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Project Title: Unstable flow in repellent and sub-critically repellent soils: theory and management implications

Investigators

Principal Investigator (PI):

Rony Wallach

Co-Principal Investigator (Co-PI):

Tammo Steenhuis

Collaborating Investigators:

Ellen R. Graber

David DiCarlo

Yves Parlange

Institutions

Hebrew University of Jerusalem

Cornell University, Ithaca NY

The Volcani Center, Israel

University of Texas, Austin

Cornell University

Keywords *not* appearing in the title and in order of importance. Avoid abbreviations.

Contact angle, finger flow, overshoot, dynamic contact angle, fatty acids, porous media, capillary, water penetration, imbibition

Abbreviations commonly used in the report, in alphabetical order:

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US: \$169,000

Total: \$ \$353,000

Signature
Principal Investigator

Signature
Authorizing Official, Principal Institution

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Publication Summary (numbers)

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Refereed (published, in press, accepted) BARD support acknowledged		5	2	7
Submitted, in review, in preparation			3	3
Invited review papers			1	1
Book chapters				
Books				
Master theses		1	1	2
Ph.D. theses		2	1	3
Abstracts				
Not refereed (proceedings, reports, etc.)				

Postdoctoral Training: List the names and social security/identity numbers of all postdocs who received more than 50% of their funding by the grant.

Cooperation Summary (numbers)

	From US to Israel	From Israel to US	Together, elsewhere	Total
Short Visits & Meetings		2	1	3
Longer Visits (Sabbaticals)		1		1

Description Cooperation:

Exchanges of ideas, and discussion of various problems and solution concerning experimental design and output of simulations were carried out between Wallach and Graber (Israel) and Steenhuis and Parlange (US) via emails, and during the visits of the Israeli researchers to Cornell, as well as at a meeting on water repellent soils that took place in Bratislava, Slovakia. An intensive and long-term cooperation on the core issue of the project, namely, the effect of contact angle on flow in porous media, was made between Wallach and DiCarlo (currently a professor at UT Austin), whereby Wallach spent a sabbatical year at UT with DiCarlo. This cooperation yielded a paper and a research proposal that was submitted to the USDA-ARS, and plans to submit a research proposal to BSF for the next call. Wallach and Graber have coordinated efforts closely on the laboratory experiments and model development in Israel with MSc. and Ph.D. students. Steenhuis and Parlange have coordinated efforts closely on measurement the effect of relation between colloids, contact angle, and flow and transport.

Patent Summary (numbers)

	Israeli inventor only	US inventor only	Joint IS/US inventors	Total
Submitted				
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Abstract

Water repellency causes unstable wetting fronts that result in water moving in preferential flowpaths through homogeneous soils as well in structured soils where macropores enhance the preferential flow pattern. Water repellency is typically associated with extended water ponding on the soil surface, but we have found that repellency is important even before the water ponds. Preferential flow fingers can form under conditions where the contact angle is less than 90° , but greater than 0° . This means that even when the soil is considered wettable (i.e., immediate penetration of water), water distribution in the soil profile can be significantly non-uniform. Our work concentrated on various aspects of this subject, with an emphasis on visualizing water and colloid flow in soil, characterizing mathematically the important processes that affect water distribution, and defining the chemical components that are important for determining contact angle. Five papers have been published to date from this research, and there are a number of papers in various stages of preparation.

Achievements

Research Problem

Water repellency has been reported for soils around the world under different climates and land uses (Wallis and Horne 1992; Doerr et al. 2000; Woche et al. 2005; De Jonge et al., 1999). Considerable research has shown that soils can become water-repellent through natural processes (Bond, 1972; Dekker and Ritsema, 1994; DeBano, 2000a; Dekker & Ritsema, 2003) as well as due to human activity such as application of wastewater effluent, as found in Israel (Wallach et al 2005; Graber et al. 2006). Water repellency causes unstable wetting fronts that result in water moving in preferential flowpaths through homogeneous soils as well in structured soils where macropores enhance the preferential flow pattern (Nektarios et al (2006). In some cases more than 80% of the percolating water is transported through preferential-flow paths, bypassing large fractions of the soil matrix and resulting in reduced capacity to filter and retain pollutants (Ritsema and Dekker, 1994, 1996).

Water repellency is typically associated with extended water ponding on the soil surface, but research has shown that repellency is important even before the water ponds (Tillman et al. 1989; Wallis et al. 1991; Hallett and Young 1999; Hallet et al., 2001; Bauters et al. 1998). Water can infiltrate without ponding, but unstable wetting fronts nevertheless form, resulting in water bypassing the bulk of the root zone. The soil characteristic curves for such porous media show that even when water does not pond, the matric potential at the water entry value is still negative, indicating a contact angle of less than 90 degrees. This was termed by Tillman et al. (1989) as “subcritical repellency.” Lamparter et al. (2006) confirmed the importance of subcritical hydrophobicity in a sandy soil and found that subcritical repellency reduced water infiltration rates by factors of 3 to 170 compared with non-repellent soil. Preferential flow was observed at this site earlier under natural rainfall conditions (Deurer et al., 2001).

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Soil water repellency in soils is recognized as widespread in some areas, but subcritical repellency is usually not recognized because it is a subsurface phenomena that is difficult to observe if water does not pond at the surface. Subcritical repellency becomes apparent only after experimental measures are applied, such as blue dye tracers, expensive multi-probe TDR equipment or observation in sand slab imaging apparatus. In this research project, we were interested in investigating the ramifications of subcritical repellency on water flow in soils.

The effects of water repellency are manifest at three scales: here termed *soil profile*, *representative elementary volume* and *pore scale*. At the *soil profile* scale (i.e. soil pedon scale, several meters in each dimension), water repellency causes unstable wetting fronts that form fingered flow patterns. Finger flow was initially observed in water infiltration into initially dry wettable soils at rates much less than the saturated conductivity (Hill and Parlange, 1972; Selker et al., 1992a,b; and Yao and Hendrickx, 1996). More recently the same flow pattern was shown to occur for subcritical and water-repellent soils. Theory for describing these flow patterns has been well developed (Raats, 1973; Parlange and Hill, 1976; Selker et al., 1992a,b; Liu et al., 1994; Geiger and Durnford, 2000; DiCarlo, 2004), but, as shown by DiCarlo (2005 and 2006), parameters are not consistent between experimental sets. The culprit here is that the discrete processes at the wetting front are not yet well understood, a critical deficiency as we seek to develop management techniques to prevent water repellency under organic wastewater application, for example.

Wetting front processes can be best examined at the *Representative Elementary Volume* (REV) scale and at the *pore scale*. The REV scale (also called Darcy scale) is sufficiently large to average what happens at discrete pores. We consider pressure and moisture content measurements taken in a 1 cm thick slab chambers to represent the REV scale. At this scale we find that there is a thin, nearly saturated layer near the surface that distributes water in fingers. Fingers are saturated at each tip and decrease in moisture content above it. The high moisture content behind the finger tip wetting front has been denoted 'saturation overshoot'. As predicted by Raats (1973), Selker et al. (1992a) showed experimentally that saturation overshoot is associated with pressure overshoot. The origin of the saturation overshoot occurs at the individual pore scale, where recent advances in microscopy have made it possible to directly observe the processes. It is now possible to observe water menisci in three dimensions with confocal microscopes and new digital light microscopes. These techniques can be used for observing flow processes in subcritically water-repellent soils.

Original Research Hypotheses

We posited three hypotheses for this research, from which our research objectives were drawn:

- 1) It is generally well known that water repellency effects occur when water ponds at the surface with contact angles of 90 degrees or larger. Repeated irrigation with organic-containing wastewater or application of organic amendments such as sludge can create repellent soils with critical ($\theta > 90$) or subcritical ($\theta < 90$) contact angles. We posit that subcritically repellent soils can exhibit unstable flow resulting in fingered (bypass) flow for a wide range of soils, flow rates and initial water contents.
- 2) Subcritical water repellency will express itself dynamically at the profile scale, the REV scale and, most importantly, at the pore scale. At the pore scale, newly developed visualization techniques in conjunction with confocal and digital

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microscopy will enable us to make measurements of water menisci radii and contact angles. These will be measured statically and dynamically for a range of repellencies. The contact angle expresses itself at the REV scale through varying degrees of moisture content overshoot at the wetting front and can be measured with conventional techniques. At the profile scale, the moisture content overshoot will determine the extent of fingered flow, and the subsequent water distribution pattern. We will measure and correlate the water repellency effects over these three scales.

3) Velocity of water flow, water repellency, grain roughness and wastewater type all affect the contact angle at the pore scale, which affects the moisture content overshoot at the REV scale and in turn water distribution in the soil profile. Observations at the three scales are needed so that the long-term effects of wastewater irrigation and consequent subcritical water repellency can be understood. This understanding will allow development of management methods to avoid future problems with soils becoming water repellent, leading to inefficient use of limited irrigation water resources.

Summary of Principal Research Findings:

1. Role of contact angle on flow of water in wettable porous media

Four model substrates based on uniformed size quartz sand (0.3-0.5 mm) were prepared to have permanent, less than 90° contact angles ($CA \approx 30^\circ$ for S100, $CA \approx 40^\circ$ for S450, $CA \approx 55^\circ$ for S1000, and $CA \approx 75^\circ$ for S1500). The plume shape and spatial water content distribution within the plume in S100 and S1500 media were considerably affected by the water application rate during the wetting and subsequent redistribution stages alike. The elongated plumes that were obtained for the lower water application rates become bulbous as water application rate increases. This trend in plume shape is more prominent for the S1500 than the S100 medium. The plume size depends on the water application rate; its area is smaller with higher average moisture content for higher water application rate. The plumes in the S100 medium have a regular shape, as usually obtained for a point source in regular soils. The irregular and even tortuous shaped (for lower water application rates) plumes in the S1500 medium demonstrate the effect of the medium's contact angle on water flow. Beyond their effect on the plume shape and size, the water application rate and medium's contact angle affect the water content distribution within the plumes. Considering first the wetting stage, the internal water content distribution is nearly uniform at high water application rates and turns non-uniform as water application rate decreases. This tendency found a distinctive disposition in the S1500 medium, where the water content gradient was negative with height and water accumulation behind the wetting front. Unlike infiltration into porous media of 0° contact angle, in which water applied to surface as a point source would have negative water content gradient, $\partial\theta/\partial z$, and matric potential gradient, $\partial h/\partial z$ (z directed downward) along any radial direction, this was not true for the wettable non-zero contact media studied here. The water content distribution within the plumes in the current study did not follow such distributions and gradients. A uniform water content distribution along horizontal cross sections and generally positive water content gradients along vertical cross sections were obtained in spite of the fact that all four media are wettable. The generally positive water content gradient along the vertical cross sections are made from nearly zero gradient at the upper part of the plume that turns positive at its lower

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part, i.e., saturation overshoot. The positive water content gradient extends as water application rate decreases and contact angle increases. As during the redistribution, part of the profile is drying while the other is wetting, capillary hysteresis may play a role, such that infiltration and redistribution require different approaches regarding the role of the characteristic curve on water flow.

Manuscript in preparation.

The results of this study support the major postulate (Hypothesis 1) underlying this BARD project: that even in initially repellent soils, flow fingers are in fact formed in the soil that is under sub-critical repellent conditions. The difference between repellent and a priori sub-critically repellent soils is that in repellent soils, $\theta > 90$ around the periphery of the finger (and at the finger tip), while in sub-critically repellent soils, θ is always < 90 .

2. Dynamics of water penetration into capillaries of varying cross-section and contact angle

Capillary flow in circular tubes has long been known to be quite well described by the Lucas-Washburn equation, in which Lucas and Washburn considered only the capillary force at the meniscus and the friction force inside a horizontal tube assuming the parabolic Poiseuille velocity distribution, while the gravity and inertial effects were neglected. Studies on the vertical infiltration of liquid into porous media have shown that gravity typically needs to be accounted for when modeling liquid infiltration. Hence, accurate models for gravity-driven infiltration into capillary tubes are needed. In this paper, capillary flow in non-uniform cross-sectional capillaries is investigated analytically. The analysis starts from the Navier–Stokes equations (NSE) and a governing equation is derived by the integration of the axial momentum equation over the liquid volume. The analysis has been developed by assuming a parabolic distribution for the velocity component in the primary flow direction and has considered the secondary flow components based on mass conservation. Compared to the classic Lucas–Washburn equation and the existing non-uniform capillary model equations, the proposed model incorporates the inertial terms and the viscous terms for non-uniform geometries. The derived nonlinear, second-order differential equation is complex and a MatLab code has been developed to solve the equation numerically by using the adaptive Runge–Kutta–Fehlberg method. The model is first validated by comparing with the solutions of the existing model equations for the circular cylindrical tubes, rectangular cylindrical microchannels, and convergent–divergent (C–D) and divergent–convergent (D–C) capillaries. The proposed model is then applied to capillaries with parabolic varying wall, simple sinusoidal wall, and divergent sinusoidal wall. The non-uniform geometry effects are investigated in detail. Fluxes lower than the soil saturated hydraulic conductivity are simulated by slug flow in the capillaries. The slug flow mechanism will be upscaled in the bundle of capillaries to generate saturation profile of unsaturated infiltration into subcritical repellent soils, and model output is compared with experimental data. The effects of different system parameters (capillaries geometry, contact angle, income flux intensity) on the formation of saturation overshoot will be analyzed by changing the values of these parameters.

Manuscripts (2) in preparation.

To now, the simulation results, especially those for capillaries with large variations of cross section, show that there are significant effects of non-uniform geometry in the

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cases studied. This model will be extended for cases with non-zero contact angle. Other results obtained by the model that has been developed so far depict the flow patterns for continuous and slug flow in uniform and sinusoidal-varying capillaries of different contact angles.

3. Role of divalent fatty acid salts in soil water repellency

In an earlier study, we had concluded that the surface-active, soil-derived organic substances in aqueous soil extracts do not contribute to wetting dynamics, and that the molecules adsorbed on the surface of the soil particles must play the major role in explaining contact angle. It was thus hypothesized that insights into the nature of the hydrophobic surface could be obtained by observing how solution chemistry affected repellency extent. Therefore, the effect of pH and counterions on the persistence of soil water repellency was examined. Repellency persistence was found to increase at elevated pH in the presence of Ca^{2+} but not Na^+ , to increase at high cation concentrations, and to decrease with increasing temperature. These results were explained by the behavior of monolayers of long-chain fatty acids on solid and liquid substrates. Other hydrophobic film-forming compounds, including long-chain alkanes, longchain amines, and hydrophobins, cannot account for the observations. A conceptual model for repellency in soils was developed: (i) fatty acid headgroups are complexed with cations at positively charged surfaces and via divalent cation bridges at negatively charged surfaces, with chains facing outward, rendering the surface hydrophobic; (ii) these complexed fatty acid molecules have a relatively slow rate of reorientation when contacted by water; and (iii) there are relatively few easily hydrated hydrophilic moieties at the surface. The factors that determine whether a hydrophobic film will form at soil surfaces, and the stability and longevity of that film, include the abundance and nature of fatty acids and other components at particle surfaces, the mineralogy of the substrate, and the chemistry of the soil solution. This model explains many observed inconsistencies of repellent soils, including spatial and temporal variability, development on soils of differing acidities, changes in repellency upon heating, and more. In accordance with the model, we suggested that the molarity of ethanol droplet test is an indirect measure of the fatty acid abundance and strength of attachment at surfaces, and not of the initial contact angle.

Published as: Graber, E.R., Tagger, S. Wallach, R. (2009). Role of divalent fatty acid salts in soil water repellency. Soil Science of America Journal, 73: 541-549

4. Rapid one-step method for total fatty acids in soils and sediments

In this study, a method was developed to extract and methylate total fatty acids (TFA) from soils and sediments using an acid-catalyzed esterification/transesterification approach; the TFA method was compared with other methods in common use for fatty acids in soils. The developed method is significantly more successful in extraction and methylation of total soil and sediment fatty acids as compared with other methods. It also extracts long-chain hydrocarbons from soils and sediments. The TFA method is relatively simple and rapid, has high reproducibility, substantially reduced solvent use, and can easily accommodate a large number of samples at the same time. The optimized TFA method is based on a combined 'one-step' acid-catalyzed approach often employed for biological tissues, oils, feedstuff, and leafy materials. Acid-catalyzed methylation is effective under many conditions, and

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methyates all fatty acids, including free fatty acids, fatty acid esters and amides, and fatty acid salts via both esterification and transesterification pathways. Used in conjunction with other methods, the TFA method can help to provide information about the distribution of ester-linked fatty acids and free fatty acids or fatty acid salts in soils and sediments.

Published as: Graber, E.R. and Tsechansky, L. (2009) Rapid one-step method for total fatty acids in soils and sediments. Soil Science of America Journal v. 74: 42-50

5. Effect of microbial activity at the pore scale on preferential flow

Recently, the interactions between soil structure and microbes have been associated with water transport, retention and preferential or column flow development. Of particular significance is the potential impact of microbial extracellular polymeric substances (EPS) on soil porosity (i.e., hydraulic conductivity reduction or bioclogging) and of exudates from biota, including bacteria, fungi, roots and earthworms on the degree of soil water repellency. These structural and surface property changes create points of wetting instability, which under certain infiltrating conditions can often result in the formation of persistent preferential flow paths. Moreover, distinct differences in physical and chemical properties between regions of water flow (preferential flow paths) and no-flow (soil matrix) provide a unique set of environmental living conditions for adaptable microorganisms to exist. In this review, special consideration is given to: (1) the functional significance of microbial activity in the host porous medium in terms of feedback mechanisms instigated by irregular water availability and (2) the related physical and chemical conditions that force the organization and formation of unique microbial habitats in unsaturated soils that prompt and potentially perpetuate the formation of preferential flow paths in the vadose zone.

Published as: Morales, V.L., Parlange J. -Y., Steenhuis, T.S. Are preferential flow paths perpetuated by microbial activity in the soil matrix? A review. J. Hydrology, Volume: 393: 29-36.

6. Impact of dissolved organic matter on colloid transport in the vadose zone

Although numerous studies have been conducted to discern colloid transport and stability processes, the mechanistic understanding of how dissolved organic matter (DOM) affects colloid fate in unsaturated soils (i.e., the vadose zone) remains unclear. This study aims to bridge the gap between the physicochemical responses of colloid complexes and porous media interfaces to solution chemistry, and the effect these changes have on colloid transport and fate. Measurements of adsorbed layer thickness, density, and charge of DOM-colloid complexes and transport experiments with tandem internal process visualization were conducted for key constituents of DOM, humic (HA) and fulvic acids (FA), at acidic, neutral and basic pH and two CaCl_2 concentrations. Polymeric characteristics reveal that, of the two tested DOM constituents, only HA electrosterically stabilizes colloids. This stabilization is highly dependent on solution pH which controls DOM polymer adsorption affinity, and on the presence of Ca^{+2} which promotes charge neutralization and inter-particle bridging. Transport experiments indicate that HA improved colloid transport significantly, while FA only marginally affected transport despite having a large effect on particle

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charge. A transport model with deposition and pore-exclusion parameters fit experimental breakthrough curves well. Trends in deposition coefficients are correlated to the changes in colloid surface potential for bare colloids, but must include adsorbed layer thickness and density for sterically stabilized colloids. Additionally, internal process observations with bright field microscopy reveal that, under optimal conditions for retention, experiments with FA or no DOM promoted colloid retention at solid-water interfaces, while experiments with HA enhanced colloid retention at air-water interfaces, presumably due to partitioning of HA at the air-water interface and/or increased hydrophobic characteristics of HA-colloid complexes.

Published as: Morales, V.L.; Zhang, W., Gao, B., Lion, L.W., Bisogni, J.J. Jr., McDonough, B.A., Steenhuis, T.S. 2011. Impact of dissolved organic matter on colloid transport in the vadose zone: Deterministic approximation of transport deposition coefficients from polymeric coating characteristics. Water Research, Volume 45, Issue 4, Pages 1691-1701.

7. Colloid transport and retention in unsaturated porous media: effect of colloid input concentration

Colloids play an important role in facilitating transport of adsorbed contaminants in soils. Recent studies showed that under saturated conditions colloid retention was a function of its concentration. It is unknown if this is the case under unsaturated conditions. In this study, the effect of colloid concentration on colloid retention was investigated in unsaturated columns by increasing concentrations of colloid influents with varying ionic strength. Colloid retention was observed in situ by bright field microscopy and quantified by measuring colloid breakthrough curves. In our unsaturated experiments, greater input concentrations resulted in increased colloid retention at ionic strength above 0.1 mM, but not in deionized water (i.e., 0 mM ionic strength). Bright field microscope images showed that colloid retention mainly occurred at the solid–water interface and wedge-shaped air–water–solid interfaces, whereas the retention at the grain–grain contacts was minor. Some colloids at the air–water–solid interfaces were rotating and oscillating and thus trapped. Computational hydrodynamic simulation confirmed that the wedge-shaped air–water–solid interface could form a “hydrodynamic trap” by retaining colloids in its low velocity vortices. Direct visualization also revealed that colloids once retained acted as new retention sites for other suspended colloids at ionic strength greater than 0.1 mM and thereby could explain the greater retention with increased input concentrations. Derjaguin–Landau–Verwey–Overbeek (DLVO) energy calculations support this concept. Finally, the results of unsaturated experiments were in agreement with limited saturated experiments under otherwise the same conditions.

Published as: Wei Zhang[†], Veronica L. Morales[‡], M. Ekrem Cakmak, Anthony E. Salvucci, Larry D. Geohring, Anthony G. Hay, Jean-Yves Parlange and Tammo S. Steenhuis. Environ. Sci. Technol., 2010, 44 (13), pp 4965–4972.