency (SWR) which causes drought issues, such as localized dry spots (LDS), on sand-based turfgrass systems. However, residual effects are often short-lived and repeated application of wetting agents are typically required. Alternatively, certain groups of wetting agents were developed to remove the hydrophobicity causing organic compounds (HOCs), thus providing extended control of SWR. This study investigated the effects of Matador, OARS, and pHAcid on removing HOCs and reducing SWR in a laboratory experiment. Naturally occurring hydrophobic sand was collected from an LDS area on a 7-year old putting green and packed into sand columns utilizing a PVC tube system. Selected wetting agents were then applied at their highest label rates to the top of the columns. Twenty-four hours after application, the treated columns were washed three times with deionized water. Sequentially, leachates from the application and each wash event were collected to determine the volume of leachate and for measurement of dissolved organic carbon (DOC) and particulate organic carbon (POC). Solid phase organic carbon (SOC) and SWR of the treated sands were determined as well. While pHAcid treatment and the water control showed minimal influence on SOC, both treatments induced higher SWR with an increase of molarity of ethanol droplet test (MED) values from 2.2 M to >3 M. Sand treated by OARS showed enhanced water

holding capacity, although the effect diminished after the second wash. In comparison, Matador resulted in 100% and 300% more DOC and POC output in the leachate than OARS, and completely transformed the hydrophobic sand to wettable media. Although OARS reduced SWR to a minimum level, it sorbed strongly to the sand which resulted in 27% greater organic carbon content in treated sand, compared to untreated sand. The mechanisms of different wetting agents are unclear and their long-term effects following repeated application are yet to be determined.

*Keywords:* Hydrophobic organic coating, soil hydrophobicity, soil water repellency, surfactant, wetting agents.

## Introduction

It is reported extensively that under typical vegetation-growing conditions most soil types eventually become water-repellent to a certain degree, especially sandy soils (Ellies and Hartge, 1994; Tucker et al., 1990; Wallis and Horne, 1992). Soil water repellency (SWR) results in uneven water distribution in the soil profile, and often leads to localized dry spot (LDS) on sand-based turf systems such as golf course tees and putting greens (Wilkinson and Miller, 1978).

From an interface energy point of view, lower solid surface free energy ( $\gamma$ ) usually leads to weaker attractions between the solid and liquid phases (Roy and McGill, 2002). Although soil minerals, such as silica sand, are polarized and have high energy surfaces (Lewin et al., 2005), microorganism and plant biological activities often result in coverage of minerals by organic materials that tend to be nonpolar with low  $\gamma$  (Doerr et al., 2000). Previous studies have attributed the development of SWR to humus, including biomolecules such as waxes (Franco et al., 1995), fatty acids (Graber et al., 2009; Mainwaring et al., 2004), as well as humic substances (De Blas et al., 2010). Accumulation of organic compounds in soils is often inevitable, as a natural outcome of soil microbial activity of plant debris decomposition (Feeney et al., 2006). However, the accumulation of nonpolar organic coatings and development of SWR on sand-based growing media can be mitigated by wetting agents (Cisar et al., 2000; Kostka, 2000). Most wetting agents are nonionic surfactants, which have amphiphilic structures consisting of polar hydrophilic heads and nonpolar hydrophobic tails. Due to the high affinity among nonpolar structures, once wetting agents are watered in through irrigation/precipitation, these amphiphilic surfactants attach their nonpolar tails onto nonpolar hydrophobic surfaces, and subsequently increase the overall soil hydrophilicity

by facing the polar end towards the by-passing water (Cisar et al., 2000; Dekker et al., 2005; Kostka, 2000). Addition of wetting agents can reduce  $\gamma$  of tap water from 48 mN m<sup>-1</sup> to 32 mN m<sup>-1</sup> or lower depending on the wetting agent selected and rate used, hence facilitating spontaneous wetting and water infiltration of the treated hydrophobic sand (Song et al., 2014).

In addition to effects on wettability and water infiltration, research efforts have also been focused on removal of organic coatings that cause SWR. Karnok et al. (1993) conducted a field study on a sand-based golf course putting green and investigated the effect of high pH solution on SWR. After consecutive application of NaOH at 0.1 M with 12 mm ponding for three days, the authors discovered significant removal of humic substances and a reduction of SWR from strong to moderate level. However, repeat applications of NaOH led to substantial increase of soil pH from 5.9 to 8.3, which may negatively impact plant growth. Alternative research approach to SWR removal includes investigation of actinomycetes, such as *Streptomyces spp.* (Roper, 2004), *Rhodococcus spp.* (McKenna et al., 2002), and *Mycobacterium spp.* (Dunkelberg et al., 2006), as a bioremediation approach. The concept behind this approach is to utilize these wax-dependent metabolizing bacteria and bio-surfactant producing bacteria (Lang and Philp, 1998; Roper, 2004) to decompose complex organic hydrophobic coatings and reduce surface  $\gamma$ . However, this approach has proven to be time-consuming and results are highly environment-dependent.

Some wetting agents might be able to remove/extract organic coatings as well. Frankewich and Hinze (1994) conducted a laboratory experiment and evaluated certain nonionic surfactants for extracting and concentrating hydrophobic organic species from

water via a micelle-mediated phase separation method at the cloud point. The authors found that nonionic surfactant with polyoxyethylene glycol monoethyl ether showed greater than 66% extraction efficiency on a series of phenols and anilines, including chlorinated phenols (88 to 90% extraction) and dinitroanilines (76 to 98% extraction). While the nonpolar and hydrophobic features of soil organic matter (OM) have been related to aromatic structures such as phenolic groups and chlorinated hydrocarbons (Karickhoff et al., 1979; Richardson and Epstein, 1971), it is reasonable to hypothesize that certain wetting agents have the potential to extract/remove hydrophobic organic substances from soil. Thus, the objective of this study was to investigate the effect of selected wetting agents on removal of hydrophobic organic coatings from sand surfaces and their influences on SWR.

## **Materials and Methods**

### *Experiment setup*

Naturally occurring water-repellent sand was collected from the LDS area on a 7-year old putting green constructed based on United States Golf Association (USGA) recommendations and air-dried under room temperature. Sands were passed through a 2-mm sieve to remove plant residues and thoroughly mixed for future use. The degree of SWR was determined as high via the molarity of ethanol droplet test (MED) (King, 1981) with a result of 2.2 molar (M).

Sand column systems were built using PVC tubes (Georg Fischer Harvel LLC, Easton, PA) with 5.08 cm internal diameter and 0.48 cm wall thickness. The tube bottoms were covered with a layer of fine synthetic fabric (maximum opening size <0.05 mm) to retain sand particles but permit liquid drainage. A total of 254 g of sand was packed

uniformly into the PVC soil columns to a depth of 7.80 cm, yielding a bulk density of 1.66 g cm<sup>-3</sup>. Particle density of the sand was measured as 2.68 g cm<sup>-3</sup>, and porosity was determined to be 37.8 % and equivalent to a pore volume of 58 ml.

#### *Treatment application*

Wetting agents included in this experiment were Matador (100% alkyl block polymer; EnP Investments LLC., Mendota, IL), OARS (80% polyoxyalkylene polymers and 10% potassium salt of alkyl substituted maleic acid; AQUA-AID Inc., Rocky Mount, NC), and pHAcid (combination of a blend of acidifying agents and a high molecular weight nonionic surfactant; Numerator Technologies Inc., Sarasota, Florida). A non-treated control, distilled deionized (DD) water only, was also included. All wetting agents were mixed with DD water at the highest label rates at 50, 29, and 267 ml L<sup>-1</sup> for Matador, OARS, and pHAcid, respectively. To saturate the sand profile, 70 ml of wetting agent solutions were slowly applied to the sand columns from the top without causing ponding. At 24 hours after treatment, sand columns were washed with a pore volume (58 ml) of DD water three repeated times, with a 30-minute interval between each wash to allow complete leaching.

#### *Measurements and statistics*

All leachates drained from the bottom were collected for volume measurement, before they were acidified using H<sub>2</sub>SO<sub>4</sub> to pH < 2 to remove inorganic carbon and stored at 4 °C in the dark for measurement of dissolved organic carbon (DOC) and particulate organic matter (POC). After drying to a constant weight at 50 °C, the washed sand columns were tested for water repellency again via the MED method. In order to compare overall organic carbon change in the sand profile before and after treatment, solid phase

organic carbon (SOC) in the untreated and treated sands was measured utilizing LECO TruSpec CN Carbon/Nitrogen analyzer (LECO Corporation, St. Joseph, MI).

Determination of DOC was performed by filtering 0.5 ml of leachate through a 0.45  $\mu\text{m}$  Acrodisc nylon membrane syringe filter (Pall Corporation, Port Washington, NY), before analysis using a Shimadzu TOC-VWP analyzer (Kyoto, Japan) equipped with an autosampler ASI-V. The amount of DOC in wetting agent solutions was also determined for comparison of organic carbon (OC) input. Remaining leachate were then centrifuged at 10,000 x g for 15 minutes to remove and concentrate particles in solution. The collected particles were then dried at 105  $^{\circ}\text{C}$  for 12 hours prior to determination of mass. Particulate organic matter (POM) content was determined via combustion at 550  $^{\circ}\text{C}$  for 12 hours (Page, 1982), and POC content was determined using a conversion factor, where POC equals to 58% of POM (Pribyl, 2010).

The experimental design for this study was a complete, randomized design with three replications, and the entire experiment was repeated once. Analysis of variance was conducted using the PROC GLM procedure of SAS 9.4 (SAS Institute, Cary, NC). There was no treatment by study interaction for all measurements; thus, data of the two experiments were pooled together and significant means were separated based on Fisher's Protected LSD at  $P < 0.05$ .

## **Results and Discussions**

### ***Effects on water infiltration/retention***

Leachate volumes collected from all leaching event showed significant differences for different treatments (Table 3.1). Although all treatments were applied at a volume (70 ml) greater than the estimated pore volume (58 ml) of the sand profiles, sand

columns treated with Matador and OARS nearly retained all solution applied. In comparison, water-treated control columns and pHAcid-treated columns retained 54 and 58 ml waters, respectively, which approximately equivalent to the estimated pore volume. After the first wash with a pore volume of water (58 ml), sand columns treated with Matador exhibited increased water drainage that resulted in 76% of the applied water volume draining from the columns. OARS-treated sand columns, however, showed significantly greater water retention and only leached out 28% of the applied volume. The water and pHAcid treatments resulted in leachates of 67% or 71% of the applied volume, respectively. Following the second and third washes, water held in both OARS- and Matador-treated columns decreased to 3%~5% of the volume applied in each washing event (Table 3.1). In comparison, pHAcid-treated columns and the control columns retained 3 or 6 ml more water after the second wash, respectively. After the third wash, no significant differences in water retention were observed between the wetting agent-treated columns and the column treated with only water.

The effects of wetting agents on soil physical properties are influenced by their chemical properties (Zontek and Kostka, 2012). Mobbs et al. (2012) evaluated four wetting agents and found no noticeable effect of the wetting agents on improving water movement. However, lower capillary rise and unsaturated hydraulic conductivity in wetting agent-treated sand was observed, indicating reduced sand surface tension and increased soil water retention. Likewise, Oostindie et al. (2008) observed greater water content in soil cores treated with a nonionic copolymer wetting agent, compared to the untreated cores. In contrast, a nonionic wetting agent intended to improve water drainage resulted in substantially lower soil water content in treated soil (Karagunduz et al., 2001).

Additionally, an effect on water movement enhancement has been reported in multiple publications (Feng et al., 2001, 2002; Karnok and Tucker, 2008; Song et al., 2014), where disparities in water movement were attributed to differences in wetting agent chemistry and hence, their influence in water retention.

### ***Effects on DOC and POC in leachate***

The amount of DOC and POC found in leachates following the four leaching events, including leachates collected after treatment and after the first, second, and third washes, showed a similar trend (Table 3.2). The greatest amount of DOC and POC leached from the sand columns were found in the leachates of the first washing, with exceptions for pHAcid-treated and control columns where no statistical differences were found in leachate POC following sequential washes. After the second wash, Matador and OARS caused a 5- to 15-fold greater amount of DOC leaching out, respectively, than the control, while Matador continually showed the greatest amount of DOC and POC in the leachates, approximately 2.4 or 6.2 times of the output by application of OARS, respectively (Table 3.2).

When DOC or POC data from four leachate fractions from each treatment was combined, it appeared that majority of OC output in the leachates was in the DOC form, where the total DOC output from Matador- or OARS-treated columns accounted for approximately 12 or 23 times of related POC, respectively (Table 3.3). Matador also caused significant leaching of POC, with at least 3.4-fold greater total POC output than the other treatments. However, total DOC output of Matador and OARS contribute only 92% and 51% of the OC input from the treatments, respectively, where all wetting agents included in this experiment are 100% water-soluble and in DOC form. Consequently, it is

not clear if or how much of the leached DOC from Matador- or OARS-treated sand columns were associated with the wetting agents applied DOC. The cumulative OC (COC) output in leachate was further calculated by summing the total DOC and POC (Table 3.3). Due to the dominant presence of DOC in leachates, COC showed a similar trend as total DOC. The COC output from Matador-treated sand columns was 1,751 mg, comparable to its OC input of 1,765 mg. However, OARS-treated columns leached only 50% of the OC introduced to the sand system, suggesting a stronger sorption of OARS components to the sand. Cumulative OC output from pHAcid- and water-treated sand columns were statistically similar (Table 3.3), indicating minimum influence of pHAcid on soil OC. The pHAcid and water treatments moved out comparable amounts of OC from the columns, indicating a minimal ability of pHAcid to interact with OC in this experimental system.

Soil organic matter can be fractionated into POM and dissolved organic matter (DOM), which reflect POC and DOC carbon sources, respectively. The fraction sizes of POM range from 0.45  $\mu\text{m}$  to 2.0 mm (Bormann et al. 1969). As the fabric adhered to sand columns had a maximum opening of 0.05 mm, collected POM had a fraction sizes possibly ranging from 0.45  $\mu\text{m}$  to 0.05 mm, which is attributed to the fine particulate organic carbon (FPOC) fraction (0.45  $\mu\text{m}$  to 0.1 mm) (Fisher and Likens 1973). It has been reported that FPOC an important role in the formation of water-stable soil aggregates (Puget et al., 2000; Tisdall and Oades, 1982) and increasing the solid-liquid contact angle and SWR even at low concentrations (Franco et al., 1995; McGhie and Posner, 1980). Extraction or redistribution of POM often involves intensive laboratory-based physical procedures, such as ultrasonic dispersion and high speed centrifugation

followed by extensive water flushing (Franco et al., 1995; Oorts et al., 2005). As a result, removal of POM even at a relatively low quantity by routine management practices, such as wetting agent application, can be desirable for mitigating SWR.

Dissolved organic carbon is usually defined as organic materials that can pass through a 0.45  $\mu\text{m}$  pore size filter (Kalbitz et al., 2000). The main portion of soil DOC comes from complex and high molecular weight fractions including humic substances (Herbert et al., 1995; Kalbitz et al., 2000). However, an organic material with size  $< 0.45 \mu\text{m}$  cannot be considered as DOC if it's hydrophobic and not dissolving in soil solution. Studies have found that DOC can be fractionated into a hydrophobic component that contains more aromatic humic and humic acids, and a hydrophilic component which consists of simpler aliphatic chains (Chen et al., 2003; Guggenberger et al., 1994). This amphiphilic nature imposed a potential high affinity between the applied wetting agents who also have amphiphilic structures and surface DOC coatings, leading to the observed sorptive effect of OC in Matador and OARS.

### ***Effects on sand SOC and SWR***

After wetting agent treatment and all wash events, SOC content in the sand systems were determined (Fig. 3.1). Matador-treated sand had statistically same SOC as what untreated sand initially had. In contrast, OARS-treated sand accumulated 27% additional SOC, and applications of pHAcid and water only treatment reduced up to 16% SOC, compared to the untreated sand.

Following wetting agent treatment and three washes, Matador-treated sands exhibited no SWR and the treatment returned the sand to a wettable condition with a MED value of 0 molar (Fig. 3.2). As a result, Matador maintained the overall SOC

content (Fig. 3.1) and completely reverse SWR. Sand treated with OARS also showed minimal SWR (0.2 molar MED value) (Fig. 3.2), which was expected based on the significant sorption of OARS compounds to the sand (Fig. 3.1). The pHAcid and water treatments slightly reduced SOC of the sands (nominally for the water treatment); however, sand treated with pHAcid or water exhibited elevated SWR with MED values up to 50% greater than the untreated sand.

The differential effects of Matador and OARS on sand SOC content are likely related to their chemical properties. Matador contains 100% alkyl block polymers, and OARS consists of 80% polyoxyalkylene polymers and 10% potassium salt of alkyl substituted maleic acid, and 10% additional inert ingredients. Although published information that specifically discusses the sorption of different nonionic surfactants on soil organic matter are limited, it is suggested that the sorption of polyoxyalkylene block copolymers on soil organic matter occurs due to strong lipophilicity of the copolymers (Nace, 1996). A high log octanol-water partition coefficient ( $K_{ow}$ ) value was observed for a polyoxyalkylene block copolymer, suggesting strong potential for copolymer sorption to soil organic matter (Nace, 1996). These properties of polyoxyalkylenes in OARS also likely explain the extended residual effect of OARS on water retention, compared with other treatments (Table 3.1). For Matador, the actual alkyl block polymer is unknown and inadequate information is available to thoroughly elucidate the apparent ‘non-significant’ effect of Matador on SOC content in the sand (Fig. 3.1). However, based on our data, we postulate that Matador could replace at least a portion of the organic coatings on the sand with surfactant molecules.

According to the pHAcid label, the acidifying agents in this product are aimed to manage the inorganic carbon fraction of soil (Ca and Mg carbonates), which consists of insoluble salts that can rapidly precipitate from the soil solution (Ogino et al., 1987). Recycled water or well water often contains excessive amount of carbonate that increases soil pH and forms a substantial amount of insoluble salts (Harivandi, 2004). With application of pHAcid, soil pH can be acidified to release  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions into solution through the dissolution of insoluble carbonates, reducing the amount of clogging caused by Ca and Mg carbonate deposits. Additionally, high sodium content in golf course water recycling irrigation systems has been a concern (Harivandi, 2004), because increased  $\text{Na}^+$  in the soil disrupts and disperses small soil particles that can block soil micropores (Duncan et al., 2000; Gupta et al., 1984). The enhanced  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  solubility/concentration in soil solution can increase the overall soil electrolyte level and counteract this negative effect from excessive  $\text{Na}^+$ , thus stabilizing soil structure (Beltrán, 1999). The sand-based USGA putting green soil system has less than 3% clay content and a 35 to 55% total porosity with 15 to 30% air-filled macropores (USGA, 2004); therefore, the influence from pHAcid on USGA putting greens was expected to be less significant than on a native soil-based turf systems.

It is important to mention that the treated and washed sands were oven dried at 50 °C for 2 weeks to achieve constant weight before testing for SWR, and previous studies have indicated that oven-drying of moist water-repellent soil samples can lead to an increased SWR (Dekker et al., 1998; Franco et al., 1995). Under field conditions, temperatures at the soil surface can reach > 50 °C thus stimulate SWR development (Rose, 1968). The cause of increased SWR in water- and pHAcid-treated sand after drying may be related to:

1) mechanically forced the release of hydrophobic particles from plant tissues during drying (Neinhuis and Barthlott, 1997); 2) heating and/or biological process-triggered release of organic substances from wax globules/hydrophobic coatings that were originally present within the soil matrix (Franco et al., 1995); 3) build-up of new hydrophobic substances from plants or microorganisms (Doerra and Thomasb, 2000); and 4) heating induces a significant shift of organic compound forms from high-molecular-weight fatty acids and aliphatic species to shorter fatty acids (< C12) and aromatic compounds, leading to increased SWR (Atanassova and Doerr, 2011). As the sand was oven-dried at 50 °C, the main reason of increased SWR by the water control could be the second or fourth mechanism: heating triggered release/activation and/or transformation of the hydrophobic compounds.

## **Conclusions**

This study showed that wetting agents such as Matador and OARS can significantly improve water retention of water-repellent sand, with OARS providing longer residual effect. The chemical properties of wetting agents influenced their ability to interact with organic coatings on sand, and data collected after single application of Matador and OARS suggests that these properties contributed to the sorption effect of wetting agent monomers or desorption effect of POC, which facilitated the increase of surface wettability. The OARS molecules exhibited strong sorption to the hydrophobic sand, thus causing substantial accumulation of OC in the sand system. Although the overall SOC in the Matador-treated sand remained unchanged after treatment, it removed significant more POC from the system than other treatments while eliminated SWR. Our data suggested a possible replacement of hydrophobic organic coatings, especially the

POC portion, by the wetting agent molecules in Matador. OARS also successfully reduced the SWR to minimal values, while pHAcid and water only treatments increased sand SWR. As pHAcid and water showed negligible impacts on organic matters in sand, the increasing of SWR is likely attributed to the heating/drying cycles which released and/or activated the hydrophobic compounds in the sand system. Future studies may need to clarify the mechanisms of different wetting agents at the molecular level and their chronic effects after repeated applications.

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**Table 3.1.** Leachate volume (ml) collected after treatment applications and after the first, second, and third washes of the wetting agent-treated sand columns. Sand columns treated with water were included as a non-treated control.

Treatments <sup>†</sup>	Leachate volume			
	Ttreatment	First wash <sup>‡</sup>	Second wash	Third wash
----- ml -----				
Matador	1 c3 <sup>§</sup>	44 a2	55 a1	55 ab1
OARS	1 c3	16 d2	55 a1	56 a1
pHAcid	12 b4	41 b3	52 b2	55 b1
Water	16 a4	39 c3	49 c2	54 ab1

<sup>†</sup>All treatments were applied at 70 ml.

<sup>‡</sup>Treated sand was washed with one pore volume of water (58ml) at 24 hours post-treatment.

<sup>§</sup>Means in the same column followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 3.2.** Dissolved and particulate organic carbon (DOC and POC; mg) in leachates collected after treatment applications and after the first, second, and third washes of the wetting agent-treated sand columns. Sand columns treated with water was included as a non-treated control.

Treatments	Treatment	First wash	Second wash	Third wash
----- DOC (mg) -----				
Matador	48 a3 <sup>†</sup>	1238 a1	295 a2	34 a3
OARS	40 a3	516 b1	153 b2	34 a3
pHAcid	18 b2	51 c1	25 c2	11 b2
Water	11 b2	28 d1	18 c12	13 b12
----- POC (mg) -----				
Matador	1 a3	108 a1	26 a2	1 a3
OARS	1 a2	17 b1	7 b2	6 a2
pHAcid	0 a1	7 c1	5 b1	3 a1
Water	0 a1	7 c1	7 b1	6 a1

<sup>†</sup>Means in the same column for the same parameter followed by the same letter were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

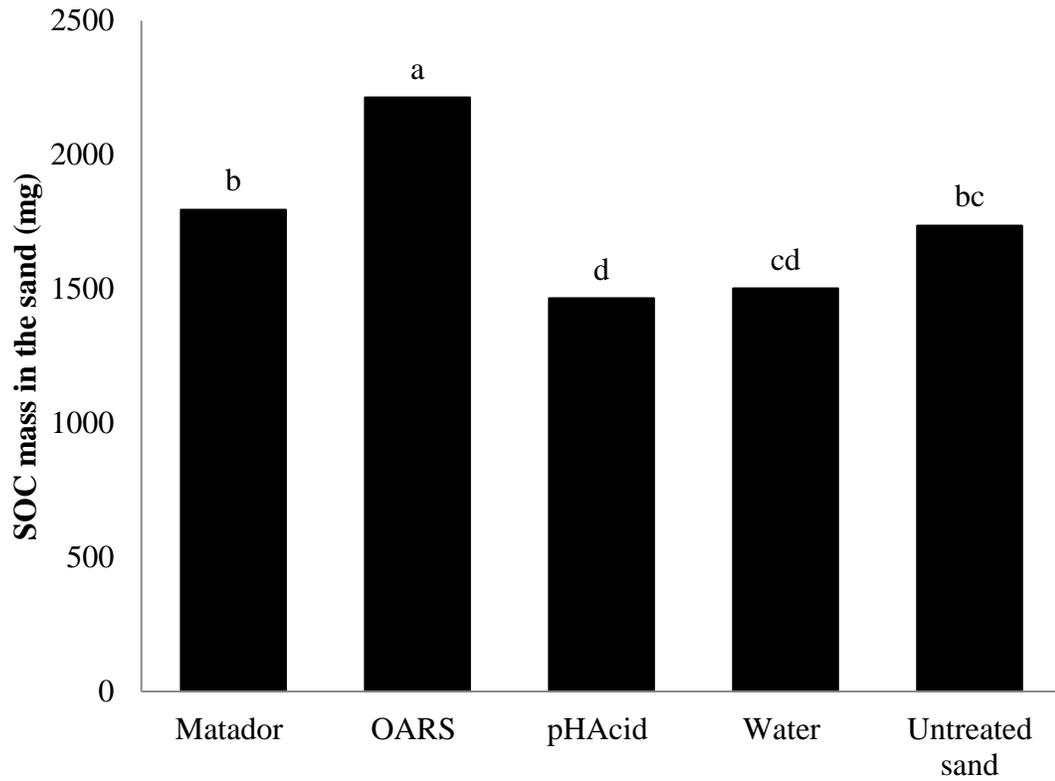
**Table 3.3.** Summary of organic carbon (OC; mg) input from different wetting agents, and total dissolved or particulate organic carbon (DOC or POC; mg), and cumulative organic carbon (COC; mg) in leachates after treatment application and sequential washes. Sand columns treated with water was included as a non-treated control.

Treatments	Treatment OC input	Total DOC in leachates	Total POC in leachates	COC <sup>†</sup> in leachates
----- mg -----				
Matador	1765 a <sup>‡</sup>	1615 a	137 a	1751 a
OARS	1409 b	721 b	31 b	752 b
pHAcid	23 c	105 c	20 b	121 c
Water	0 c	70 d	16 b	90 c

<sup>†</sup>Cumulative organic carbon (COC) is the sum of total DOC and POC.

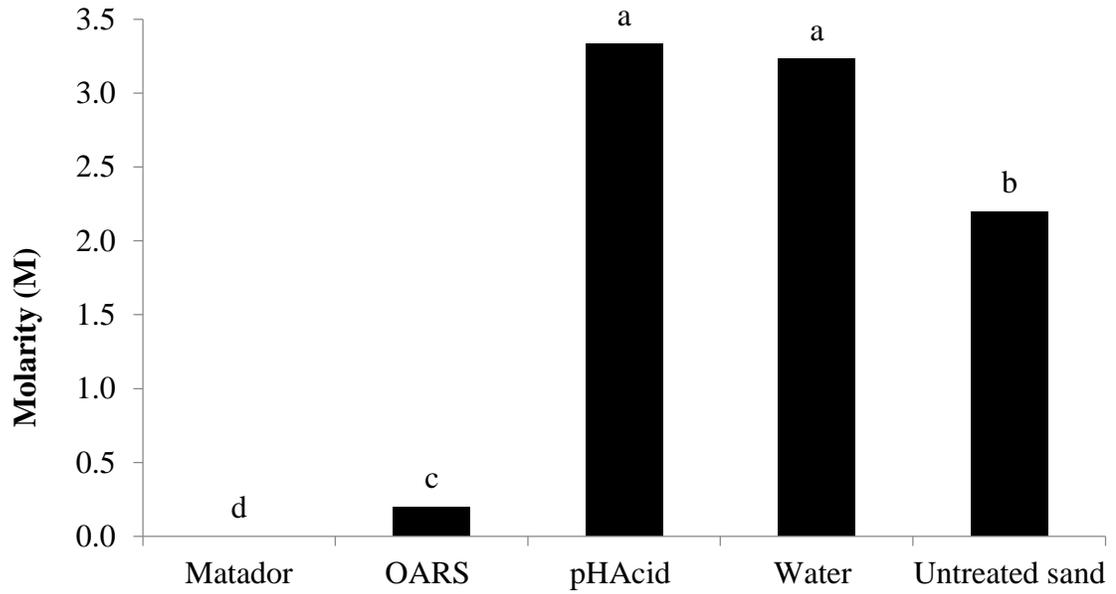
<sup>‡</sup>Means in the same column followed by the same letter were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Figure 3.1.** Solid phase organic carbon (SOC) content (mg) in treated and untreated sands. Bars labeled with the same letter were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



**Figure 3.2.** Soil water repellency (SWR) determined by molarity of ethanol droplet (MED; M) test. Bars labeled with the same letter were not significantly different based on

Fisher's Protected LSD at  $P < 0.05$ .



## Chapter III: Part Two

### Effects of Selected Wetting Agents on Water Repellent Sands: Underlying Mechanisms

Enzhan Song<sup>1</sup>, Keith W. Goyne<sup>2</sup>, Robert J. Kremer<sup>2</sup>, Stephen H. Anderson<sup>2</sup>, Xi Xiong<sup>1\*</sup>

<sup>1</sup>Division of Plant Sciences, University of Missouri, Columbia, MO 65211, USA

<sup>2</sup>School of Natural Resources, University of Missouri, Columbia, MO 65211, USA

#### Abstract

Traditional wetting agents/soil surfactants have been developed to temporarily mitigate soil water repellency (SWR) causing drought issues in sandy soils, such as localized dry spots (LDS) on golf course putting greens. However, reapplications at monthly or even shorter intervals are usually required to continuously address SWR. More recently developed wetting agents, such as OARS (organic acid removal system), purportedly remove hydrophobic organic compounds (HOCs), thus directly addressing SWR for long-term control. This study compared the effects of OARS and an innovative block copolymer, Matador, in hydrophobic sand (HS) and fresh sand (FS) on soil water retention, HOC removal, and SWR, with the goal of explaining the underlying wetting mechanisms. Commercial United States Golf Association (USGA) putting green sand was used as FS and the top 5 cm of sand from a LDS area on a 7-year old USGA putting green was harvested as the HS source. Wetting agents mixed at their highest label rates and a water control were applied to the surface of re-packed soil columns that drained freely. After 24 hours, treated columns were washed three separate times with one pore volume of deionized water. Leachate from treatment applications and each wash were collected to determine the volume of leachate and for measurement of dissolved organic

carbon (DOC) and particulate organic carbon (POC). Sequentially, triple-washed sand columns were dried at 50 °C and subjected to two more cycles of treatment/washing/drying. At end of the three cycles, solid phase organic carbon (SOC) of the sands was measured via combustion and SWR was quantified using the molarity of ethanol droplet test (MED). Both Matador and OARS removed POC from HS and FS systems, while Matador showed evidence of replacing soil DOC with surfactant monomers of the formulation with minimum hydrophobicity (MED=0). In contrast, surfactant monomers of OARS sorbed to HS and FS as illustrated by 16 and 44% SOC increases, respectively. Consequently, hydrophobicity significantly increased from the original MED values of 2.2 (HS) and 0.0 (FS) to 4.3 and 0.3, respectively. The results indicated different mechanisms of addressing SWR between the two wetting agents. Matador was effective at replacing HOC from the sand system; however, OARS appeared to mainly add monomers into the sand system, leading to increased SWR after repeated treatment, rewetting, and drying cycles.

*Keywords:* Repeated surfactant application, soil water repellency, hydrophobic organic coating solubilization, surfactant adsorption, critical micelle concentration, surfactant working mechanisms.

## Introduction

Soil water repellency (SWR) is a common issue on sand-based golf course putting greens (Ellies and Hartge, 1994; Tucker et al., 1990; Wallis and Horne, 1992; Wilkinson and Miller, 1978), and wetting agent application has been the most effective means to mitigate corresponding symptoms, such as localized dry spot (LDS) (Cisar et al., 2000; Karnok, 2006; Kostka, 2000).

Microbially decomposed plant materials are considered the primary source of soil hydrophobic organic compounds (HOCs) (Feeney et al., 2006; McGhie and Posner, 1980; McGhie and Posner, 1981; Sun et al., 1999), which includes humic substances (de Blas et al., 2010) and biomolecules derived from microbes and plants such as waxes (Franco et al., 2000) and fatty acids (Graber et al., 2009; Mainwaring et al., 2004). These components of soil organic matter (SOM) tend to be nonpolar and have low solid surface free energy/surface tension ( $\gamma_s$ ) (Doerr et al., 2000). As a result, organic materials often occur as coating on mineral particle surfaces which decrease  $\gamma_s$  and increases overall soil hydrophobicity (Kern et al., 1986).

Most wetting agents are formulated with non-ionic surfactants consisting of amphiphilic molecules with polar hydrophilic heads and non-polar lipophilic/hydrophobic tails. Such characteristics allow wetting agents to attach their lipophilic tails with non-polar hydrophobic particle surfaces while the polar end can interact with soil water, thus wetting the system (Cisar et al., 2000; Dekker et al., 2005; Karnok et al., 2004; Kostka, 2000). Specialized wetting agents, such as OARS, also aim to remove HOCs through solubilization/desorption of the organic coatings and flushing from the system through irrigation. It is, however, important to note that the amphiphilic

properties of surfactants may increase the affinity of HOCs to soil particles. Research had reported countering effects on the ability of surfactants to enhance infiltration after repeated usage of strong soil absorptive surfactants (Urrestarazu et al., 2008).

Investigation of non-ionic surfactant sorption onto different soil minerals has found a positive correlation between mineral silica content and the sorption of nonylphenol ethoxylates commonly used in wetting agents (Shen, 2000). Considering that wetting agents are primarily applied to silica sand-based soil media in putting greens, the sorption of surfactant ingredients onto sand surfaces is expected. Further, Sun et al. (1995) found positive correlation between apparent soil–water distribution coefficients ( $K_d$ ) and surfactant concentration when a micelle-forming surfactant was applied below its critical micelle concentration (CMC). However, a negative correlation between  $K_d$  and surfactant concentration was observed when the same surfactant was applied above the CMC. These reports indicated the possibility of solubilization/partitioning of HOC, but only when surfactant micelles start to form and precipitate on soil particles. The objective of this study was to investigate the influence of selected wetting agents on SOM in hydrophobic and fresh sand surface systems following repeated applications at label rates.

### **Materials and Methods**

Hydrophobic sand (HS) was prepared by homogenizing and drying sand collected from a water repellent area on a United States Golf Association (USGA) standard putting green. Consistent strong hydrophobicity levels in the green were validated via the molarity of ethanol droplet test (MED) with a value of 2.2 molar (M) (King, 1981; Watson and Letey, 1970).

To mimic water movement influences on wetting agent function, 254 g of the prepared HS or fresh wettable sand (FS) was packed into PVC tubes (Georg Fischer Harvel LLC, Easton, PA) to a depth of 7.80 cm. The tubes have 5.08 cm internal diameter and 0.48 cm thickness and one end was covered by a layer of fabric with maximum openings < 0.05 mm to retain the sand. Bulk densities of HS and FS columns were 1.66 g cm<sup>-3</sup> and 1.74 g cm<sup>-3</sup>, and particle densities of HS and FS were measured as 2.68 g cm<sup>-3</sup> and 2.76 g cm<sup>-3</sup>. Thus, the porosity was determined as 38% for HS columns and 37% for FS columns which was equivalent to a pore volume of 58 ml and 54 ml, respectively. Treatments included Matador (100% alkyl block polymer), OARS (80% polyoxyalkylene polymers and 10% potassium salt of alkyl substituted maleic acid), and a distilled, deionized (DD) water control. The liquid surface tension at 0.5, 1, 2, and 3 times label rates was determined by an Attension Teta Lite tensiometer (Biolin Scientific, Inc., Linthicum Heights, MD) to create the surface tension-concentration relation curve (Fig. 3.3). One time label rate was used in this study where 70 ml of treatment solutions were applied from the top of each sand column without creating a ponding pressure. After 24 hours, treated sand columns were washed three times with three pore volumes of DD water (i.e., one pore volume per wash). Triple-washed sand columns were dried at 50 °C for 7 days. Subsequently, the entire process of treatment application, triple washing, and drying was repeated twice more for all treatments. Leachates from all individual treatment and wash events were collected for each column, then acidified pH < 2 and stored at 4 °C in the dark. The leachate volume, dissolved organic carbon (DOC), and particulate organic carbon (POC) mass contents were measured next. At the completion of all washing/drying cycles, sand samples were collected from each column for

determination of solid phase organic carbon (SOC) mass content and hydrophobicity via MED test.

Separation of POC from solution was performed by centrifuging the leachate at 10,000 x g for 15 minutes at 4 °C, followed by removal of the supernatant solution. Complete separation of POC from solution was further ensured by centrifuging supernatant through nylon membrane filter centrifuge tubes (Corning® Costar® Spin-X® centrifuge tube filters) with a pore size of 0.45 µm. No particles were observed on the filter after centrifugation. Solids separated from solution were dried at 105 °C for 12 hours, followed by a measurement of particle mass. Particles were combusted under 550 °C for 12 hours, cooled, and weighed (Nelson and Sommers, 1982). Particulate organic matter content of the leachate was calculated as the mass loss after combustion, then the POC content was calculated using 58% organic matter to organic carbon (OC) conversion factor (Pribyl, 2010). Supernatant solution collected after centrifuge filtration of the leachate was analyzed for DOC concentration using a Shimadzu TOC-VWP analyzer (Kyoto, Japan) equipped with an autosampler ASI-V, and DOC mass content was calculated based on the leachate volume and obtained DOC concentration. Content of SOC as % by weight in treated and untreated (initial substrates) sand samples were measured utilizing LECO TruSpec CN Carbon/Nitrogen analyzer (St. Joseph, MI), then the SOC mass content was calculated based on total sand mass.

The experimental design for this study was a complete randomized design with three replications, and the entire study was repeated once. Analysis of variance was conducted using the Proc GLM procedure of SAS 9.4 (SAS Institute, Cary, NC). No treatment by study interactions were found for all measured parameters, thus the data

from the two studies were pooled to provide six replicates per treatment. Significant mean separations were performed based on Fisher's Protected LSD at  $P < 0.05$ .

## **Results and Discussion**

The relationship between the surface tension of water and the concentration of applied wetting agents showed a decreasing trend for both wetting agents as wetting agent concentration increased to two (OARS) and three (Matador) times the label rate (Fig. 3.3). At higher concentrations, surface tension was generally stable, indicating that the critical micelle concentration (CMC) had been reached (Burlatsky et al., 2013; Kile and Chiou, 1989). Results suggested that the concentrations of both wetting agents at normal label rates were not sufficient to saturate the solution with surfactant monomers.

Results of leachate volume, DOC, and POC collected from the three application cycles are presented in Tables 3.4, 3.5, and 3.6, respectively. Each application cycle had four individual leachate collection events, including leachate of the treatment application and leachates of the first, second, and third washes. Due to water alone significantly increasing hydrophobicity of HS to a severe level (MED value at 3.4 M) after only one application cycle (Fig. 3.4), no data is shown for water alone treatment in the second and third application cycles for HS (Tables 3.4, 3.5, and 3.6).

### ***Effects on leachate volume***

Leachate volume indirectly represented treatment influence on soil hydrologic aspects, such as hydraulic conductivity and water holding capacity. In the HS system, OARS and Matador treatment applications (70 ml) yielded a maximum of 3.8 ml of leachate following wetting agent application (Table 3.4), even though the total pore volume was only 58 ml. Results indicated increased water holding capacity by the wetting agents. The enhanced water holding capacity of OARS-treated HS extended to

the first wash event following the first application event which yielded only 15.5 ml of leachate, which was significantly less than the other treatments (Table 3.4). Meanwhile, Matador-treated HS yielded the greatest leachate volume (46.6 ml) in first wash event, thus indicating improved infiltration upon treatment (Table 3.4). However, a similar trend was not observed in HS system during the second and third application/wash cycles. Treatment effects on leachate volume gradually abated in the second and third wash events in all three application cycles for the HS system (Table 3.4). Furthermore, the comparison between HS and FS showed opposite influence from the wetting agents on leachate volume in the second and third wash events of the first application cycle, where Matador and OARS tended to facilitate infiltration with significantly more leachate yield than water in the HS system, but both treatments resulted in significantly less leaching in FS system, compared to water (Table 3.4).

Previous studies have reported similar differentiated effects of various types of soil surfactants on soil hydraulic properties. Some observed enhanced soil water retention and increased water holding capacity than untreated material without improved water movement in water repellent soil (Mobbs et al., 2012; Oostindie et al., 2008). Many others found improved water infiltration/drainage or lower soil water content in treated hydrophobic soil (Feng et al., 2001; Feng et al., 2002; Karagunduz et al., 2001; Karnok and Tucker, 2008; Song et al., 2014). These results suggest that wetting agents with different chemical properties may act through different mechanisms. While data are lacking for the effects of wetting agents on water movement in hydrophilic/wettable soil, some have stated that soil surfactants may not be beneficial in healthy, hydrophilic soils (McFarland et al., 2002; Miller et al., 1975). However, significantly reduced water

leaching in FS (Table 3.4) can be a potential reference for utilizing wetting agents under hydrophilic soil conditions to provide enhanced water holding capacity and thus reduced chemical leaching.

### ***Effects on OC***

Measurements of DOC and POC mass content in the leachates showed three consistent trends for the HS and FS systems in all three application cycles (Tables 3.5 and 3.6). First, DOC dominated the overall OC leached out from the wetting agent treated sand with 7 to 103 times higher mass than POC. Second, most of the DOC leached out after the first wash event, but POC was more evenly distributed in the three wash events. Lastly, sum DOC output in leachate from the Matador treatment was consistently greater (up to 20%) than the OARS treatment for the HS and FS systems (Tables 3.5 and 3.6). Although the HS system showed similar DOC mass loss in the first wash leachate among the three application cycles within each treatment, the amount of DOC in the first wash leachate from the FS system increased from 484.6 mg to 586.3 mg to 736.9 mg for OARS and from 599.4 mg to 619.4 mg to 733.9 mg for Matador, following sequential three application events (Table 3.5). This pattern indicated an initial coating/adsorption of surfactant monomers on the FS surface, but greater leaching of the wetting agents after repeated applications. This trend is attributed to reduced surfactant reactivity with the sand following the previous treatment due to the increased development of a surfactant coating on the particles.

Although SOC mass content in the untreated HS was four-fold the amount in FS, SOC measured in the treated HS and FS showed the same pattern (Fig. 3.5). Water only treatment significantly reduced SOC in the treated HS and FS systems, compared to the

untreated HS and FS sand. Matador-treated sands also had statistically similar SOC than untreated HS and FS, while OARS significantly increased the SOC in treated HS and FS systems. To better translate the data, total dissolved, particulate, and cumulative organic carbon (TDOC, TPOC, and TOC) collected from all application cycles were calculated, and compared with total OC input from the three applications (Table 3.7). Data suggested true removal of POC from the HS system by Matador and OARS with 11- to 6-fold greater TPOC, compared to water control. However, SOC in both HS and FS sand system did not change significantly after three applications of Matador, which is correlated with the comparable TOC (2982 mg) and total OC input (2997) of Matador. More significant results were observed in OARS treated HS, where 3864 mg total OC input from the OARS applications only resulted in 2574 mg TOC output, which is a 33% loss of total OC input into the HS system (Table 3.7). In addition to significantly higher SOC in the OARS treated HS than untreated HS (Fig. 3.5), indicating sorption of OARS organic molecules into the HS system.

Similar trend was observed in FS system, with 6 and 33 % decrease TDOC output in the Matador and OARS leachates, respectively, compared to corresponding total OC input (Table 3.7), indicating coating/adsorption of surfactant monomers on the FS surface originally free of HOC. Strong adsorption of nonionic surfactant onto clean sand has been reported previously by Bera et al. (2013). The authors conducted X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) experiments to prove the adsorption of nonionic surfactant on silica sand. While XRD results showed a high purity of silica sand, FTIR spectra of nonionic surfactant-treated sand showed a C-H bond stretching vibration shifting from  $2920\text{ cm}^{-1}$  to  $2927\text{ cm}^{-1}$ , in addition to a vibration at  $1888\text{ cm}^{-1}$ ,

due to adsorption of surfactant ethoxylate groups to the sand surface. A fitted Langmuir adsorption isotherm also showed a positive correlation between surfactant concentration and adsorption to the sand particles, but increases in adsorption ceased at the CMC. The CMC is the minimum aqueous concentration of a surfactant when monomers start to saturate in the solution and aggregate into micelles (Edwards et al., 1994; Rosen, 1989). The CMC value is determined by the surfactants' structure and composition, but is influenced by environmental conditions such as temperature and ionic strength of the solution (Edwards et al., 1994; Rosen, 1989). The micelles orient in a way where monomer non-polar tails are in maximum contact with each other creating a hydrocarbon-like core while their hydrophilic polar heads face outside and interact with water (Cui et al., 2008). Normally, following an increase of surfactant concentration, surface tension of the surfactant solution will decrease to the CMC and reach a constant value (Burlatsky et al., 2013; Kile and Chiou, 1989). According to this concept, both Matador and OARS were not able to reach its CMC at label rates (Fig. 3.3). However, compared to Matador-treated FS, the numerically small yet significantly higher MED index of OARS treated FS (Fig. 3.4) indicated a different orientation of OARS monomers on the surface of FS when applied at a rate below the CMC.

It is important to mention that both wetting agents only have soluble compounds thus the OC input would be in DOC form. As a result, it is difficult to isolate the hydrophobic coating portion of DOC from wetting agent input DOC in the final collected TDOC. However, POC detected in the leachate likely originated from the HS. As a result, a replacing effect of POC by Matador monomers was expected as Matador efficiently removed POC from water-repellent sand system with significant TPOC output yet

balanced SOC in Matador-treated and untreated HS (Fig. 3.4; Table 3.7). Compared to the overall SOC quantity in untreated HS system, the mass of Matador reduced SOC might be not significant (Fig. 3.5), but the surfactant did mitigate hydrophobicity in the HS system (Fig. 3.4). While Matador output respectively 345%, 106%, and 136% POC of what OARS did during the three application cycles completed for the HS system (Table 3.6), respectively, Matador also eliminated hydrophobicity of HS yet OARS doubled the MED value of HS (Fig. 3.4). Results suggested a significant role of POC on soil hydrophobicity. It has been reported that addition of low concentration of POC could significantly increase solid-liquid contact angle and SWR (Franco et al., 1995; McGhie and Posner, 1980). Removing of small amount of potential hydrophobicity causing POC by wetting agent applications can be a beneficial practice for long term SWR control/prevention under field conditions. The disappearance of hydrophobicity for Matador-treated HS suggested that the adsorbed molecules were able to arrange/orient themselves in a way that would not jeopardize the wettability of the sand even at a rate less than the CMC (Fig. 3.3), most likely due to their hydrophilic end facing into solution (Cui et al., 2008).

### ***Effects on SWR***

Three repeated application cycles of OARS or Matador showed opposite impacts on HS, where OARS significantly increased hydrophobicity of treated HS to > 4 M (extreme) and Matador reduced hydrophobicity to none (0 M) (Fig. 3.4). None of the treatments created much hydrophobicity on FS (Fig. 3.4), but OARS significantly increased the MED test index of FS from 0 M to 0.2 M. Data indicated an alteration of

physical or chemical properties on the OARS-treated FS surface that may induce increased surface tension.

The significant amount of OC addition into HS by OARS also significantly increased the MED hydrophobicity index (Fig. 3.4), suggesting excellent soil adsorption property in HS but also strong countering effects on water movement. Our results were very similar to Urrestarazu et al. (2008), who discovered increased water holding capacity, reduced wettability and air capacity by reused soil surfactants, possibly due to increased water adhesion/cohesion in the micropores and even reduced pore space. Furthermore, multiple studies related to remediation of soil organic contaminants have reported little or no effect on solubilization of HOCs (Haigh, 1996), or even increased precipitation of HOCs on soil particles (Laha et al., 2009) when surfactants were applied at less than the CMC. Our data suggested a stronger OC adsorption than the removing effect of OARS less than the CMC. More importantly, the unsaturated monomers from OARS may act alone and/or interact with original HOCs on HS that induced further hydrophobicity, instead of forming hydrophilic micelles.

Even though water alone was able to remove significant amount of OC from the HS system by one application and triple-wash cycle (Fig. 3.5; Table 3.7), the dramatically increased hydrophobicity of water-treated HS (Fig. 3.4) suggested that the OC collected in the water treatment leachate was more likely to be water extractable organic carbon (WEOC). It is important to distinguish DOC and WEOC in this case, as WEOC included both DOC and POC that can be directly dissolved or mechanically removed by water only (Chantigny, 2003). Limited contribution of hydrophobic substances (<30%) in WEOC under normal extraction temperature (20°C, 24 h) has been

reported by Nkhili et al. (2012). It was obvious that the residual OC in the HS system after removal of WEOC would contribute to further induction of soil hydrophobicity.

## **Conclusions**

The two tested wetting agents had different sorption and partitioning mechanisms when reacted with the soil OC. Matador showed an efficient SWR reduction and POC replacing effect with significant output of TPOC yet consistent before- and after-treatment SOC content in the HS system. OARS did not directly cause HOC removal, instead OARS showed a strong sorptive effect of its own nonionic surfactant monomers in the HS system that induced more soil hydrophobicity with repeated applications. Additionally, the wetting agents showed a sorption effect of their surfactant monomers in the FS system but only OARS altered the sand hydrophobicity with an increased MED index, which was consistent with its influence on HS. Thus, it is reasonable to predict that long-term repeated application of Matador on either a newly established or a putting green exhibiting hydrophobicity will provide prevention and mitigation effects on SWR. However, repeated application of OARS, especially at a lower than CMC rate may lead to further buildup of hydrophobicity on areas with SWR issues or even induce hydrophobicity on fresh sand. Obviously, although the experimental conditions used in an advertisement may be ideal for a product's action, the same positive results may not be achieved under soil conditions with different chemical and physical properties. Further research is needed to investigate the effects of tested wetting agents at higher concentrations, as well as to validate their actual working mechanisms at the microscopic/molecular level.

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**Table 3.4.** Treatment effects on leachate volume of hydrophobic and fresh sand systems after the first, second, and third applications and sequential washes.

Treatment	Application cycles	Treatment†‡	1st Wash§	2nd Wash	3rd Wash
<b>Hydrophobic sand</b> †					
	First application	----- Volume (ml) -----			
OARS		1 b3¶	16 c2	55 a1	56 a1
Matador		0 b3	47 a2	56 a1	56 a1
Water		17 a3	39 b2	49 b1	54 b1
	Second application				
OARS		4 a3	47 a2	55 a1	56 a1
Matador		0 b3	45 b2	56 a1	56 a1
	Third application				
OARS		1 b3	45 a2	55 a1	56 a1
Matador		4 a3	45 a2	56 a1	56 a1
<b>Fresh sand</b>					
	First application				
OARS		19 a4	44 a3	52 b1	51 c2
Matador		17 b3	44 a2	52 b1	53 b1
Water		16 c3	42 b2	54 a1	54 a1
	Second application				
OARS		16 c3	43 b2	52 b1	52 a1
Matador		17 a3	42 c2	52 ab1	51 b1
Water		21 b3	47 a2	52 a1	52 a1
	Third application				
OARS		21 b4	45 a3	52 b1	52 b2
Matador		14 c3	44 b2	51 c1	52 b1
Water		24 a3	40 c2	53 a1	53 a1

† Results of hydrophobic and fresh sand system were presented, respectively.

‡ All treatment solutions were applied at 70 ml.

§ Treated sand was washed with one pore volume of water at 58ml for hydrophobic sand and 54ml for fresh sand.

¶ Means in the same column of hydrophobic or fresh sand system followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row of hydrophobic or fresh sand system followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 3.5.** Treatment effects on dissolved organic carbon (DOC) of hydrophobic and fresh sand systems after the first, second, and third applications and sequential washes.

Treatment	Application cycles	Treatment	1st Wash	2nd Wash	3rd Wash	Sum§
<b>Hydrophobic sand†</b>		----- DOC (mg) -----				
	First application					
OARS		16.9 a4‡	516.3 b1	153.1 b2	34.4 a3	720.7 b¶
Matador		0.2 b4	667.3 a1	180.4 a2	20.6 ab3	868.5 a
Water		11.0 ab2	28.3 c1	17.9 c12	12.8 b2	70.0 c
	Second application					
OARS		51.7 a3	616.0 b1	150.0 b2	36.1 a3	853.8 b
Matador		5.3 b3	707.3 a1	184.8 a2	26.4 a3	923.8 a
	Third application					
OARS		13.5 b3	655.9 b1	149.8 a2	35.5 a3	854.7 b
Matador		60.0 a3	698.2 a1	165.5 a2	20.9 a4	944.6 a
<b>Fresh sand</b>						
	First application					
OARS		223.6 a2	484.6 b1	74.2 a3	25.4 a4	807.8 b
Matador		229.4 a2	599.4 a1	69.2 a3	10.6 b4	908.6 a
Water		4.7 b3	17.9 c2	36.1 b1	29.0 a1	87.7 c
	Second application					
OARS		176.0 b2	586.3 b1	74.0 a3	19.4 b4	855.7 b
Matador		250.6 a2	619.4 a1	62.8 a3	11.9 b4	944.7 a
Water		12.7 c2	20.3 c2	38.9 b1	33.7 a1	105.6 c
	Third application					
OARS		84.2 b2	736.9 a1	80.4 a2	21.7 a3	923.2 a
Matador		120.9 a2	733.9 a1	71.9 b3	19.1 a4	945.8 a
Water		10.5 c2	19.5 b1	23.1 c1	22.8 a1	75.9 b

† Results of hydrophobic and fresh sand system were presented, respectively.

‡ Means in the same column of hydrophobic or fresh sand system followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row of hydrophobic or fresh sand system followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

§ Sum of the DOC collected from application, the 1st, 2nd, and 3rd washes for each treatment.

¶ Mean separation of the sum DOC data was conducted individually, where means in hydrophobic or fresh sand system followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 3.6.** Treatment effects on particulate organic carbon (POC) of hydrophobic and fresh sand systems after the first, second, and third applications and sequential washes.

Treatment	Application cycles	Treatment	1st Wash	2nd Wash	3rd Wash	Sum§
<b>Hydrophobic sand†</b>		----- POC (mg) -----				
	First application					
OARS		1.3 a3‡	17.2 b1	7.2 b2	5.8 a2	31.6 b¶
Matador		0.1 a3	89.1 a1	16.2 a12	3.8 a2	109.2 a
Water		0.3 a2	7.0 c1	6.7 b1	6.4 a1	20.4 b
	Second application					
OARS		13.6 a23	21.5 b1	17.3 a12	8.8 a3	61.2 a
Matador		0.0 b2	57.4 a1	5.4 b2	2.4 a2	65.1 a
	Third application					
OARS		3.0 a3	8.8 b3	24.4 a1	16.4 a2	52.5 a
Matador		7.5 a2	55.4 a1	3.2 b2	5.1 b2	71.3 a
<b>Fresh sand</b>						
	First application					
OARS		9.0 a1	1.9 a2	6.8 a1	2.4 a2	20.1 a
Matador		5.3 b1	3.2 a12	0.8 b3	1.3 a23	10.6 b
Water		7.5 a1	2.7 a2	2.3 b2	0.6 a2	13.1 b
	Second application					
OARS		3.1 a1	2.0 b1	2.0 a1	2.3 a1	9.3 a
Matador		3.3 a1	3.8 a1	1.0 a2	0.9 ab2	9.1 a
Water		1.2 b1	1.3 b1	1.5 a1	0.3 b1	4.2 b
	Third application					
OARS		3.2 a2	10.5 a1	1.1 a2	1.8 a2	18.4 a
Matador		1.7 b2	3.8 b1	1.6 a2	1.8 a2	8.9 b
Water		1.0 b1	0.3 c1	0.3 b1	0.1 a1	1.9 c

† Results of hydrophobic and fresh sand system were presented, respectively.

‡ Means in the same column of hydrophobic or fresh sand system followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row of hydrophobic or fresh sand system followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

§ Sum of the DOC collected from application, the 1st, 2nd, and 3rd washes for each treatment.

¶ Mean separation of the sum DOC data was conducted individually, where means in hydrophobic or fresh sand system followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 3.7.** Total dissolved, particulate, and cumulative organic carbon (TDOC, TPOC, and TOC†) collected from all application cycles.

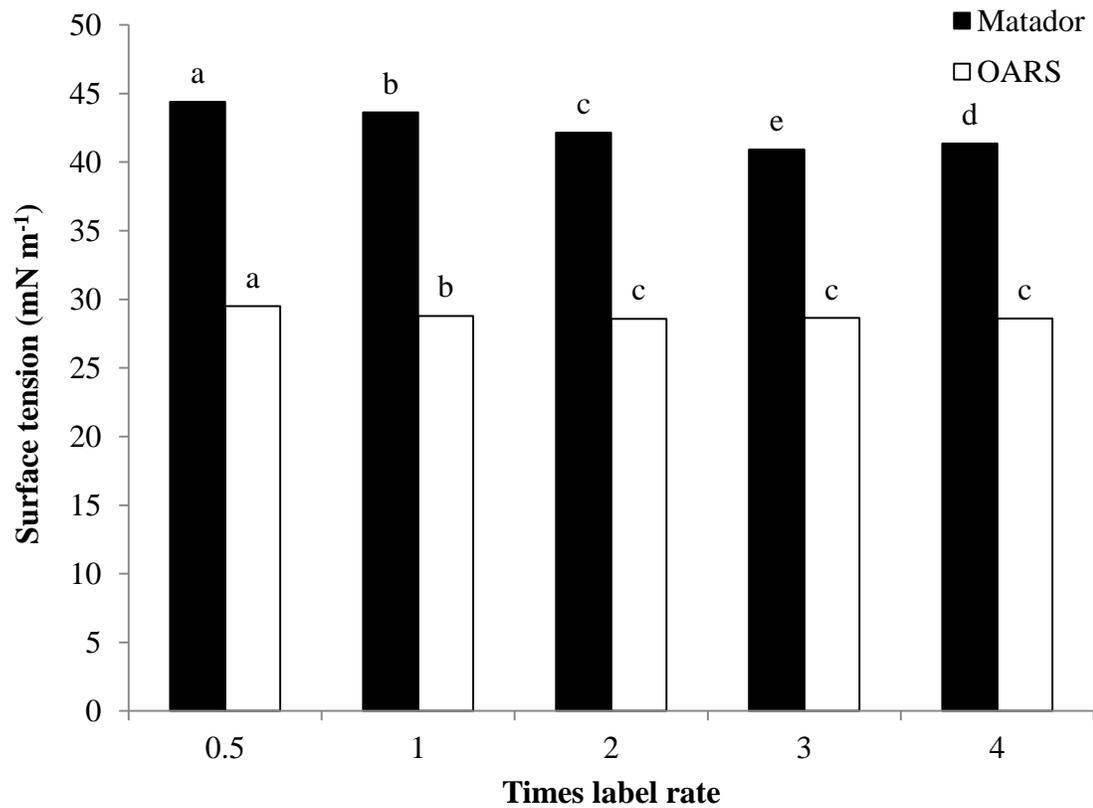
Treatments	TDOC	TPOC	TOC	Total OC input§
<i>Hydrophobic sand</i> ----- mg -----				
OARS	2429 b‡	145 b	2574 b	3864 a
Matador	2736 a	246 a	2982 a	2997 b
Water	70 c	20 c	90 c	0 c
<i>Fresh sand</i>				
OARS	2587 b	48 a	2635 b	3864 a
Matador	2799 a	29 b	2828 a	2997 b
Water	269 c	19 b	288 c	0 c

† Total dissolved and particulate organic carbon (TDOC and TPOC) was the sum of DOC and POC collected from all three applications cycles, respectively for hydrophobic or fresh sand system. Total organic carbon (TOC) was calculated by summing the TDOC and TPOC for each treatment.

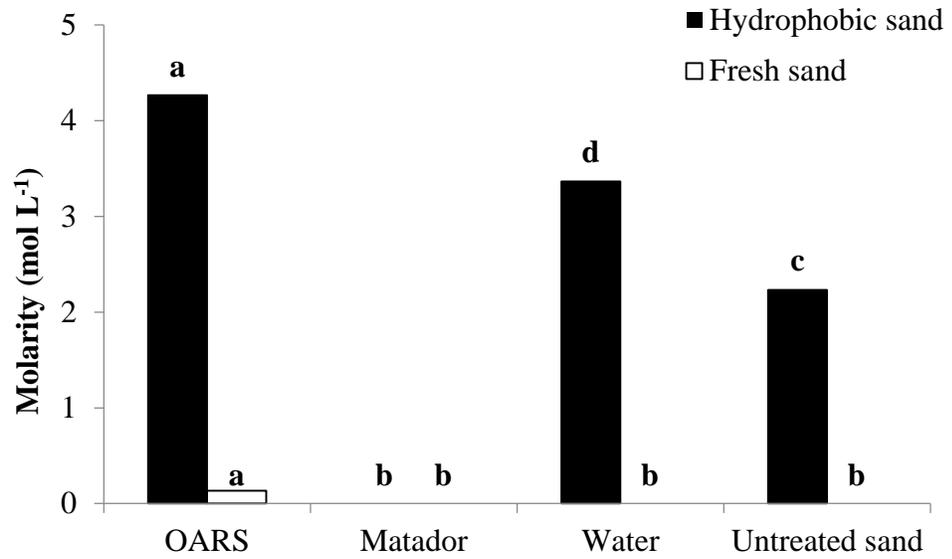
‡ Means in the same column of hydrophobic or fresh sand system followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

§ Total organic carbon (OC) input from three applications is consistent for both hydrophobic and fresh sand systems.

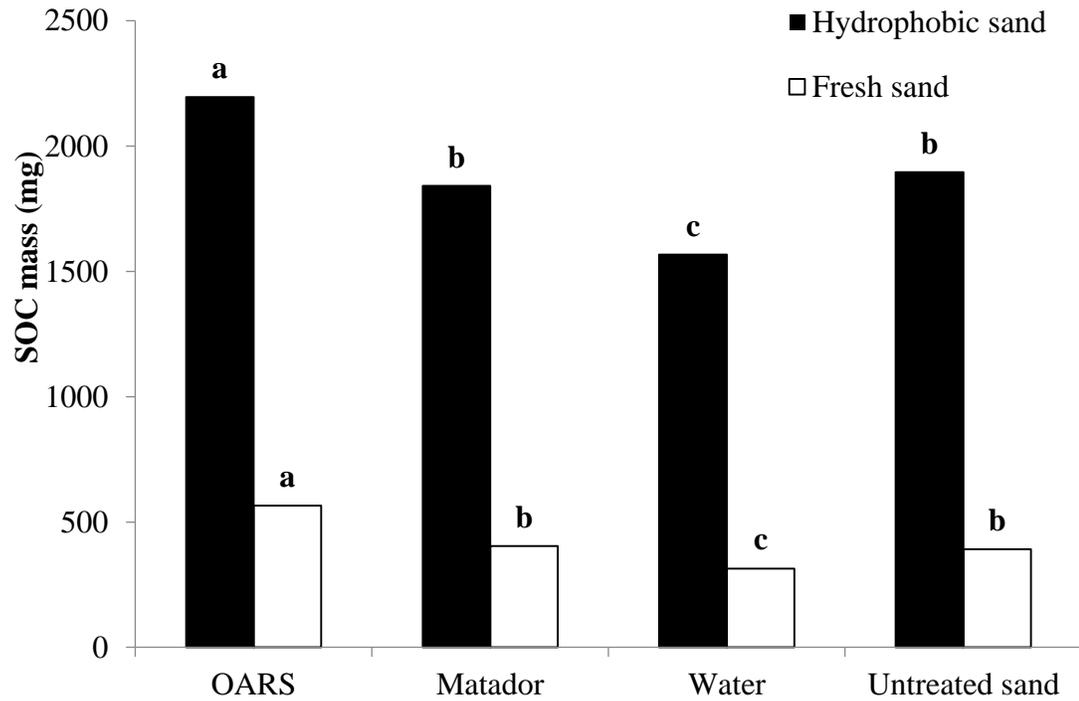
**Figure 3.3.** Relationship between the surface tension of solution and the concentration of applied wetting agents. Both Matador and OARS were tested at 0.5, 1, 2, 3, and 4 times their label rates and the actual respective concentrations were 12.5, 25.0, 50.0, 75.0, and 100.0 ml L<sup>-1</sup> for Matador and 14.4, 28.8, 57.6, 86.4, and 115.2 ml L<sup>-1</sup> for OARS. Bars labeled by the same letters within each wetting agent are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



**Figure 3.4.** Hydrophobicity of untreated and treated hydrophobic sand and fresh sand determined by molarity of ethanol droplet (MED) test after final application cycles. Bars labeled with the same letter within each graph are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



**Figure 3.5.** Solid phase organic carbon (SOC) mass content in the untreated and treated hydrophobic sand and fresh sand systems after final applications cycles. Bars with the same letters are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



## Chapter IV

### Influence of Repeated Application of Selected Wetting Agents on Soil Water Repellency and Microbial Communities

Enzhan Song<sup>1</sup>, Robert J. Kremer<sup>2</sup>, Keith W. Goyne<sup>2</sup>, Stephen H. Anderson<sup>2</sup>, Xi Xiong<sup>1\*</sup>

<sup>1</sup>Division of Plant Sciences, University of Missouri, Columbia, MO 65211, USA

<sup>2</sup>School of Natural Resources, University of Missouri, Columbia, MO 65211, USA

#### Abstract

Previous studies have validated that microbial degradation of soil organic matter (SOM), mainly plant materials, is the primary process of producing hydrophobic compounds in soil. Application of wetting agents is the primary technique used to mitigate soil water repellency (SWR) on sandy soils, especially localized dry spot (LDS) issues on sand-based golf course putting greens. However, the long-term influence of monthly or shorter repeated application intervals on microbial communities is unknown. The goal of this study was to investigate the effects of six selected wetting agents on turf and soil physical and biological properties after repeated applications under field conditions. The study was conducted in 2015 and 2016 on a creeping bentgrass (*Agrostis stolonifera*) putting green with existing SWR. Turfgrass and SWR responses were visually assessed or measured via the molarity of ethanol droplet (MED) test. Soil microorganism community changes were evaluated by phospholipid fatty acid (PLFA) analysis, and then correlated with the turfgrass and soil parameters for comprehensive interpretation. The weather conditions in 2015 and 2016 were significantly different, and the treatment effects were generally masked by the more dominant factor of precipitation. Overall, Hydro-Wet and Matador reduced soil moisture and microbial activity, and 2- to 4-fold lower disease

coverage than other wetting agents, even in the driest period of 2016. In contrast, Cascade Plus and OARS helped the soil to hold more water but also increased fungal disease occurrence. Tournament-Ready showed medium water movement and retention capability; while the glucose derived active ingredients of Tournament-Ready appeared to contribute to increasing PLFA abundance of individual microbial communities. Although pHAcid did not mitigate SWR, it potentially reduced soil pH and promoted competition from pathogenic fungal groups under drought stress conditions, resulting in > 4-fold higher disease coverage than the control during the early season of 2016. Overall, microorganisms were influenced indirectly by the capability of different wetting agents to adjust soil moisture as well as environmental conditions, mainly precipitation and temperature.

## **Introduction**

Soil water repellency (SWR) is a common problem on intensively managed turf land, especially on sand-based growing media such as putting greens (Karnok and Tucker, 1989; Wilkinson and Miller, 1978). When SWR exists, water will move in the soil profile following preferential flow patterns with randomly distributed wetting fronts and result in localized dry spots (LDS). This issue is particularly problematic in sand media (Nektarios et al., 1999; Wang et al., 2000) primarily due to the large size yet small specific surface area of sand particles which tend to be covered by soil organic matter (SOM) more frequently, compared to smaller size minerals such as clay (Karnok and Tucker, 1989; Larsbo et al., 2008; Roberts and Carbon, 1972). Consequently, these SOM coatings reduce the overall sand surface free energy ( $\gamma$ ) and increase soil hydrophobicity (Doerr et al., 2000; Kern et al., 1986; Tucker et al. 1990). Although SWR has not been

fully explained, previous studies validated the crucial role of microbial decomposition of plant materials in forming soil hydrophobic organic coatings (Czarnes et al., 2000; Doerr et al., 2000; Feeney et al., 2006; Sun et al., 1999).

To manage water-repellency, especially LDS on putting greens, wetting agents containing amphiphilic molecules with polar (hydrophilic) and nonpolar (hydrophobic) affinities are applied to the soil surface. Turf managers use wetting agents for different purposes, including enhancement of water infiltration, improving water retention, and promoting lateral water movement for moisture uniformity. Numerous studies have been conducted to investigate the direct impact of wetting agents on turf quality and soil physical properties. For instance, laboratory studies have been conducted to investigate the impact of wetting agents on water infiltration, wetting front instability, preferential flow, and the relationship between wetting agents and ponding depth ( $h_o$ ) or water entry pressure ( $h_w$ ) (Carrillo et al., 2000; Feng et al., 2001; Nektarios et al., 1999; Ritsema et al., 1993; Wang et al., 2000).

Few studies have attempted to identify/classify the actual hydrophobicity causing microorganisms. Savage et al. (1969) conducted a very interesting research almost a half century ago to investigate the effects of some soil fungi on water repellency in silica sand, and identified two groups of hydrophobicity causing fungi: *Aspergillus sydowi* and *Penicillium nigricans*. Karnok and Tucker (2001) conducted a field study investigating the effect of a flutolanil fungicide and wetting agent through individual or mixed applications on a water repellent putting green sand. They found that two applications of flutolanil fungicide alone in early June and July reduced hydrophobicity from an initial strong level in June to moderate level by the end of August. Results indicated a

significant relationship of microorganisms, especially fungal activities, with soil water repellency in sand media. Previous studies have also investigated relationships between surfactants and biodegradability, such as the effect of temperature on surfactant degradation, effects of surfactants on SOM degradation, surfactant stimulation of microbial enzyme production, co-degradation of surfactants containing glucose, surfactant toxicity to marine microorganisms, and effects of surfactants on phenanthrene degradation (Jin et al., 2007; Poremba et al., 1991; Reese and Maguire, 1969; Rouse et al., 1994; Takamatsu et al., 1996; Zeng et al., 2007). However, no research has evaluated the direct influence of wetting agent application on soil microbial structure/activity, as well as the long-term effects on SWR under field conditions.

Thus, this study was conducted to investigate the impact of repeated applications of selected wetting agents on turfgrass performance, microorganism community, and soil hydrophobicity. Wetting agents were selected based on their different physical and chemical characteristics and their effects on hydrophobic sand that have been evaluated in previous laboratory studies.

## **Materials and Methods**

This two-year field study was carried out on a creeping bentgrass (*Agrostis stolonifera*) USGA putting green at the University of Missouri Turfgrass Research Center, Columbia, MO, where LDS has been an issue. Treatments included six wetting agents applied monthly from May to September in 2015 and 2016 at the highest labeled rates, and an untreated control (Table 4.1). Changes in SWR were monitored monthly from May to October by the molarity of ethanol droplet test (MED) (King, 1981; Watson and Letey, 1970). Five soil cores from the top 10 cm were randomly collected from each

plot on a monthly basis before wetting agent application and air-dried at room temperature for 2 weeks. Samples were then evaluated for the SWR via MED test. The soil samples collected in May and October of each year were also used for phospholipid fatty acid (PLFA) analysis to assess soil microbial community composition following the extraction procedure described by Buyer and Sasser (2012).

Soil samples between 2.0 to 2.5 g were freeze-dried before total lipid contents were extracted and fractionated into glycol, neutral, and polar lipid fractions. The polar lipid fraction was trans-esterified by mild alkali into the form of fatty acid methyl esters. The recovered PLFA (methyl esters) were identified and quantified by an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a flame ionizer detector. The chromatographic responses were converted to molar responses by an internal standard, and peaks were compared with a database of known microbial fingerprints for determination of the molar responses of taxonomic microbial groups such as fungi (Frostegård et al., 1993; Frostegård and Bååth, 1996), mycorrhizae (Unger et al., 2009) and arbuscular mycorrhizae (AM) fungi (Olsson, 1999), aerobic and anaerobic bacteria (Unger et al., 2009), and actinomycetes (Unger et al., 2009) (Table 4.2). The PLFA concentrations of various microbial groups were calculated based on the mass of soil sample and reported as  $\text{pmol g}^{-1}$  soil (Buyer et al., 2010).

Volumetric water content (VWC, v/v %), percent LDS coverage (%), and percent disease coverage (%) were monitored weekly to represent soil moisture related parameters. Turf parameters included turf quality and phytotoxicity ratings (1 to 9 scale where 1 means total turf death and 6 is the minimum acceptable value), as well as normalized difference vegetation index (NDVI) for canopy color/density performance

evaluation that was determined by a Trimble GreenSeeker (Trimble Inc., Sunnyvale, CA).

Plots were 1.5 by 1.5 meters in size and arranged in a randomized complete block design with four replications; the study was conducted in 2015 and 2016. Analysis of variance was conducted using the Proc GLM procedure of SAS 9.4 (SAS Institute, Cary, NC). Significant mean separations were performed based on Fisher's Protected LSD at  $P < 0.05$ .

## **Results and Discussion**

### ***Weather Conditions of 2015 and 2016***

Temperature and precipitation data at the research location in 2015 and 2016 are presented in Fig. 4.1. Similar temperature patterns were observed from April through November in both years but the monthly average precipitation showed significant variations. The amount of precipitation in April, May, and June of 2015 was 50%, 100%, and 300% more than corresponding months of 2016. While the study was initiated in mid-May and finished in mid-October, the wet early summer of 2015 led to high moisture levels in the topsoil (12 cm) and no significant treatment effects on volumetric water content were observed. However, reduced precipitation in early 2016 provided ideal drought conditions that were desired for this study. Consequently, there was a significant interaction between year and treatment effects, and the data for each year will be discussed separately.

### ***Soil property and turf parameter results of 2015***

All wetting agents proven to be safe with monthly applications where no treatment injury (phytotoxicity) was observed for all treatments in both years. Although greater

precipitation in early 2015 led to consistent topsoil moisture that masked the influence of wetting agents on visually assessed turf quality and amount of LDS, significant differences among treatments were found for disease coverage and NDVI (Fig. 4.2) with no interaction between treatments and monthly rating. Although NDVI of the different treatments were statistically variable, the actual NDVI values ranged between 0.802 (untreated control) and 0.810 (Tournament-Ready), indicating above-acceptable turf performance (Xiong et al., 2007). Furthermore, the NDVI results were similar to the results of visually assessed turf quality. Although all wetting agents numerically increased disease occurrence compared to the untreated control, only OARS and pHAcid treated plots showed statistically greater disease coverage than the control with more than a 0.5-fold increase (Fig. 4.3).

Different from the in-field measured parameters (Fig. 4.2 and 4.3), the hydrophobicity (MED) test showed significant interactions between treatment and repeated monthly applications at different month after initial treatments (MAIT) (Table 4.3) in 2015. While soil hydrophobicity gradually built up in untreated control plots, wetting agent-treated plots generally reached a peak MED value around 3 M at 1 MAIT and further development of soil hydrophobicity was prevented. Matador was the only treatment that consistently decreased the MED values (3.1 to 2.4 M) in 1 to 4 MAIT. However, soil hydrophobicity deteriorated for all treated plots at 5 MAIT (Table 4.3), which could be related to the reduced precipitation (< 5 cm) in September and October of 2015 (Fig. 4.1). Cascade Plus, Matador, and OARS consistently maintained the lowest MED values, especially during the drought months of 2015 (3 and 5 MAIT) (August and October). Results indicated a superior residual effect of Cascade Plus, Matador, and

OARS on SWR mitigation. Our previous study discovered significantly different residual effects for various wetting agents, where Cascade Plus-treated sand exhibited extended re-wettability (Song et al., 2014). Although no previous studies have investigated the residual effects of Matador and OARS, studies comparing the wetting efficiency and longevity of early wetting agents, Soil Penetrant (100% alkyl polyoxyethylene ethanol) and Aqua-Gro (50% polyoxyethylene esters of cyclic acid and 50% polyoxyethylene ether of alkylated phenols), reported longer wetting effects from Aqua Gro (Mustafa et al., 1969; Osborn et al., 1969), which is formulated similarly to Matador and OARS (Table 4.1).

#### ***Soil property and turf parameter results of 2016***

Due to a more complex precipitation pattern in 2016, different statistical results were found in the 2016 dataset. Treatment effects were individually significant for NDVI, VWC, and LDS coverage (Fig. 4.2, 4.4, and 4.5), but also significantly interacted with repeated rating intervals on disease coverage and turf quality (Tables 4.3 and 4.4). Although most wetting agents increased the topsoil moisture, Cascade Plus and OARS were the only two treatments that retained a significantly greater VWC ( $> 17.2\%$ ) than the untreated control. Uniquely, Hydro-Wet and Matador numerically reduced the VWC of treated plots from 16.7 % (untreated control) to 16.6 and 16.5%, respectively (Fig. 4.5). As a result, LDS and NDVI data showed highly correlated patterns when compared with VWC results. Matador treated plots had significantly greater LDS coverage than the other treatments while Cascade Plus and OARS-treated plots showed the lowest LDS occurrences (Fig. 4.5), although the average % LDS coverage was less than 2.5% for all treatments. In contrast, Cascade Plus and OARS treatments resulted in the highest NDVI

(> 0.82) while Hydro-Wet and Matador had statistically similar NDVI as the untreated control (Fig. 4.2). A significant increase in NDVI related to increased irrigation was similarly reported by Xiong et al. (2007).

The complicated precipitation pattern across different months of 2016 led to a significant interaction between treatment effects and timing of repeated turf rating for disease coverage (Table 4.3). An early summer drought in 2016 between April and July resulted in only 2.5 cm of precipitation in June (1 MAIT). Consequently, disease occurrence was consistently lower than 1.5% for most treatments through 0 to 2 MAIT, with exception for Cascade Plus, OARS, and pHAcid which induced significantly greater disease (> 4.5%) in the driest month (1 MAIT) (Table 4.3). The disease occurrence pattern was correlated with the capability of the wetting agents to maintain topsoil moisture (Fig. 4.4). More importantly, the tendency of OARS and pHAcid to enhance disease occurrence was consistent in both 2015 and 2016 (Fig. 4.3 and Table 4.4). It is reasonable that OARS could potentially increase pathogenic fungal growth as it reduced SWR and promoted soil moisture (Table 4.3 and Fig. 4.4) (Couch et al., 1960). However, enhanced pathogen growth, mainly the Dollar spot fungal pathogen (*Sclerotinia homoeocarpa*) in pHAcid treated plots, may be the result of reduced soil pH that favors fungi over other microorganisms (Smith and Doran, 1996; Rousk et al., 2009). The acidifying agents in pHAcid are intended to reduce soil pH and release  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from inorganic carbonates that deposit rapidly and create clogging effects in the soil (Ogino et al., 1987). Greater precipitation in July 2016 (26.5 cm) facilitated pathogen infestation, leading to significantly increased disease coverage between 4 and 8% for all plots at 3 MAIT (Table 4.4). When precipitation decreased more than 100% in August

(12.2 cm), disease occurrence was suppressed naturally among treatments and masked treatment effects at 4 MAIT. Increased precipitation and cooler temperatures in September 2016 caused disease reoccurrence in all plots ( $> 3\%$ ), although no significant treatment effects were detected (Table 4.4).

Although all treatments generally resulted in NDVI values  $> 0.8$  in 2016 (Fig. 4.2), visually evaluated turf quality is considered a more comprehensive assessment of aesthetic aspects, such as uneven turf density or under-canopy disease patch and dry spots, that might be not be captured by NDVI-measuring instrument. As a result, a significant interaction between treatment effect and repeated rating timing was found for turf quality in 2016 (Table 4.4). While no severe LDS ( $< 2.5\%$ ) (Fig. 4.5) was observed in the treatments, disease occurrence significantly influenced turf quality rating. Increased disease coverage at 1 MAIT in the Cascade Plus, OARS, and pHAcid treatments was severe enough to reduce turf quality to barely acceptable and unacceptable ratings of 5.0, 6.5, and 4.5 (Table 4.5), respectively. Further, increased disease coverage at 3 MAIT (July 2016) significantly deteriorated turf quality for all treatments to a rating of  $\leq 6.0$ . Overall, turf quality and disease coverage were negatively correlated.

The hydrophobicity results from MED tests showed a similar treatment by timing of turf rating interaction but trends were different in 2016 than 2015 (Table 4.3). First, wet and cool conditions of November and December 2015 with an average monthly precipitation of 17.7 cm and air temperature of 7.4 °C (Fig. 4.1), contributed to reduced MED at the beginning (0 MAIT) of the 2016 study (Table 4.3). Studies have reported a strong positive correlation between soil temperature and soil microbial activity. For example, Mikan et al. (2002) discovered a dramatic increase of microbial respiration rate

at higher temperatures with surprisingly 4.6 or greater temperature coefficients ( $Q_{10}$ ) when temperature rises from 0.5 to 14 °C. While plant growth was reduced in December 2015, temperatures > 5 °C may have extended microbial degradation and further reduced hydrophobic organic materials. Dry conditions in May and June 2016 allowed soil hydrophobicity to quickly return and peak by 1 or 2 MAIT for all treatments (Table 4.3). Cascade Plus, Hydro-Wet, Matador, and OARS further significantly reduced the MED from 2.6 or greater to 2.2 or less by 5 MAIT. Clearly, most wetting agent applications reduced the soil hydrophobicity from an initial strong level (MED = 3.0) to a medium level (MED  $\leq$ 2.4) by the end of the two-year study, except for pHAcid (Table 4.3).

#### ***PLFA analyses of Soil Microbial Community Structure***

To evaluate repeated treatment effects on soil microbial communities, soil samples from the surface 10-cm depth were collected during May and October in 2015 and 2016 for PLFA analysis. Due to differences in weather between 2015 and 2016 (Fig. 4.1), only a significant sampling time effect with a masked treatment impact was detected. While only significant treatment effects were found in 2016, there was a significant interaction between treatment effect and sampling time on aerobic bacteria, anaerobic bacteria, actinomycetes, arbuscular mycorrhizae, and total mycorrhizae and bacteria (Tables 4.6 and 4.7) when the data of the first sampling (May 2015) was excluded. It has been documented that long-term applications are often require to make significant changes to soil microbial community structures in grassland, even with application of fungicide or fertilizers which causes more direct impact to soil microorganisms (Michelsen et al., 1999). The appears to be non-effective first year wetting agent

treatments may simply due to a lack of reaction/responding time after only one year of applications.

For the May 2016 sampling, soil samples were collected before the first treatment of the second-year study, following the five monthly treatments applied in 2015. The PLFA contents of all microorganism groups in Hydro-Wet and Matador-treated plots were significantly or numerically lower than in untreated control plots (Tables 4.6 and 4.7). Results indicated a general suppression of microbial communities in Hydro-Wet and Matador-treated soil. Suppressed PLFA content was highly correlated with the reduced soil moisture induced by Hydro-Wet and Matador that resulted in the lowest soil VWC in 2016 (Fig. 4.4). Reductions of anaerobic bacteria PLFA by both wetting agents (Table 4.6) indicated an increased aerobic/dryer soil environment, which aligned with the VWC results (Fig. 4.4). Additionally, pHAcid applications led to reduced PLFA contents of anaerobic bacteria, actinomycetes, arbuscular mycorrhizae, and mycorrhizae (Tables 4.6 and 4.7). Considering the high VWC in pHAcid treated plots (Fig. 4.4), the acidic pH conditions created by this unique wetting agent may have contributed to suppressed microbial growth. In contrast, Tournament-Ready increased overall microbial community abundance while all other wetting agents generally resulted in reductions, compared to the untreated control (Tables 4.6 and 4.7). The active ingredients of Tournament-Ready contain 62% of alkylpolyglycoside and siloxane solution, and alkylpolyglycoside is formulated from glucose derivatives and fatty alcohols (Hill et al., 2008). This high carbohydrate formulation of Tournament-Ready may provide a preferred energy/food source for many microorganisms and enhance microbial growth.

The 55 cm of total precipitation in the summer of 2016 (July to September) imposed dramatic influences on microbial communities in soil samples collected during October 2016 (Fig. 4.1; Tables 4.6 and 4.7). Consistent results were observed only in pHAcid-treated plots in which significantly greater PLFA contents than other wetting agents for aerobic and anaerobic bacteria, actinomycetes, arbuscular mycorrhizae, and mycorrhizae (Tables 4.6 and 4.7). While the MED test showed that all the other wetting agents significantly reduced soil hydrophobicity by the end of this study (Table 4.3), pHAcid was the only treatment with no effects except deteriorated SWR. As a result, it is reasonable to believe that other treatments facilitated water movement under heavy rainfall in July, August, and September of 2016, causing excessive leaching of soil nutrients that may have benefited microbial metabolism (Helen et al., 2008; Suzanne et al., 1992; Ying et al., 2012). Under such circumstances, the microbial community may prefer the less water-penetrable but more stable soil environment in pHAcid treated plots, leading to 18 to 34% greater aerobic bacteria PLFA, 10 to 23 % greater anaerobic bacteria PLFA, 12 to 23 % greater actinomycetes PLFA, 18 to 36 % greater arbuscular mycorrhizae PLFA, and 10 to 42% greater mycorrhizae PLFA than the other treatments (Tables 4.6 and 4.7).

Overall, the dataset between October 2015 and October 2016 showed a significant influence of precipitation pattern in 2015 and 2016 on the PLFA contents for related microbial groups (Fig. 4.1 and 4.6; Tables 4.6 and 4.7). However, it is important to point out that, when compared the results across the timeline within different treatments, OARS and Tournament-Ready are the only two wetting agents that maintained PLFA level of actinomycetes in the drought early summer of 2016 (May) (Fig. 4.1 and Table

4.6). Meanwhile, the two wetting agents also showed the lowest MED values (hydrophobicity) at 0 MAIT (May) in 2016 (Table 4.3). Previous studies have shown a bioremediation effect on hydrophobic coatings with addition of actinomycetes, such as *Streptomyces spp.* (Dunkelberg et al., 2006; Roper, 2004), *Rhodococcus spp.* (Roper, 2004), and *Mycobacterium spp.* (Dunkelberg et al., 2006; Roper, 2004). These laboratory-based studies consistently observed significant reduction of SWR by wax metabolizing (*Streptomyces spp.* and *Mycobacterium spp.*) and bio-surfactant producing bacteria (*Rhodococcus spp.*) (Lang and Philp, 1998; Roper, 2004; Walter et al., 1991). Our results indicated the effect of Tournament-Ready and OARS to protect actinomycetes competition/growth under dramatic seasonal changing of environmental conditions, thus potentially promoting degradation of hydrophobic coatings that induce SWR.

## **Conclusions**

Environmental conditions, especially precipitation, influenced soil moisture levels and unavoidably interfered with final results of this drought-stress dependent field study. Within the same timing under same conditions, Hydro-Wet and Matador tended to facilitated water infiltration/leaching and reduce soil water content, which further led to a reduced overall microbial growth. Conversely, Cascade Plus and OARS retained soil moisture in the sandy system and caused more fungal disease issues. Tournament-Ready appeared to be a well-balanced wetting agent that performed satisfactorily for both water infiltration and retention aspects. Moreover, the high carbohydrate content of Tournament-Ready active ingredients may contribute to enhanced microbial activities. As a unique product that targets inorganic hydrophobicity causing carbonates, pHAcid did

not reduce SWR in the sand based soil system relative to the other wetting agents. More importantly, the acidic nature of pHAcid may negatively impact soil microbial health through enhanced growth/competition of plant pathogenic fungal groups. Overall, influences of wetting agents on microbial groups were mainly related to ability/capability to adjust soil moisture. Products with readily degradable active ingredients may promote growth of beneficial microbial groups under stress conditions, drought in this case, and thereby suppress disease pathogens.

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**Table 4.1.** List of selected wetting agents and their application rates.

Wetting agent	Active ingredients	Rates (ml L <sup>-1</sup> )
Untreated control		
Cascade Plus	10% alcohol ethoxylates, 90% polyethylene and polypropylene glycols	62
Hydro-Wet	87.5% poloxanlene, 2-butoxyethanol	
Matador	100% polyalkylene Glycol	47
OARS	80% Polyoxyalkylene polymers	27
pHAcid	10% Potassium salt of alkyl substituted maleic acid 100% blend of acidifying agents and a high molecular weight nonionic surfactant	250
Tournament-Ready	62% alkylpolyglycoside and siloxane solution 38% polyalkoxylate blend	62

**Table 4.2.** Phospholipid Fatty acid (PLFA) markers and the associated categories of organism used in this study.

Microbial group	Markers	Related Literatures
Fungi	18:2w6 cis	Frostegeård et al., 1993; Frostegeård and Bååth, 1996
Mycorrhizae	16:1w5, 18:2w6,9	Unger, et al., 2009
Arbuscular mycorrhizae (AM)	16:1w5 cis	Olsson, 1999
Bacteria	10:0B, 12:0b, 12c alcohol 14:0i, 15:00, 15:00 all 15:0a, 15:0i, 15:1cy 16:0, 16:0Me 10, 16:1x7 16:1x7t, 16c alcohol, 17:0a 17:0cyc, 17:0i, 17:1x7i 17:0me10, 17:1x6, 18:1x7 18:1x7c, 19:0cyc19:0cyc	Unger, et al., 2009
Aerobic bacteria	16:1x7, 16:1x7t, 18:1x7	
Anaerobic bacteria	15:1cy, 17:0cyc, 19:0cyc	
Actinomycetes	16:0Me 10, 17:0me10	
Gram-negative bacteria	10:0B, 12:0b, 12c alcohol, 17:0cyc	
Gram-positive bacteria	i14:0, a16:0, i15:0, a15:0, i16:0, i17:0, a17:0	Harwood and Russell, 1984
Protozoa	20:2w6, 20:4w6	Ringelberg et al., 1997

**Table 4.3.** Soil hydrophobicity influenced by different treatments and determined by molarity of ethanol droplet (MED) test at 0, 1, 2, 3, 4, and 5 months after initial treatment (MAIT) in 2015 and 2016.

Treatments	0MAIT	1MAIT	2MAIT	3MAIT	4MAIT	5MAIT
<b>2015</b> ----- mole L <sup>-1</sup> -----						
Control	3.0 a2†	3.1 b12	3.3 a1	3.4 a1	3.3 a1	3.3 a1
Cascade Plus	2.9 a1	2.9 b1	2.9 cd1	2.9 cd1	2.3 d3	2.6 c2
Hydro-Wet	3.0 a1	3.1 b1	3.0 bcd1	3.1 bc1	2.6 c2	2.9 b1
Matador	3.0 a1	3.1 b1	2.9 cd12	2.7 d23	2.4 d4	2.6 c34
OARS	3.0 a12	3.1 b1	2.8 d23	3.0 cd12	2.3 d4	2.7 bc3
pHAcid	2.9 a3	3.4 a1	3.2 ab2	3.3 ab12	2.9 b3	3.1 ab23
Tournament-Ready	3.0 a12	3.1 b1	3.1 abc1	3.1 bc1	2.3 d3	2.7 bc2
<b>2016</b> ----- mole L <sup>-1</sup> -----						
Control	2.6 a2	3.3 a1	3.2 a1	3.1 a1	3.0 a1	3.1 a1
Cascade Plus	2.5 ab12	2.6 b1	2.4 d123	2.2 bc23	2.4 b123	2.1 bc3
Hydro-Wet	2.4 ab12	2.5 b12	2.6 cd1	2.3 bc2	2.2 b23	2.0 c3
Matador	2.5 ab12	2.7 b1	2.5 cd1	2.1 c3	2.5 b12	2.2 bc23
OARS	2.3 b2	2.6 b1	2.7 bc1	2.3 bc2	2.3 b2	2.1 bc2
pHAcid	2.5 ab2	3.1 a1	3.0 ab1	2.9 a1	3.0 a1	3.0 a1
Tournament-Ready	2.4 ab1	2.5 b1	2.6 cd1	2.4 b1	2.5 b1	2.4 b1

† Means in the same column of 2015 or 2016 followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row 2015 or 2016 followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 4.4.** Disease percent coverage (%) influenced by different treatments at 0, 1, 2, 3, 4, and 5 months after initial treatment (MAIT) in 2016.

Treatments	0 MAIT	1 MAIT	2 MAIT	3 MAIT	4 MAIT	5 MAIT
	----- % disease -----					
Control	1.0 a2†	0.8 b2	0.0 a2	4.0 a1	0.8 a2	3.3 b1
Cascade Plus	1.3 a2	5.0 a1	0.3 a2	7.3 a1	0.8 a2	4.8 ab1
Hydro-Wet	0.3 a2	1.3 b2	0.0 a	4.0 a1	0.0 a	3.3 b1
Matador	0.5 a3	1.5 b3	0.8 a3	7.0 a1	2.8 a23	5.3 ab12
OARS	1.3 a3	6.5 a1	0.8 a3	6.8 a1	2.0 a23	5.8 a12
pHAcid	1.0 a3	4.5 a23	0.8 a3	8.0 a1	1.0 a3	3.8 ab2
Tournament-Ready	0.8 a2	0.8 b2	0.0 a2	5.8 a1	1.0 a2	4.8 ab1

† Means in the same column followed by the same letters were not significantly different

based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 4.5.** Turf quality† influenced by different treatments at 0, 1, 2, 3, 4, and 5 months after initial treatment (MAIT) in 2016.

Treatments	0 MAIT	1 MAIT	2 MAIT	3 MAIT	4 MAIT	5 MAIT
	----- turf quality -----					
Control	7.5 a1‡	8.0 a1	6.3 c2	6.0 a2	7.8 a1	6.5 a2
Cascade Plus	7.8 a1	6.0 cd34	7.5 ab12	5.3 ab4	7.0 ab123	6.5 a23
Hydro-Wet	7.8 a1	7.8 a1	7.0 abc12	6.0 a3	7.3 ab12	6.8 a23
Matador	7.8 a1	6.8 bc12	6.5 bc23	4.8 b4	6.0 b23	5.5 b34
OARS	7.8 a1	5.5 d3	7.3 abc12	5.8 ab3	6.5 ab123	6.0 ab23
pHAcid	7.8 a1	6.3 cd23	7.8 a1	5.0 ab4	7.0 ab12	6.5 a23
Tournament-Ready	7.5 a1	7.5 ab1	7.0 abc12	5.8 ab3	7.3 ab12	6.3 ab23

† Turf quality was rated based on a 1 to 9 scale, where 1 means total turf death and 6 is the minimum acceptable quality.

‡ Means in the same column followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

**Table 4.6.** Treatment effect on different microbial groups based on the phospholipid fatty acid (PLFA) † data of October 2015, May 2016, and October 2016.

Treatments	PLFA groups	Oct-2015	May-2016	Oct-2016
	Aerobic bacteria	----- pmol g <sup>-1</sup> -----		
Cascade Plus		15257 a2‡	16631 ab12	18973 b1
Hydro-Wet		14598 a2	15275 ab2	19629 b1
Matador		14801 a2	14281 b2	18863 b1
OARS		14115 a2	16287 ab12	18640 b1
Tournament-Ready		13803 a2	17751 a1	17301 b1
Control		15290 a2	17226 a2	19282 b1
pHAcid		15538 a2	15436 ab2	23112 a1
	Anaerobic bacteria			
Cascade Plus		7963 a12	7443 ab2	8825 b1
Hydro-Wet		7788 a2	7227 ab2	8996 b1
Matador		7392 a2	6663 b2	8763 b1
OARS		7591 a2	7596 ab2	8684 b1
Tournament-Ready		7414 a2	7978 a2	8511 b1
Control		7887 a2	7989 a2	9488 b1
pHAcid		8109 a2	6852 b3	10450 a1
	Actinomycetes			
Cascade Plus		6277 a2	5151 a3	7749 b1
Hydro-Wet		6025 a2	4933 a3	7620 b1
Matador		5861 a2	4791 a3	7485 b1
OARS		5891 a2	5395 a2	7449 b1
Tournament-Ready		5758 a2	5508 a2	7310 b1
Control		6112 a2	5482 a2	8057 b1
pHAcid		6351 a2	4760 a3	9014 a1
	Mycorrhizae			
Cascade Plus		6310 a2	6366 ab2	9700 bc1
Hydro-Wet		6114 a2	6203 ab2	10583 ab1
Matador		6016 a2	5693 b2	10759 b1
OARS		6063 a2	6606 ab2	10175 bc1
Tournament-Ready		5944 a2	6842 ab2	9179 c1
Control		6554 a2	7135 a2	10288 bc1
pHAcid		6733 a2	6104 ab2	12615 ba1
	Bacteria			
Cascade Plus		34044 a2	32893 abc21	39722 b1
Hydro-Wet		32563 a2	30998 abc2	40744 b1
Matador		32189 a2	28860 c2	40064 b1

OARS	31762 a2	33181 abc2	39015 b1
Tournament-Ready	31096 a2	35351 a12	37147 b1
Control	34048 a2	34894 ab2	41424 b1
pHAcid	35201 a2	30605 bc2	47965 a1
Total			
Cascade Plus	80809 a2	82866 ab21	106885 b1
Hydro-Wet	77349 a2	78767 ab2	108350 b1
Matador	84649 a2	73416 b2	108242 b1
OARS	76413 a2	84461 ab2	105577 b1
Tournament-Ready	74249 a2	88412 a1	99578 b1
Control	81764 a2	87586 a2	111399 b1
pHAcid	83377 a2	77603 ab2	128253 a1

† Phospholipid fatty acid (PLFA) contents were PLFA concentrations based on the mass of soil sample as  $\text{pmole g}^{-1}$  soil.

‡ Means in the same column of individual sampling time in each microbial group followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row of individual sampling time in each microbial group followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

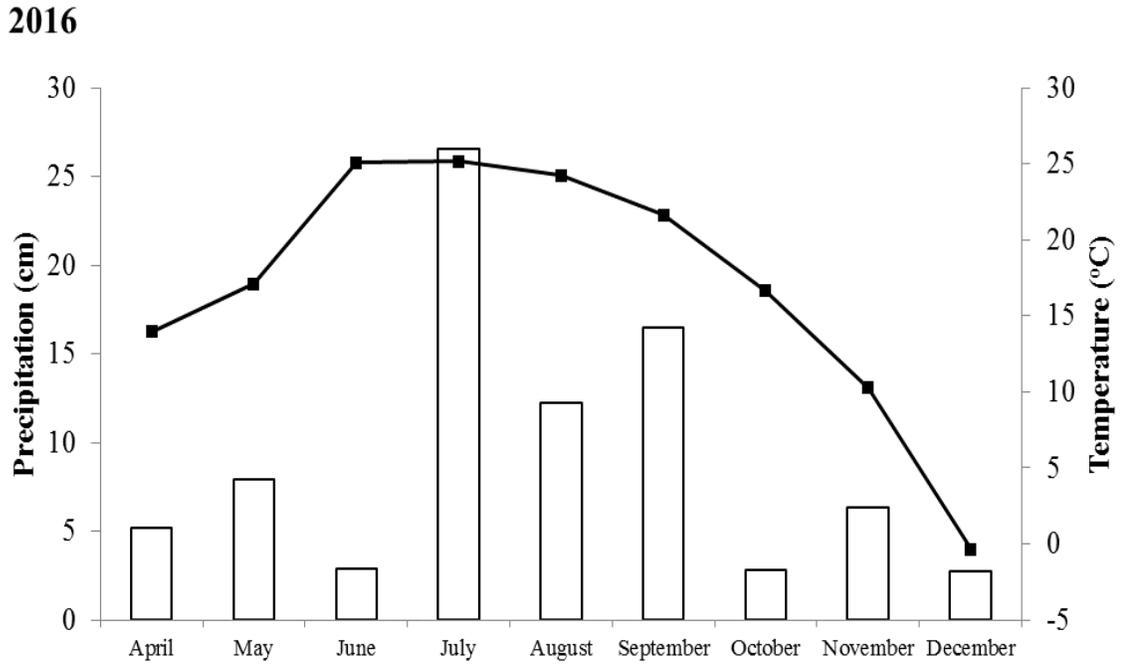
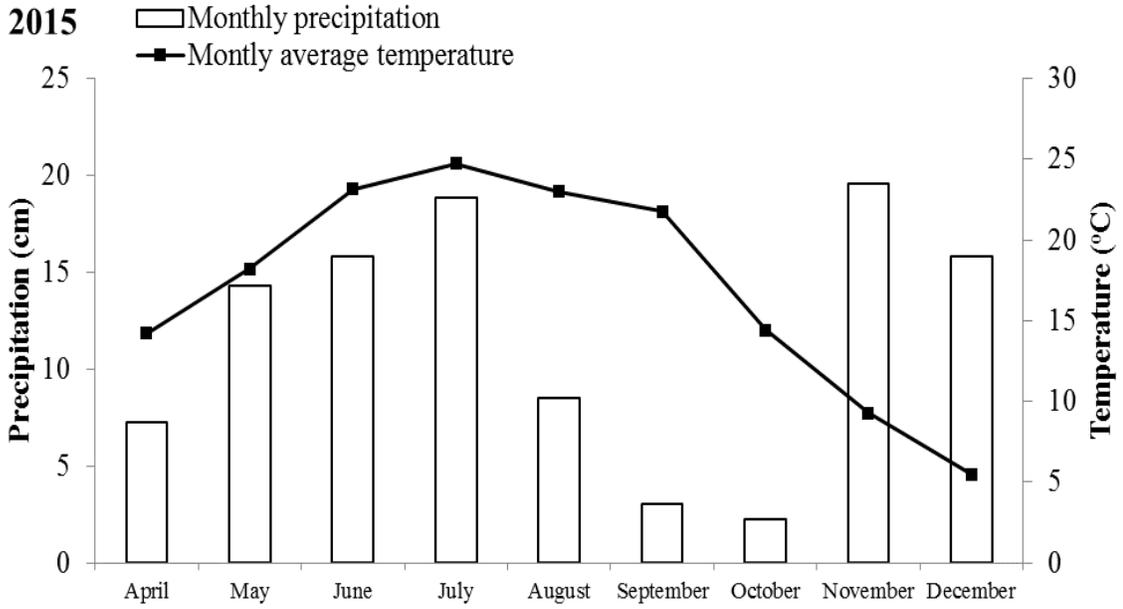
**Table 4.7.** Treatment effect on additional microbial groups based on the phospholipid fatty acid (PLFA) † data of October 2015, May 2016, and October 2016.

Treatments	PLFA groups	Oct-2015	May-2016	Oct-2016
	Gram-positive bacteria	----- pmol g <sup>-1</sup> -----		
Cascade Plus		13274	10693 ab2	14633 b1
Hydro-Wet		12480	10054 ab3	14322 b1
Matador		12255	9484 b3	14343 b1
OARS		12327	11063 ab2	14122 b1
Tournament-Ready		11986 b2	11493 a2	13809 b1
Control		13059	11273 a3	14952 b1
pHAcid		13776 a2	9838 ab3	17110 a1
	Gram-negative bacteria			
Cascade Plus		18176 a2	19427 bc12	21210 b1
Hydro-Wet		17643 a2	18177 bc2	21974 b1
Matador		17532 a2	16838 c2	21062 b1
OARS		17088 a2	19224 ab12	20793 b1
Tournament-Ready		16809 a2	20821 a1	19640 b1
Control		18308 a2	20338 ab12	22119 b1
pHAcid		18644 a2	17959 bc2	25570 a1
	Eubacteria			
Cascade Plus		10199 a2	9348 bc2	11772 b1
Hydro-Wet		9957 a2	9031 bc2	11780 b1
Matador		9391 a2	8343 c2	11542 b1
OARS		9732 a2	9676 ab2	11456 b1
Tournament-Ready		9462 a2	10016 a12	11178 b1
Control		10125 a2	9899 ab2	12289 b1
pHAcid		10401 a2	8671 bc3	13764 a1
	Arbuscular mycorrhizae			
Cascade Plus		4640 a2	4810 ab2	6456 bc1
Hydro-Wet		4398 a2	4629 ab2	7049 b1
Matador		4260 a2	4327 b2	7146 b1
OARS		4278 a2	4914 ab2	6708 bc1
Tournament-Ready		4182 a3	5215 a2	6158 c1
Control		4674 a2	5369 a2	6962 bc1
pHAcid		4863 a2	4597 ab2	8400 a1

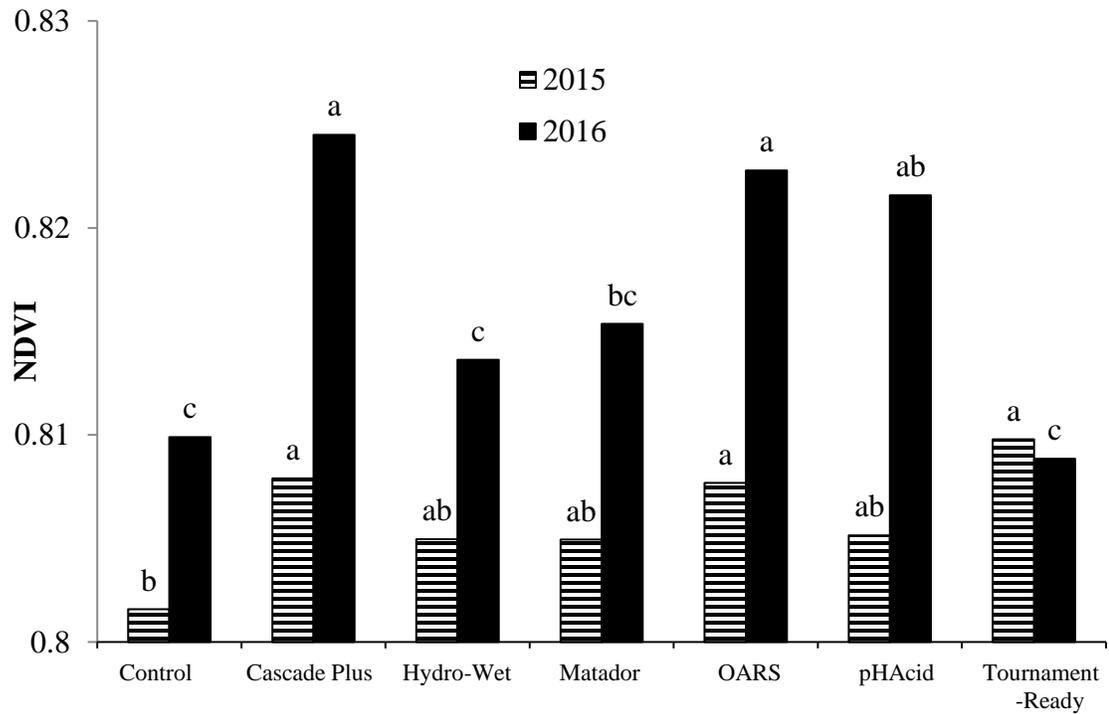
† Phospholipid fatty acid (PLFA) contents were PLFA concentrations based on the mass of soil sample as pmole g<sup>-1</sup> soil.

‡ Means in the same column of individual sampling time in each microbial group followed by the same letters were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ ; means in the same row of individual sampling time in each microbial group followed by the same numbers were not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .

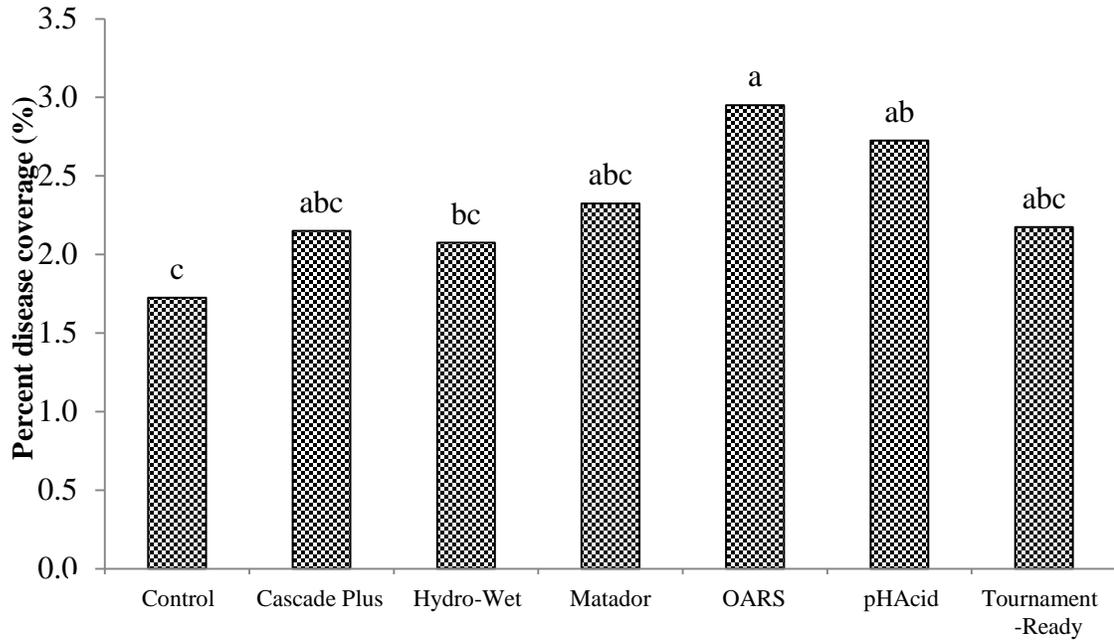
**Figure 4.1.** Average monthly precipitation and air temperature from April to December in 2015 and 2016.



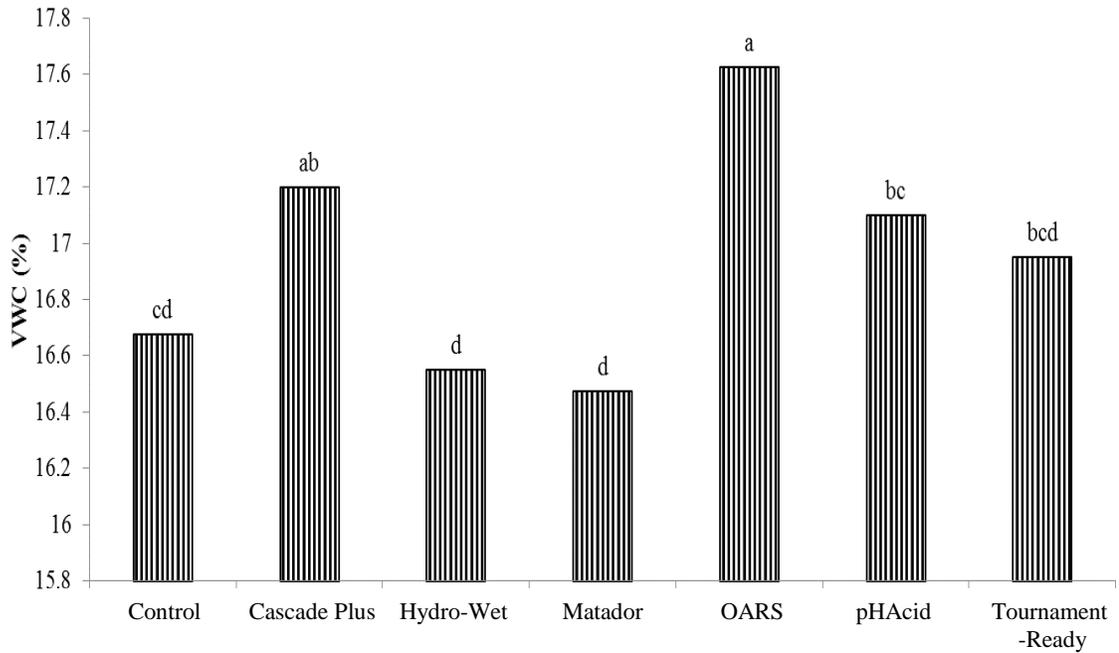
**Figure 4.2.** Average normalized difference vegetation index (NDVI) of canopy color/density performance influenced by different treatments in 2015 and 2016. Bars of 2015 or 2016 labeled by the same letters are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



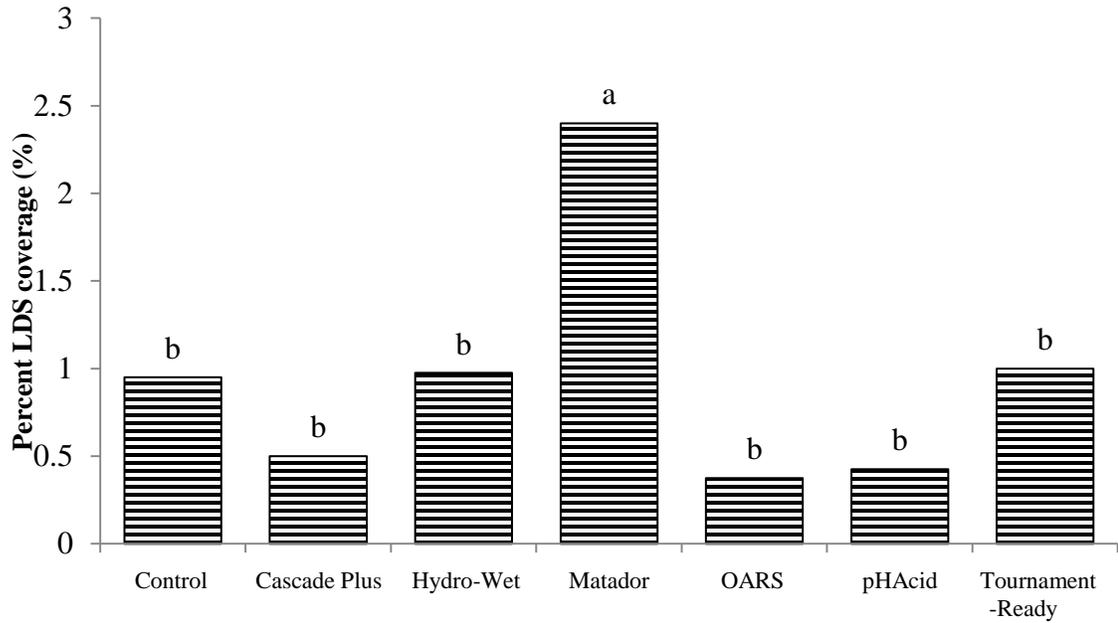
**Figure 4.3.** Average percent disease coverage (%) influenced by different treatments in 2015. Bars labeled by the same letters are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



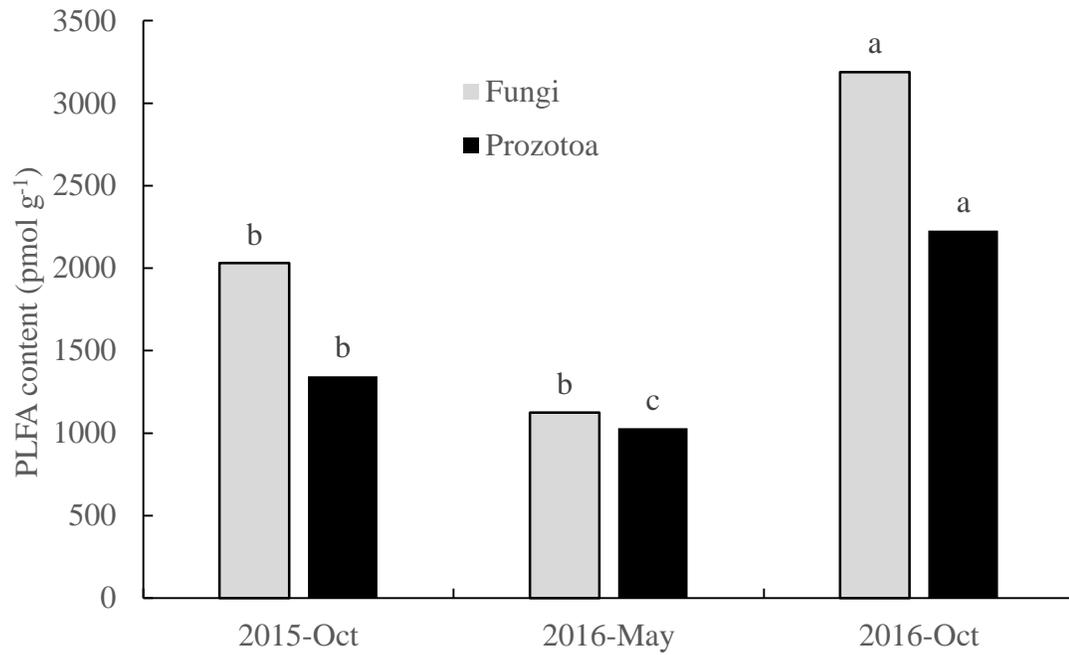
**Figure 4.4.** Average soil volumetric water content (VWC, v/v %) influenced by different treatments in 2016. Bars labeled by the same letters are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



**Figure 4.5.** Average percent localized dry spot coverage (LDS, %) influenced by different treatments in 2016. Bars labeled by the same letters are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



**Figure 4.6.** Average phospholipid fatty acid (PLFA) contents ( $\text{pmol g}^{-1}$  soil) of fungi and prozotoa groups for soil samples collected in October 2015, May, and October 2016. Bars of the three timings within each microbial group labeled by the same letters are not significantly different based on Fisher's Protected LSD at  $P < 0.05$ .



## VITA

Enzhan Song was born in Wuhan, a big city sitting on the Chang Jiang river in China. He spent his happy childhood in Wuhan until he graduated from high school in 2004, and enrolled in the turfgrass management education program in Beijing Forestry University (BFU), at Beijing, China. This is a co-hosted program between BFU and Michigan State University (MSU) which aimed at improving the professionalism of China turfgrass management industry.

During the undergraduate study, Enzhan was able to take an internship on a golf course at Naples, FL, in the USA for half year, and his interests in turf management was further extended, and decided to pursue a graduated degree after graduation. After five years' study, Enzhan graduated with his Bachelor's degree in June 2009, and found an opportunity to study aboard that summer at University of Missouri, Columbia. Since then, he has been studying under his advisor Dr. Xi Xiong for 8 year. Enzhan graduated with his Master's degree in 2012, with focus on weeds control in Crop, Pest, and Soil Management area and was able to publish multiple papers with the help from Dr. Xiong and his committee member Dr. Reid Smeda and Dr. He Qiong.

Life started to change significantly for Enzhan in 2012, as he got married with his wife Xiaowei Pan in December 2012, and one year later they had their first baby girl on March 14, 2013.

Enzhan kept working as a Ph.D. student for Dr. Xiong in 2012 with research emphasis switched to soil water repellency and wetting agent related topic. As a result, he luckily found three soil scientists: Dr. Anderson, Dr. Goyne, and Dr. Kremer as his committee who are experts in soil physics, soil chemistry, and soil microbiology, respectively. They published two papers related to wetting agents influences on soil hydrology in hydrophobic sand system in 2014, with another two currently in preparation.

In March 2017, Enzhan took a successful interview at Eltopia, WA and accepted the job offer as a research scientist for Agriculture Development Group, Inc.. The new and exciting chapter of life just opened for him, and his family.