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Water quality and surfactant effects on the water repellency of a sandy soil ☆

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SUMMARY

Differences in irrigation water quality may affect the water repellency of soils treated or untreated with surfactants. Using simulated irrigations, we evaluated water quality and surfactant application rate effects upon the water repellency of a Quincy sand (Xeric Torripsamment). We used a split plot design with two irrigation water qualities, three surfactant application rates, two irrigations, and 12 sampling depths as fixed effects, with four replications. Each water quality × rate × irrigation combination was a main plot and depth was a repeated-measures subplot. A slightly water repellent Quincy soil (average water drop penetration time, WDPT, of 2.5 s) was packed in 25-mm lifts (or layers) to a bulk density of 1.6 Mg m^{-3} into 0.15-m-high × 0.105-m-diameter plastic columns. We studied a nonionic surfactant, a blend of an ethylene oxide/propylene oxide block copolymer and an alkyl polyglycoside. We sprayed the surfactant at rates of 0, 9.4, and 46.8 L ha^{-1}, diluted with reverse osmosis water (RW) to apply 187 L ha^{-1} of solution, onto the soil surface of each packed column. About 1 and 5 days after surfactant application, columns were sprinkler irrigated with either RW or well water (WW). The WDPT was then measured with depth on soil air-dried after the first and after the second irrigation. After the first irrigation, WDPT at depths from 97 to 117 mm averaged across surfactant rates reached a maximum of 28 s, regardless of irrigation water quality. WDPT was greatest at 117 mm with RW but only at 97 mm with WW. After the second irrigation, maximum WDPT was 1202 s at 139 mm with RW but only 161 s at 117 mm with WW, nearly 7.5 fold less than with RW. WDPT was greatest near the wetting front, irrespective of water quality. We conclude that irrigation water containing modest amounts of electrolytes or salts, in this case mostly salts of Ca^{2+}, reduces water repellency in the presence or absence of surfactant. Our experimental results may also help explain erratic surfactant performance under rainfed conditions where neither water quality nor depth of infiltration can be fully controlled.

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1. Introduction

Water quality affects both the aggregation and dispersion of soil colloidal material and has been linked through these to many important soil phenomena, including surface sealing and crusting, infiltration, runoff, illuviation, and erosion. Because of the potent interaction between water quality and various constituents in soil and on particle surfaces, water quality may also influence the wettability of soils. Soils untreated or treated with wetting agents, or surfactants, may respond differently to waters differing in quality.

A water repellent soil is one that resists wetting (Doerr et al., 2000). Water repellency is likely due to hydrophobic organic compounds that coat or partially coat soil particle surfaces (DeBano et al., 1970; Wallis et al., 1991). Hydrophobic compounds may be either (1) non-polar aliphatic hydrocarbons, nearly insoluble in water, or (2) polar hydrocarbons with one end of a carbon chain being hydrophilic and the other hydrophobic (Doerr et al., 2000). Sandy soils easily become water repellent because of their small surface area (Doerr et al., 2000). Water repellent soils are found worldwide (Mataix-Solera and Doerr, 2004; Wallis et al., 1991; Wallis and Horne, 1992; Dekker et al., 2005 and references cited therein).

Water repellent soils in highly managed environments like turf grass and agricultural fields are often treated with surfactants, organic molecules that reduce the surface tension of water (Fernández Cirelli et al., 2008; Laha et al., 2009). Surfactant molecules are amphiphilic; they possess both hydrophilic and hydrophobic functional groups, as do polar hydrophobic compounds (Haigh, 1996).

Despite sorption on clay and organic matter, surfactants can move through soil profiles (Miller et al., 1975; Miller and Letey, 1975). The leaching of surfactants depends upon (1) the properties of the applied surfactant as well as the soil receiving it, and (2) the surfactant concentration in the applied solution (Miller et al., 1975). Depending on the concentration of surfactant present and on the amount of surfactant on soil particle surfaces, different sorption regimes may exist (Adeel and Luthy, 1995; Laha et al., 2009). This may account for the difficulty in describing and

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☆ Manufacturer or trade names are included for the readers' benefit. By including names, the USDA-ARS implies no endorsement, recommendation, or exclusion.

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modeling the effects of relatively low surfactant concentrations upon surfactant movement through soil (Miller et al., 1975).

There is disagreement in the literature whether relatively low concentrations of surfactants can mobilize hydrophobic compounds in soil profiles (Haigh, 1996; Grasso et al., 2001; Scheunert and Korte, 1985). Adding low concentrations of surfactant to soil-water systems is thought to reduce the leaching of hydrophobic organic compounds because the hydrophobic compounds sorb to the surfactant compounds that, in turn, are strongly sorbed to the soil (Laha et al., 2009). However, Scheunert and Korte (1985) found that a relatively low surfactant concentration (10 mg kg^{-1} in the uppermost 10 cm of soil) increased, rather than decreased, the mobilization of hydrophobic organic compounds, possibly by physically affecting near-surface soil sorption sites for water repellent compounds. By reducing surface tension and facilitating water entry into, and displacement of water-repellent substances from sidewalls of fine pores, surfactants at relatively low concentrations were thought to enhance movement of hydrophobic compounds (Fernández Cirelli et al., 2008; Laha et al., 2009).

Doerr et al. (2000) reported that prolonged hydration of a water repellent soil decreased water repellency. They speculated that it was due to the rearrangement of amphiphilic hydrophobic compounds on particle surfaces. Upon rearrangement, bonds joining hydrophobic substances to particle surfaces may weaken or break.

Hydrophobic materials may also be liberated from particle surfaces by physical means. Hydrophobic compounds can be removed from sand particle surfaces by mechanical agitation in water (Roberts and Carbon, 1971) or cultivation followed by irrigation (Jamison, 1946).

Haigh (1996) also speculated that surfactant effects on the movement of water-repellent substances may be the net effect of different mechanisms operating concurrently. Though hydrophobic organic compounds are sorbed onto soil organic matter (Zhou and Zhu, 2005), the soil organic matter can itself move, carrying the sorbed hydrophobic compounds with it. Movement of organic matter may transport applied surfactants similarly.

Water repellency generally decreases as soil water content increases (Doerr et al., 2000). Water repellency often decreased or rapidly disappeared at the soil surface during simulated rainfall (Zwolinski, 1971) or in both the surface and subsurface after heavy precipitation (Ritsema and Dekker, 1994; Ritsema et al., 1997). Jaramillo et al. (2000) speculated that excessive precipitation thinned water repellent horizons.

These findings suggest that water passing through repellent soil alters the effects of hydrophobic organic compounds at the surface, transports those compounds through soil, or both. The water flowing through repellent soils and any resulting changes in water repellency with depth need to be closely examined during or shortly after water application (Ritsema et al., 1997).

Calcareous lithology, divalent cations, or electrolytes in the soil solution have been reported to affect water repellency (Cerdà and Doerr, 2007; Mataix-Solera and Doerr, 2004). Cerdà and Doerr (2007) suspected that water repellency may not develop in calcareous soil. Indeed, Roberts and Carbon (1972) held that alkaline conditions prevented water repellency. For acid soils, liming reduced water repellency (Karnok et al., 1993; van't Woudt, 1959).

Rao and He (2006) reported that surfactant sorption onto soil also increased as solution ionic strength increased. In addition, Haigh (1996) noted that electrolytes in solution increased the solubility and mobilization of hydrophobic compounds in soils treated with anionic and cationic surfactants. Electrolyte effects upon the efficacy of nonionic surfactants, in contrast, are thought to be minimal because charge interactions play no part in the formation of clusters of uncharged surfactants in solution (Haigh, 1996). Fernández Cirelli et al. (2008) noted that nonionic surfactants were little affected by Ca^{2+} or Mg^{2+} ions. Electrolyte effects upon the water repellency of soils, whether untreated or treated with nonionic surfactants, warrant additional study.

To sustainably manage and protect soils in agricultural areas, more information is needed on the manner in which hydrophobic organic compounds (1) interact with all classes of surfactants (Fernández Cirelli et al., 2008), and (2) attach to and detach from particle surfaces (DeBano and Letey, 1969; Doerr et al., 2000). Unresolved questions still exist regarding movement of hydrophobic substances by water where electrolytes are present either in the soil or in irrigation water or rainfall. Thus, the objective of the study was to evaluate the effects of water quality and surfactant application upon the water repellency of a Quincy sand.

2. Materials and methods

2.1. Surfactant and soil properties

The study was conducted at the USDA-ARS Northwest Irrigation and Soils Research Laboratory, Kimberly, ID. We studied the commercially available, miscible surfactant IrrigAid Gold® (IGG), produced by Aquatrols Corporation of America, Paulsboro, NJ. This surfactant was chosen because it synergistically alleviated water repellency better than the sum of its two components (Bially et al., 2005). IrrigAid Gold (IGG) is a blend of two nonionic surfactants: an ethylene oxide/propylene oxide block copolymer and an alkyl polyglycoside (Bially et al., 2005). IrrigAid Gold is a light brown, odorless liquid that contains 0.17 kg active ingredient kg^{-1}, with the remaining liquid being water. As marketed, IGG has a pH of 6.4 and a specific gravity of 1.024 Mg m^{-3}. Additional properties were given by Lehrsch et al. (2011).

We studied a Quincy sand, a mixed, mesic Xeric Torripsamment (Soil Survey Staff, 2010a) (Table 1). The Quincy soil is an agriculturally important soil from the Pacific Northwest region of the US and was chosen because it sometimes exhibits soil water repellency sufficient to impair crop productivity (D. Horneck, 2009, personal commun.). The soil is present on nearly 280,000 ha, mostly in the Columbia River Basin region of Washington, Oregon, and Idaho (NRCS, 2009). We determined particle size distribution with a pipette (Gee and Or, 2002). The soil's specific surface area was measured by the Soil Survey Staff (2010b) using the ethylene glycol monoethyl ether method (Pennell, 2002). We measured Walkley-Black organic C (Nelson and Sommers, 1996), and pH using a combination electrode in a saturated paste (Robbins and Wiegand, 1990). Soluble (and readily dissolvable) cations in an aqueous saturated paste extract (Rhoades, 1996; Robbins and Wiegand, 1990)

Table 1
Properties of the Quincy sand (Ap horizon, 0- to 0.3-m depth).

Property	Value
Physical	
Particle size distribution, g kg^{-1}	
Sand (0.05–2 mm)	950
Silt (0.002–0.05 mm)	10
Clay (<0.002 mm)	40
Specific surface area, $m^2\ kg^{-1} \times 10^3$	31.5
Chemical	
Organic C, g kg^{-1}	4.6
pH (sat. paste)	6.4
Soluble Ca^{2+}, mg kg^{-1}	43.8
Soluble Mg^{2+}, mg kg^{-1}	17.0
Soluble K^{+}, mg kg^{-1}	58.7
Soluble Na^{+}, mg kg^{-1}	5.5
Electrical cond. (sat. paste ext.), dS m^{-1}	1.66
Sodium adsorption ratio (SAR), $(meq/L)^{0.5}$	0.32
Cation exchange capacity, $cmol_c\ kg^{-1}$	12.6
Base saturation, %	45

were quantified with inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Optima Model 4300 DV spectrometer (Perkin Elmer Instruments, Waltham, MA). On a saturated paste extract, electrical conductivity (EC) was determined per Rhoades (1996) and sodium adsorption ratio (SAR) per Robbins and Gavlak (1989). Cation exchange capacity (CEC) and base saturation, each at a ratio of 2 g of soil to 20 ml of extractant, were determined following the guidelines of Sumner and Miller (1996) for soils containing carbonates. The clay fraction mineralogy of the Quincy soil consisted of roughly similar amounts of montmorillonite, mica, kaolinite, and a vermiculite-chlorite intergrade, as shown in the USDA Natural Resources Conservation Service Soil Characterization Database (Soil Survey Staff, 2010b).

We collected the soil, at depths from 0 to 0.3 m, in February 2007 from a field (45°45′N 119°32′W) near Hermiston, Oregon. When sampled, the soil's water content was about 0.16 kg kg^{-1}. The soil was transported to Kimberly, ID, and stored field-moist in covered metal bins at ambient temperatures.

2.2. Column preparation

After being air-dried and well mixed by hand, Quincy soil was packed by tamping in 25-mm lifts to a nominal bulk density of 1.6 Mg m^{-3} into 0.15-m-high × 0.105-m-diameter columns of polyvinyl chloride pipe. Columns were filled with soil to within 3 mm of the column rim. Water repellency was characterized for each lift by measuring water drop penetration time, WDPT (van't Woudt, 1959), a widely used measure of the persistence of water repellency (Letey et al., 2000). To establish a baseline on the soil packed into each of the six lifts, we measured WDPT using 10 0.06-ml drops of reverse osmosis water (RW) in a laboratory at 24 °C with ca. 26% relative humidity. According to the classification scheme of Roberts and Carbon (1971), a soil sample was classified as wettable if its WDPT was <1 s, as slightly water repellent if its WDPT was 1 to <10 s, as moderately water repellent if its WDPT was 10–60 s, and as severely water repellent if its WDPT was >60 s. Soil samples with WDPTs >1 but ⩽5 s have been described as exhibiting subcritical water repellency (Cerdà and Doerr, 2007). In our study, the initial WDPT averaged across depths was 2.5 s, indicating that the Quincy soil was slightly water repellent. *In situ* Quincy sand exhibits spatial and temporal variation in soil water repellency, often being more water repellent during the drier portions of the year, summer and early fall (D. Horneck, 2009, personal commun.).

2.3. Surfactant application

Before irrigation, surfactant was sprayed directly to the soil on the surfaces of the packed columns using a backpack sprayer and a 1.52-m long, hand-held spray boom equipped with five nozzles (Spraying Systems Co. TeeJet® Model 1100050V) operated at a nozzle pressure of 172 kPa (25 PSI). We moved the boom across each column twice at a calibrated rate, first moving left to right then right to left. Tracks placed 0.36 m above the columns supported the boom to ensure uniform application height and even distribution (Christiansen's Uniformity Coeff. of 0.93; Smajstrla et al., 1997) of surfactant onto the soil in all columns. Surfactant application rates were based on 0, 1, and 5 times the manufacturer's recommended rate of 9.4 L ha^{-1} of product, diluted with RW as necessary to apply 187 L ha^{-1} of dilute solution. A 1:19 (v/v) dilution of surfactant to RW was used for the 9.4-L ha^{-1} rate and 1:3 for the 46.8-L ha^{-1} rate. We applied 0.16 ml (equivalent to a depth of <0.02 mm) of diluted surfactant to the soil on the surface of each column. No RW was applied to the controls using the backpack sprayer since the RW volume applied to the treated columns was regarded as insignificant, given (1) the evaporation that occurred after the surfactant solutions were applied, and (2) the water subsequently applied via irrigation (described below).

2.4. Irrigations

Twenty-four h after applying surfactant, we irrigated the soil in the columns for 0.25 h at 88 mm h^{-1} for the first time. Water was applied using a calibrated sprinkler simulator equipped with a single, oscillating Spraying Systems Co. VeeJet® Model 8070 nozzle mounted 3 m above the soil columns. The sprinkler, similar to that of Meyer and Harmon (1979), was operated at a nozzle pressure of 76 kPa to simulate irrigation with a median drop diameter of 1.2 mm and sprinkler droplet kinetic energy of 26.0 J kg^{-1} (Aase et al., 1998; Kincaid, 1996). Water from the flat-fan type nozzle wet the entire soil surface of each column throughout each irrigation. Our irrigation water contained no surfactant. We used well water (WW) drawn from a tap to irrigate all WW columns, and thereafter RW (Table 2) to irrigate all RW columns. We measured pH according to Thomas (1996) and, in 60-ml, unfiltered samples stabilized with 0.6 ml of saturated boric acid solution, soluble cations by ICP-OES. Each water's EC and SAR were determined on an unfiltered sample as described above. At the first irrigation of each block, soil in three additional, identically prepared columns (one treated with each of the three surfactant rates) was irrigated and immediately thereafter destructively sampled (described below). This provided the soil samples from columns irrigated only once. Between irrigations, the remaining irrigated but unsampled columns were placed in an oven at 30 °C for 3 days until their soil dried to a water content <0.04 g g^{-1}. After cooling for 16 h to reach ambient temperature, the columns were again irrigated with water of the same quality as before and sampled as previously.

2.5. Soil sampling and water drop penetration time measurements

Following the first and second irrigations, soil samples for measuring WDPT were collected in 12 increments from 0 to 150 mm. In general, samples were collected in 10-mm increments near the surface, steadily increasing to 20-mm increments near the column bottom. Specifically, samples were collected in increments with midpoint depths of 8, 13, 19, 27, 37, 46, 58, 69, 81, 97, 117, and 139 mm. Upon column disassembly immediately after irrigation, soil from each increment was mixed by hand, then placed in a tin and weighed. The soil in the tins was air-dried at 30 °C for 5 days until its water content was 0.007 g g^{-1}. Then, each sample's WDPT was measured using RW and WW as described above. Unless specified otherwise, all WDPT values reported hereafter were measured using RW.

2.6. Statistical analysis

The experimental design was a split plot in four replications, with two irrigation water qualities, three surfactant application

Table 2
Water quality of the reverse osmosis water (RW) and well water (WW) used for irrigation.

Water quality parameter	Reverse osmosis water	Well water
pH	5.7	7.6
Soluble Ca^{2+}, mg L^{-1}	0.882	54.90
Soluble Mg^{2+}, mg L^{-1}	0.051	31.98
Soluble K^{+}, mg L^{-1}	0.045	5.21
Soluble Na^{+}, mg L^{-1}	3.201	67.16
Electrical conductivity (EC), dS m^{-1}	7.2×10^{-3}	0.7
Sodium adsorption ratio (SAR), (meq/L)$^{0.5}$	2.2	1.7

rates, two irrigations, and twelve sampling depths. The design was modeled with each of the twelve water quality × rate × irrigation combinations as a main plot and depth as a subplot, with depth considered a repeated-measures factor. Because all soil columns were identical in size, our mixed-model analysis (described below) enabled us to test each of the three factors in our main plots for significance. Our response variable for subsequent statistical analyses was each soil sample's mean WDPT, calculated by excluding the highest and lowest measured WDPT and taking the arithmetic average of the remaining eight values. Before performing an analysis of variance (ANOVA), we examined the WDPT's error variance by treatment using the relationship between the WDPT treatment means and corresponding treatment standard deviations (Box et al., 1978). To do so, we first calculated a WDPT mean and standard deviation ($n = 4$) for each of the 144 treatment combinations, then regressed the log standard deviations on the corresponding log means. The fitted slope suggested the appropriate transformation to be applied to the raw data (Box et al., 1978). To stabilize the error variance, we transformed each sample's WDPT mean by adding one, then taking the common log of the sum (Steel and Torrie, 1960).

We used SAS (SAS Institute Inc., 2009) to perform an ANOVA using mixed-model procedures and a significance probability (P) of 5%, unless otherwise noted. As needed, ANOVA grouping options were used to account for heterogeneous variances in the response variables. In our ANOVA, response variable correlations among depths within main plots were accounted for using a spherical, spatial covariance structure. We separated least-squares means using t-tests of pairwise differences at $P = 0.05$. Where needed, means were back-transformed into original units for presentation.

We also determined the correlation between each sample's mean WDPT measured using WW and RW by calculating Kendall's tau-b correlation coefficient where $-1 \leqslant \text{tau-}b \leqslant +1$. Kendall's correlation coefficient is a nonparametric measure of association based on the number of concordant and discordant pairs of observations (SAS Institute Inc., 2009). Concordant observations are paired observations that increase (or decrease) together.

3. Results

3.1. Overview

Our analysis of variance findings are shown in Table 3. In terms of main effects, soil water repellency as measured by WDPT was affected most by irrigation, followed in order by sampling depth, then irrigation water quality. In contrast, surfactant application rate did not affect soil water repellency, neither as a main effect nor as part of an interaction (Table 3). Unlike Miller and Letey (1975), surfactant application rate had no effect on water repellency in our experiment, likely due to differences in surfactants, application rates, and protocols. Also, our Quincy sand with an initial WDPT of 2.5 s was only slightly water repellent, considered wettable in some classification schemes (Bisdom et al., 1993), and thus not likely to significantly respond to surfactant application (Lehrsch et al., 2011). Indeed, application rate effects were minimal. Averaged across all other main effects, WDPT was 3.2 s for the control, 3.3 s for the 9.4-L ha^{-1} rate, and 3.5 s for the 46.8-L ha^{-1} rate, all statistically similar. However, WDPT was affected by a highly significant interaction between irrigation water quality, irrigation, and sampling depth, our experiment's key interaction (Table 3).

Table 3
Analysis of variance of water drop penetration time (WDPT).

Source of variation	Degrees of freedom (df)	F-ratio's significance probability
Irrigation water quality (WQ)	1	0.430
Surfactant appl. rate (RATE)	2	>0.500
WQ × RATE	2	>0.500
Irrigation (IRR)	1	<0.001
WQ × IRR	1	0.396
RATE × IRR	2	>0.500
WQ × RATE × IRR	2	>0.500
Sampling depth (DEPTH)	11	<0.001
WQ × DEPTH	11	<0.001
RATE × DEPTH	22	>0.500
WQ × RATE × DEPTH	22	>0.500
IRR × DEPTH	11	<0.001
WQ × IRR × DEPTH	11	<0.001
RATE × IRR × DEPTH	22	>0.500
WQ × RATE × IRR × DEPTH	22	>0.500

3.2. Water drop penetration time as affected by irrigation water quality, irrigation, and sampling depth

Irrigation water quality affected WDPT (Fig. 1). Compared to initial (pre-irrigation) conditions, soil water repellency after Irrigation 1 generally decreased at depths ⩽81 mm but increased at depths ⩾97 mm (Fig. 1A). Irrigation water quality also seemed to affect the depth at which WDPT was maximum after Irrigation 1. WDPT was greatest at 97 mm when irrigated with WW but at 117 mm when irrigated with RW (Fig. 1A). WDPT for WW at 97 mm was 27.5 s, significantly greater (at $P < 0.061$) than the 16.1 s at the depth below, 117 mm. In contrast, WDPT for RW at 117 mm was 27.9 s, significantly greater (at $P < 0.083$) than the 15.5 s at the depth above, 97 mm.

Changes in WDPT with depth after Irrigation 2 (Fig. 1B) are similar in many respects to the findings after Irrigation 1 (Fig. 1A). Compared to initial conditions, WDPT was less near the surface but much greater at depth (Fig. 1B). In every case, WDPT was least above 19 mm, where surfactant effects have often been reported to be greatest (Haigh, 1996; Miller and Letey, 1975). WDPT after irrigation with RW was similar at depths from 19 to 81 mm. Regardless of irrigation water quality, water repellency was greatest below 97 mm.

There were three major differences in WDPT with depth between the first and second irrigation (Fig. 1). First, WDPT at depths ⩾97 mm was far greater after Irrigation 2 than 1. For example, WDPT after Irrigation 2, compared to 1, was 2- to 3.5-fold greater at 97 mm and 12- to 564-fold greater at 139 mm. Second, WDPT after irrigating with WW was greatest at 97 mm after Irrigation 1 but at 117 mm after Irrigation 2. Similarly, WDPT after irrigating with RW was greatest at 117 mm after Irrigation 1 but at 139 mm after Irrigation 2. Irrigating a second time applying 22 mm of either WW or RW moved the water repellency peak downward by 20 mm. Third, after Irrigation 2, WDPT for RW changed little from 117 to 139 mm.

After the second irrigation (Fig. 1B), water repellency at depth was much greater (significant at $P < 0.001$) after irrigating with RW than WW. For example, WDPT at 117 mm with RW was 1121 s, seven-fold greater than the 161 s with WW. At 139 mm, WDPT differences were even greater, 1202 s for RW compared to 47 s for WW. Stated differently, irrigation with WW rather than RW decreased WDPT after the second irrigation by 86% at the 117-mm depth and by 96% at the 139-mm depth. In contrast, WDPT at intermediate depths (69 and 81 mm) was 3–4 times greater after irrigating with WW rather than RW.

Our findings also reveal differences in WDPT from irrigation to irrigation for each water quality by comparing data shown in Fig. 1A with that in Fig. 1B for each water quality. Compared to the first irrigation, a second one significantly increased water repellency at depths ⩾97 mm for each water quality. Averaged across rates, WDPT at all depths ⩾97 mm was significantly greater after the second than first irrigation with RW (Fig. 1A vs. 1B).

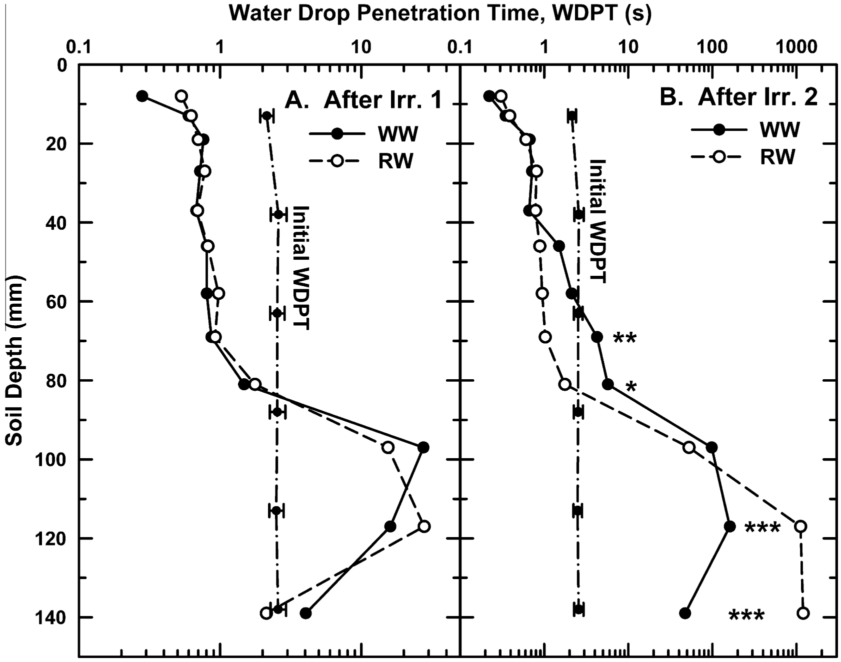

Fig. 1. Water drop penetration time (WDPT) as a function of soil depth for Quincy sand irrigated with either well water (WW) or reverse osmosis water (RW) after each of two irrigations. Data have been averaged across surfactant application rates. Within an irrigation, significant differences between water quality means at specific depths, when they occurred, are denoted with asterisks where $*$ is $P < 0.05$, $**$ is $P < 0.01$, and $***$ is $P < 0.001$. Selected means ($n = 12$) are shown with their 95% confidence limits.

Similarly, WDPT at all depths $\geqslant$69 mm was significantly greater after the second than first irrigation with WW.

Water drop penetration times measured using WW and RW were highly correlated (Fig. 2). Kendall's correlation coefficient, $r_K = +0.87^{***}$, revealed that WDPT measures would be similar whether one used WW or RW as source water for the measurement. Many WDPT values were <5 s (Fig. 2, inset).

4. Discussion

4.1. Movement of hydrophobic substances

Compared to initial conditions, soil water repellency generally decreased in the upper half of the columns but increased greatly in the lower half (Figs. 1A and B). Two possible mechanisms (I or II) may be operating. For Mechanism I, hydrophobic compounds, possibly adhering to particulate organic matter or on colloids or released from particle surfaces, are being mobilized from depths $\leqslant$81 mm and are moving with the water near the wetting front. Those compounds are being transported below the 81 mm-depth to coat wettable mineral surfaces, thus rendering them more repellent than they initially were (Fig. 1). For Mechanism II, at and above 81 mm, particle surfaces covered with hydrophobic compounds are being rendered wettable due to possible rearrangement of hydrophobic substances present there, thus decreasing WDPT. This second explanation, however, does not explain the substantial increase, compared to initial values, in WDPT at depths of 97 mm and below, the depths to which the wetting front descended after each irrigation. If Mechanism II were operating, the WDPT below the wetting front should be similar to the initially measured WDPT but, as Fig. 1 reveals, the WDPT at 97 mm and below was much greater than that measured initially. In summary, the changes observed in WDPT with depth are described better with Mechanism I than II.

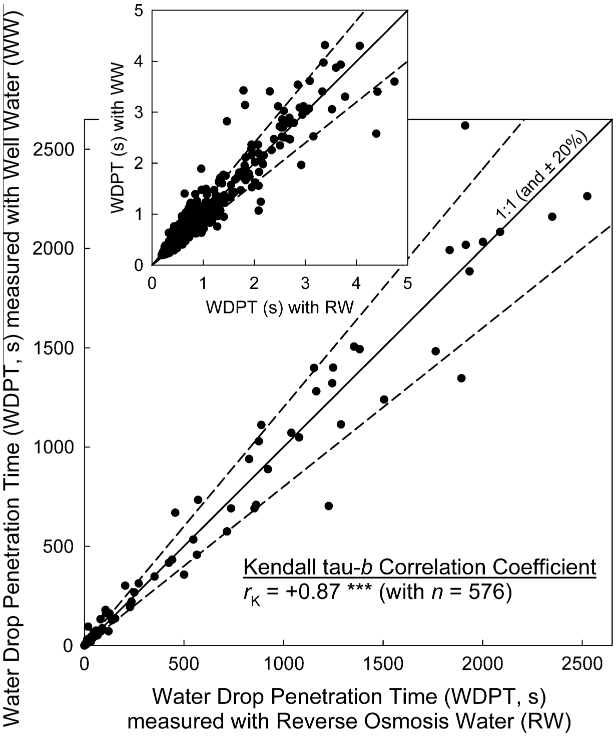

Fig. 2. Water drop penetration time (WDPT) measured using well water (WW) and reverse osmosis water (RW). The inset provides detail near the origin.

As we postulate in Mechanism I, hydrophobic compounds could have been liberated from particle surfaces in the following manner. The rearrangement of amphiphilic compounds to join their hydrophilic polar ends with water molecules may weaken the bond between the hydrophobic compounds and the soil, displacing the hydrophobic substances from the soil and rendering the particle surface wettable (Tschapek, 1984; Ma'shum and Farmer, 1985; Velmulapalli, 1993, all cited by Doerr et al. (2000)). Irrigation or rainfall may leach these displaced hydrophobic, amphiphilic compounds deeper in the soil. Once there upon drying, the amphiphilic compounds can adhere to particle surfaces and again rearrange, rendering those surfaces hydrophobic once more, increasing water repellency (Tschapek, 1984; Ma'shum and Farmer, 1985). In addition, Ritsema et al. (1998a,b) speculated that water-repellent substances were also leached through coarse-textured soil profiles as water moved through them. In their case, but not in ours, leaching occurred from preferential flow (or finger) pathways, thus contributing to the pathways' continued existence and reoccurrence at the same location from one storm to another.

Ritsema et al. (1997) noted that water repellency should not appreciably change over the short-term since much time is needed to change the quantity or quality of the water-repellent substances adsorbed on soil particle surfaces. In our study, however, we detected water repellency changes within 5 days after applying water (Fig. 1). Compared to the environment (both test and physiographic) of Ritsema et al. (1997), our environment was surely less humid and likely hotter, possibly accounting for the changes in water repellency that we observed much sooner than they postulated.

Hydrophobic substances often adsorb onto soil organic matter (Ma'shum et al., 1988; Zhou and Zhu, 2005). Fine particulate organic matter, if hydrophobic in character, causes water repellency (de Jonge et al., 1999). With movement of fine organic matter, hydrophobic organic compounds can be mobile in this way as well, imparting water repellency to the soil where they come to rest (Doerr et al., 2000). Irrigation water may be transporting this fine particulate organic matter deeper in the profile, thereby decreasing WDPT near the surface and increasing WDPT at lower depths (Doerr et al., 1996).

4.2. Water quality effects

The depth at which water repellency was greatest was a function of irrigation water quality, significantly so after Irrigation 2 (Fig. 1B). Greater water repellency in soil irrigated with RW rather than WW may be due to the fact that, per unit volume, RW contained less than 2% of the Ca^{2+} ions that WW contained (Table 2). Thus, data in Fig. 1 reveal that WDPT was greatest deeper in columns irrigated with RW than WW. All in all, irrigating with RW rather than WW resulted in WDPT being (1) much greater than that measured pre-irrigation at depths $\geqslant$97 mm, and (2) greatest at the two lowest depths after Irrigation 2. In other words, irrigating with low compared to high electrolyte water caused soil water repellency to be expressed both deeper and to a greater degree in Quincy sand. Stated differently, water repellency in slightly water repellent soil is minimized better by irrigating with water containing electrolytes rather than water essentially devoid of electrolytes, such as rainfall or melt water from high-elevation snowpacks.

Water quality affected soil water repellency (as indicated by WDPT) or, at least, the expression of it at depth in our soil profiles in both the presence and absence of surfactant (Fig. 1B). At depths $\geqslant$117 mm, divalent cations are apparently playing a role in altering the degree to which hydrophobic compounds express water repellency, minimizing the mobilization of hydrophobic compounds to those depths, or both. Like most others who study water repellency, we did not directly measure hydrophobic compound concentrations with depth in our soil columns. Therefore, we cannot definitively document such mobilization but our indirect evidence from WDPT profiles is strong. Compared to initial conditions, water with and without electrolytes consistently decreased WDPT above 81 mm (Fig. 1A) while greatly increasing WDPT at depths $\geqslant$97 mm, in general (Figs. 1A and 1B). Electrolytes may also be muting the expression of water repellency by transported hydrophobic substances, once those substances have accumulated at some depth in the profile (Fig. 1B).

We also speculate that the movement of hydrophobic compounds may be affected by water with relatively high SAR, high EC, or varying combinations of either, which in turn may affect surfactant efficacy. Haigh (1996), on the other hand, held that electrolytes would have little or no effect on the efficacy of nonionic surfactants.

As noted above, colloids may also be transporting hydrophobic substances (Zhuang et al., 2005). If so, downward movement would increase with irrigations, as Fig. 1 reveals. In addition, the few divalent salts in RW would allow the diffuse double layer of clays to expand and clay domains to disperse, facilitating the movement of colloids with attached hydrophobic compounds. In contrast, the relatively high Ca^{2+} concentrations in WW would reduce the thickness of the clay particles' diffuse double layers leading to flocculation, and thus less colloidal transport. This zeta potential effect may also inhibit the movement of surfactants, depending upon their molecular size, conformation, and degree of association with colloidal surfaces.

The leaching of hydrophobic substances with irrigation water that we postulate is also supported by data shown in Fig. 1. As water leaches a solute through a soil profile, the solute's peak typically becomes less distinct with the peak's shoulders broadening as the solute moves downward (Porro and Wierenga, 1993). This broadening of the WDPT peaks for both the WW and RW irrigations can be seen by comparing Fig. 1A with 1B. A solute's peak concentration also generally decreases as it moves downward (Leij and van Genuchten, 2002). In our experiment, in contrast, the concentration of hydrophobic compounds at depths >81 mm increased greatly from one irrigation to the next, particularly when irrigated with RW (Fig. 1).

4.3. Water repellency at column midpoints after the second irrigation

Water repellency after Irrigation 2 at depths of 69 and 81 mm was significantly greater after irrigating with WW than RW (Fig. 1B). As redistribution occurred in the soil in the columns that were slowly dried after the first irrigation, water moving upward in response to a potential gradient that developed due to evaporative water loss from the soil surface may have transported hydrophobic organic compounds upward to depths of 46–81 mm from depths of 97 mm and below in columns irrigated with WW but not RW. This upward transport of hydrophobic substances to intermediate depths via redistribution was not detected after Irrigation 1 (Fig. 1A) because the soil in those columns was destructively sampled immediately after being irrigated. This explanation is supported by observations we made in a separate study to be reported in a manuscript now in preparation. In that study as Quincy soil slowly dried, we found that mobile hydrophobic compounds apparently were transported upward in the profile by water moving as a consequence of evaporation from the soil surface. The electrolytes present in the WW but not RW might be playing a role in this upward movement of hydrophobic substances.

Another explanation, however, is plausible. Additional WW applied in the second irrigation may have stripped some of the hydrophilic surfactant from water-repellent areas on particle surfaces from depths of 69 to 81 mm, causing those surfaces to again become water repellent, thereby increasing WDPT at those depths. Such displaced surfactant compounds were likely transported farther down in the columns, there to keep water repellency in check, as Fig. 1B suggests. Miller and Letey (1975) reported that surfactant moved deeper as more and more water passed through their treated columns.

4.4. Soil handling effects

For a companion study (Lehrsch et al., 2011), a protocol was needed to obtain soil that was homogeneous with respect to its water repellency. To develop that protocol, we conducted preliminary studies with Quincy soil. We found that the WDPT varied greatly among the soil lots collected from the field, and even among batches of soil retrieved from each lot. As we worked with the soil, it became clear that handling (mixing, abrasion, tamping, etc.) altered the WDPT. Abrasion from this soil handling may have dislodged hydrophobic compounds from particle surfaces, facilitating their downward transport (Jamison, 1946; Ma'shum and Farmer, 1985).

In this study, soil disturbance, particle abrasion, or both seemed to contribute to hydrophobic compound movement and with leaching to the creation of a much more water repellent layer deeper in the soil profile (Fig. 1). In soils in agricultural production, plowing and field preparation disturb soil, abrade particles, and likely dislodge hydrophobic substances. Thereafter, water applied in the first irrigation after plowing may drive the water repellent layer deeper in the profile (Doerr et al., 1996). King (1981) reported that the application of 10–15 mm of water (as rain) with concurrent or subsequent tillage reduced water repellency, likely by dislodging and leaching hydrophobic substances. In our study, the most water repellent portion of the profile was located at the wetting front.

Erosion by wind or water can make the management of water repellent soils even more difficult. Where we collected the Quincy soil for this experiment, (1) the most water repellent soil was commonly situated on high-elevation areas in the field, and (2) wind erosion was often severe. It follows that the uppermost portion of the profile on those areas was likely eroded, exposing the more water repellent portion underneath.

In summary, sprinkler irrigating a Quincy sand translocated repellency-inducing moieties to the wetting front, concentrating them there in either surfactant-treated or untreated soils. Repeated irrigations further concentrated and drove repellency-inducing moieties deeper. When the sprinkler water contained modest amounts of calcium-rich electrolytes, the repellency at the wetting front was reduced nearly an order of magnitude. It appears that irrigating water repellent soils using water containing electrolytes (particularly Ca^{2+} salts), greatly reduces repellency in the zone where hydrophobic substances accumulate in such soils. In our study, this occurred whether or not the soil was pretreated with surfactant.

4.5. Applying the findings

Our findings of irrigation water quality effects on soil water repellency should generally be applicable to certain other classes of surfactants and to similar soils in arid and semi-arid climates. In an earlier investigation of three wettable soils that included a wettable Quincy (Lehrsch et al., 2011), surfactants with active ingredients of alkyl polyglycosides, ethylene oxide/propylene oxide block copolymers, and a blend of both did not differ in their effects on infiltration from simulated irrigations. Consequently, we speculate that irrigation water quality would have similar effects on the water repellency of sandy soils treated with these classes of surfactants. Moreover, we would expect that irrigation water quality would have similar effects on the water repellency of other coarse-textured soils, in particular those having clay mineralogy with substantial amounts of mica and montmorillonite. Heavily weathered sandy soils with much gibbsite and vermiculite, however, may not react as did the Quincy sand to these classes of surfactants and to irrigation water quality (Lehrsch, 2010, unpublished; Sullivan et al., 2009).

The hydrophobic organic compounds causing water repellency in the Quincy soil appear to be both mobile (soluble under certain conditions) and mutable (that is to say, their potency seems to be modified by handling and water quality). With additional research, it might be possible to manage both the position and thickness of the water repellent layer using soil disturbance, prescribed water quality modification, prescribed irrigation protocols, and possibly other means. An opportunity exists for the conjunctive use of calcium sources (1) in irrigation water (e.g., dissolving added gypsum in the water) or (2) on the field (e.g., applying granular gypsum to the soil). Farmers and managers of turf grass and other agricultural land may be able to control the soil depth where repellency-inducing substances accumulate. For turf grass managers, this depth should be well below that of rooting. For farmers, it should be below the depth of rooting or below the depth of annual tillage, whichever is greater. Another way to manage water repellency might be to enhance surfactant efficacy via formula modification involving calcium salts.

Our study's findings have potentially large implications for managing agricultural soils, turf grass, and fire-ravaged landscapes. In soils used to produce food and fiber, water repellency may be fought more effectively through a combination of soil manipulation, irrigation water application practices, and surfactant application. In turf grass, where new water quality challenges are emerging, integrated management of water quality and surfactants may need to be far more prescriptive than has been previously thought. Existing problems with irrigating turf grass on water repellent soil may well be exacerbated by the wide variation in kinds and quality of both organic and inorganic constituents present in municipal waters now often being re-used for irrigation. We know little on how these individual components or combinations of them might affect water repellency development in such soils. In soils from burned areas, it may be that current fire suppression techniques are actually concentrating repellency in subsoil layers, facilitated by the downward movement of water sprayed from ground level or dropped from the air for fire suppression. Furthermore, conditioning fire suppression water with salts and possibly surfactants may moderate subsoil repellency accretion or eliminate repellency altogether.

5. Conclusions

Water repellency measured by the WDPT test was affected by irrigation and irrigation water quality, but not surfactant application rate. In 150-mm deep columns of slightly water repellent Quincy sand, simulated irrigations decreased WDPT in the soil in the upper half of the columns but greatly increased WDPT in the lower half, compared to initial conditions. A second irrigation with low-electrolyte water caused water repellency to be expressed both to a greater degree and deeper in the soil. Irrigating twice with water that contained electrolytes decreased WDPT by 86% at the 117-mm depth and by 96% at the 139-mm depth, compared to irrigating with water essentially devoid of electrolytes. Farmers and land managers may be able to use electrolyte-containing irrigation water to control water repellency by depth in soil profiles. The water quality effects on water repellency found in this study may also help account for surfactant efficacy differences between rainfed and irrigated locales. Irrigating with water that contains electrolytes better controls water repellency of coarse-textured soil whether treated with a nonionic surfactant or not.

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