Effects of Surfactants Originating from Reuse of Greywater on Capillary Rise in the Soil

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Abstract
Greywater is all domestic wastewater excluding toilet effluents. Detergents contain surfactants, which account for the highest concentration of organic chemicals in average domestic wastewater. Accumulation of surfactants in greywater-irrigated soils was determined in 3 household gardens. The effect of surfactants on capillary rise in loess and sand was then tested in the range of concentrations found in the garden soils. The capillary rise of freshwater in sieved oven-dried soil mixed with different concentrations of laundry detergent solution (10% w/w moisture content) was determined. In a second setup, the soil was mixed with freshwater and the rising solution contained different concentrations of detergent solution. The introduction of laundry solution to the soils caused a significant decrease in the capillary rise over the range of concentrations that is found in greywater-irrigated soils. The effect was more noticeable in the sand than in the loess. Interestingly, in the second setup, the capillary rise of the laundry solutions in the sand was almost similar to that of freshwater, whereas in the loess the capillary rise was significantly reduced. It is suggested that accumulation of surfactants in the soil might form water repellent soils that have a significant effect on agricultural productivity and environmental sustainability.

Keywords
Capillary rise; Hydrophobic soils, Greywater; Surfactants;

INTRODUCTION

Greywater (GW) includes all the non-toilet wastewater produced by an average household including the water from bathtubs, showers, sinks, washing machines and dishwashers. The use of GW for private garden irrigation is becoming increasingly common due to the scarcity of freshwater, especially in arid and semi-arid areas. In most countries, regulations or specific guidelines for GW reuse are not available, and it is therefore often used without any significant pre-treatment, a practice mistakenly considered safe. In several states in the USA and Australia regulations for the use of GW have been established; however, these mainly consider issues associated with public health and do not take into account potential harmful environmental impacts or pollution (DHWA, 2002; ADEQ, 2003). The separation of the toilet stream from domestic wastewater generates effluents with reduced levels of nitrogen, solids, and organic matter (especially the hardly degradable fraction), but which often contain elevated levels of surfactants, oils, boron and salt. This may alter the soil properties, damage plants and contaminate groundwater (Garland *et al.*, 2000).

Detergents are the main source of surfactants in domestic wastewater, and have been recognized as being the most abundant type of organic chemical in municipal wastewater (Abu-Zreig *et al.*, 2003). Surfactants are organic molecules consisting of a hydrophilic head and a hydrophobic tail. The

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hydrophobic group contains long alkyl chain of C_{10}-C_{20}. The hydrophilic group has an electrical charge, or is polarized, and can form hydrogen bonds (Figure 1).

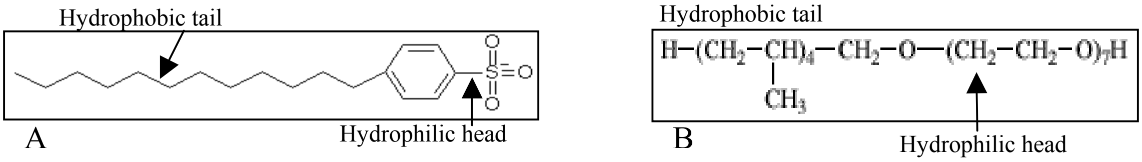

Figure 1. Demonstration of : A) Linear alkyl benzene sulphonates (anionic surfactant) and B) Linear primary AE (nonionic surfactant).

Surfactants in aqueous solutions tend to accumulate at the liquid/gas or solid/liquid interface, increasing the distance between the water molecules and therefore causing reduction of water surface tension (Kuhnt, 1993). The capillary rise (*h*) is directly related to the surface tension as described by the Young-Laplace equation (Eq. 1).

Eq. 1. $$h = \frac{2\sigma \cos \alpha}{\rho g r}$$

where σ is the surface tension of the imbibing solution in Nm^{-1}, α is the contact angle in degrees, ρ is the density of the liquid in Kgm^{-3}, g is the gravity force in ms^{-2} and r is the capillary radius in m. Consequently, if the surface tension decreases (assuming no change in contact angle), capillary force is reduced and the migration of the imbibing solution within soil pores is likely to change (Kuhnt, 1993). Capillary rise of liquids in soils is a phenomenon that can have both beneficial and detrimental effects on the soil (Smirnov *et al.*, 2003). It is an important mechanism by which plants can draw water from below the root zone, but it is also a mechanism contributing to the accumulation of salts in the soil. Very little information is available regarding the effects of surfactants commonly present in laundry and household detergents, on the hydro-physical properties of the liquid–solid system in soils in general and on the capillary rise in particular (Abu-Zreig *et al.*, 2003). There is still lack of information regarding the potential environmental pollution due to unregulated use of GW, but there is increasing evidence that it might cause environmental harm (Abu-Zreig *et al.*, 2003; Gross *et al.*, 2003). The current study was aimed at monitoring the accumulation of surfactants in soils irrigated with GW and determining their effect on capillary rise and some hydrological properties in loess and sandy soils, commonly used for gardening.

MATERIALS AND METHODS

Characterization of GW and GW-irrigated soils

Greywater was characterized bi-weekly for 12 months, in two households and a Laundromat for: anionic surfactants by the MBAS method, electrical conductivity (EC), pH, BOD_5 and COD. The tested parameters were analyzed using standard procedures (Standard Methods for the Examination of Water and Wastewater, 1998). The surfactant content in loess from 3 garden plots irrigated with GW for over a year was determined by taking 5 samples (5 cm deep) from each plot. For control, nearby plots that were not irrigated and that were irrigated with freshwater were also sampled. Surfactant analysis for soil samples was performed by its extraction with 1% sodium chloride and acetone followed by analysis of anionic surfactant by the MBAS method (Kornecki *et al.*, 1997).

Capillary rise

The impact of surfactants on the capillary rise of liquid in the soils was studied.

Soils. The effect of laundry effluents and surfactants on the capillary rise in quarry sand and native loess soils from the Negev desert, both commonly used in Israeli gardens, was studied. Fine sand (trade name “sand–100”) was obtained from “Negev Industrial Minerals Ltd.”, as raw material, and the loess was obtained from "Carmey Avdat" farm. These soils were characterized previously (Tamir, 2004) and their properties are given in Table 1.

Table 1. The properties of quarry glass sand ("Negev Industrial Minerals Ltd.") and native loess soils from the Negev Desert (after Tamir, 2004 and Negev Industrial Minerals Ltd. analytical laboratory).

Soils	pH	Organic matter (%)	Bulk density g cm^{-3}	Porosity (%)	Particle size analysis (%)		
					sand	silt	clay
Loess	7.9	0.7	1.2	50	64.3	15.6	20
Sand (–100)	8.3	0.2	1.4	40	98	1 - 2	<1

"Rising solutions". Water, laundry solution, and pure surfactant solutions were used. Arial laundry powder was purchased as a model for laundry products. The different concentrations of anionic surfactants used were prepared by mixing known amounts of laundry powder in tap water followed by measurement of anionic surfactants as described above. LABS-100, which is a common laundry anionic surfactant based on a straight alkyl chain (linear dodecyl benzene) and a blend of ethoxylated alcohols (AE) commercially named Imbentin-UMG/070 that are common laundry nonionic surfactants were used as pure surfactants. The surfactants were purchased from Zohar Dalia Ltd, Israel.

Setup. Sieved (1.4 mm mesh), oven-dried sand and loess soils that were never irrigated were mixed with one of the rising solutions of known surfactant concentration to give 10% soil moisture content (w/w). Concentrations of surfactants in the soil ranged from 0 to 100 mg Kg^{-1}. The soil was placed in a 25 cm column (2.5 cm diameter), and was covered with a fine mesh at one end. The column was attached to a balance whose base was located on the water surface of an open reservoir containing one of the rising solutions (Table 2). The weight change due to the capillary rise in the column was recorded every second and converted mathematically to the capillary height (h) (McGinnis, 2001).

Table 2. Combinations used to test the effect of capillary rise of different rising solutions in sand and loess soils that were pre-wetted with either freshwater or water containing surfactants.

Soils	Rising solutions		
	Freshwater	Laundry solution	Pure surfactants
Pre-wetted with freshwater (10% w/w)	+	+	+
Pre-wetted with solution containing surfactant (10% w/w)	+		

A similar capillary rise study was conducted with ethanol as the rising solution. Since the contact angle of ethanol is considered to be zero, solving Eq.1 for this case would yield the capillary radius (r). Assuming that the r is similar between experiments, the contact angle (index of wettability) could be obtained with the remaining capillary rise results. Each surfactant concentration was replicated 5 times. Using the capillary rise equation derived from Poiseuille's law (Eq. 2), the data was also used to determine the penetration coefficient (λ) in ms$^{-0.5}$, and the effective hydraulic conductivity (Ke) in ms^{-1}, in sand (Malik *et al.*, 1981; Abu-Zreig *et al.*, 2003).

Eq. 2. $$\frac{dh}{dt}=\frac{2\sigma r\cos\alpha}{G\mu}\frac{1}{h}-\frac{\rho g r^2}{G\mu}$$

where: dh/dt is the rate change of wetting front with respect to time in ms^{-1}, r is the equivalent pore radius in m, μ is the viscosity of the solution in Pas, G is the shape factor (8 for circular capillary of uniform diameter), σ is the surface tension in Nm^{-1}, α is the contact angle in degrees, ρ is the rising solution density in Kgm^{-3}, and g is gravity in ms^{-2}.

Analysis of the equation indicated that a plot of the capillary rise dh/dt versus the reciprocal of the capillary height 1/h is linear. The slope of this line represents the penetration coefficient λ (advance visible wetting front in dry soil per square root of time under unit hydraulic head) and the intercept represents the effective hydraulic conductivity (Ke). Differences between treatments were compared by one-way analysis of variance using SigmaStat 2.0 (SPSS, 1997).

RESULTS AND DISCUSSION

Characterization of GW and soils irrigated with GW

Greywater quality is summarized in Table 3. Detergents and soaps are the main sources of anionic surfactants and organic matter in GW (Abu-Zreig *et al.*, 2003). Concentration of anionic surfactants in GW varies significantly between sources and between dates within the same water source. Concentrations of anionic surfactants ranged between 0.7 to 44 mg L^{-1}, with an average of 17.5 mg L^{-1}. This is usually higher than the concentration in full domestic wastewater, which ranges between 1 to 10 mg L^{-1} (Henau *et al.*, 1986). The concentration of organic matter in the different sources as revealed from the BOD_5 and COD analyses also varied. The pH ranged from 7.1 to 8.1, due to the high alkalinity of the water that buffers wide pH changes, and also possibly due to alkaline chemicals in the detergents. Similarly, there was only slight additional salinity or EC in the GW, compared to local freshwater (EC = 1.2 dS m^{-1}).

Table 3. Average ± standard errors and the ranges of greywater quality parameters found in 3 domestic sources (n = 24).

Tested parameters	Household 1	Household 2	Laundromat
Anionic surfactants (mg L^{-1})	17 ± 5.4 6 -17	3 ± 0.5 0.7 – 7	26 ± 4.2 14 – 44
Electrical conductivity (dS m^{-1})	1.5 ± 0.1 1.2 – 1.7	1.3 ± 0.03 1.2 – 1.4	1.5 ± 0.0 1.3 – 1.7
pH	7.6 ± 0.1 7.1 – 7.9	7.5 ± 0.1 7.2 – 8.1	7.5 ± 0.1 7.2 – 7.9
BOD_5 (mg L^{-1})	195 ± 26 33 –324	62 ± 10 8 – 155	122 ± 24 65 - 241
COD (mg L^{-1})	474 ± 96 37 - 1240	200 ± 40 57 – 650	262 ± 34 161 - 478

Surfactants for domestic use are required to be biodegradable in most western countries (N. Garti, personal communication). Interestingly, we found a significant accumulation of anionic surfactants (up to 60 mg kg^{-1}) in soils that were irrigated with GW (Figure 2). The adsorption of surfactants on the soil particles was suggested as a possible mechanism that may prevent availability of these substances to biodegradation (Khunt, 1993). The low surfactant concentration in the native and freshwater irrigated soils is probably due to the presence of some native organic substances rather than an external source.

Capillary rise

The addition of laundry solution to the soils caused a significant decrease in the capillary rise over a range of concentrations found in GW irrigated soils (Table 4, Figures 3A, and 4A). When pure surfactants (LABS and AE) were premixed with sand at concentrations similar to those used in the laundry solution studies, the results obtained were similar to those described above, confirming that the observed changes in capillary rise were actually due to the surfactants present in the laundry solution (Figure 5). Pre-wetting the sand with LAS and AE mixture did not change the magnitude of the capillary rise, suggesting that there is no synergistic mechanism between the two substances. A possible explanation for decrease in capillary rise is embedded in the mechanism of surfactant adsorption onto soil particles. In the case of LABS, specific site surface interactions that include electrostatic bonds of negatively charged sulphonate groups with positively charged sites on the sand surface (i.e. metals), caused the adsorption of the LAS monomers with their hydrophobic tails (alkyl chains) to protrude into the aqueous phase (Ziqing *et al.*, 1995). The sorption of AE to soil components is dominated by hydrogen bonds between the ethylene oxide chain (the hydrophilic portion of the surfactant molecule) and polar soil constituents that cause the hydrophobic part of the nonionic surfactants to protrude toward the aqueous phase (Yuan and Jafvert, 1997). In both cases the outcome was increasing soil-water repellence. Analysis of the capillary rise data in the sand by the models (Eqs. 1 and 2) yielded similar trends to the experimental results. In the sand the contact angle obtained from the Young-Laplace model increased with increasing surfactant concentration (Table 4). The meaning of this increase is that cos α (Eq. 1) approaches zero and consequently the capillarity is reduced. Similarly, the penetration coefficient and the effective hydraulic conductivities that were based on the model described by Malik *et al.* (1981) also decreased (Table 4).

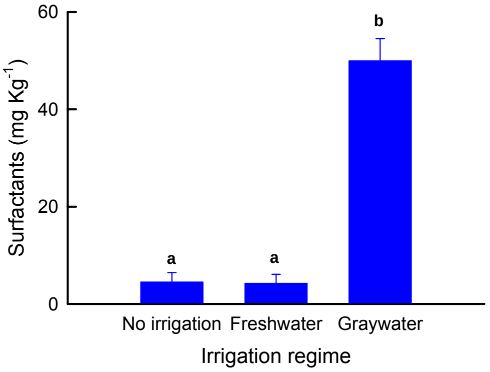

Figure 2. Concentration of anionic surfactants found in loess soils, where "Greywater" indicates the average concentration found in soils irrigated with greywater. "No irrigation" and "Freshwater" indicate the average concentration of native soils that were not irrigated or that were irrigated with freshwater, respectively (n = 5). Soils were irrigated for over 3 years. The letters a, b indicate statistical significance (p<0.05).

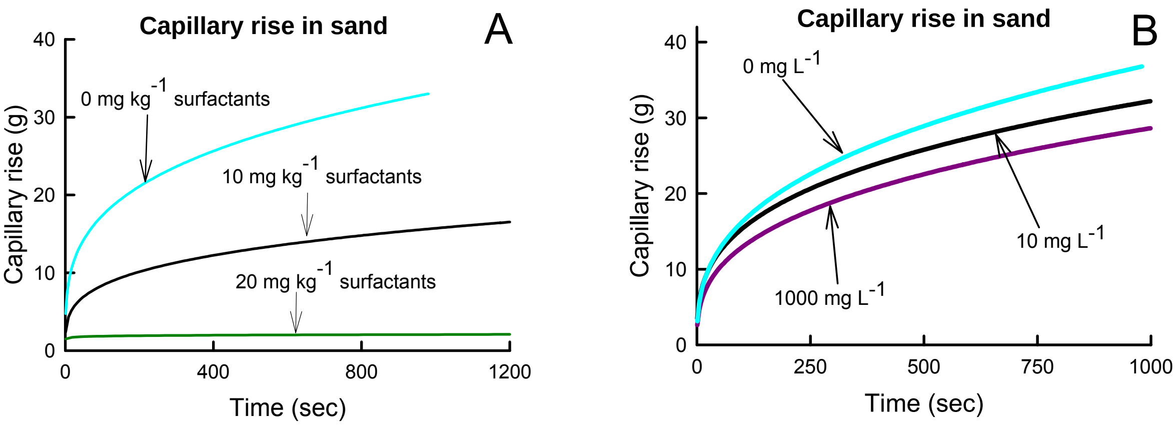

Figure 3. A. The effect of laundry detergent solution in the sand (final moisture content 10% w/w) on the capillary rise of freshwater. B. The effect of different concentrations of laundry solutions on capillary rise in sand that was pre-wetted with freshwater to give 10% (w/w) moisture content.

Table 4. Results of capillary rise (h) in loess and sand that was pre-wetted with laundry solution containing anionic surfactants after 1 h. Parameters α, λ, and Ke were obtained from the Young-Laplace equation and the equation given by Malik *et al.*, (1981). NA - not applicable.

Soils	Anionic surfactant mg kg^{-1}	Capillary rise (h) cm	*Contact angle (α) degrees	Penetration coefficient (λ) cm*s$^{-0.5}$	Effective hydraulic conductivity (Ke) cm*s^{-1}
Sand	0	13.96^{a}	48.9^{a}	0.0075^{a}	0.048^{a}
	10	9.10^{b}	64.6^{b}	0.00073^{b}	0.0078^{b}
	20	1.33^{c}	86.4^{c}	0	0
	100	0.88^{c}	87.6^{c}	0	0
Loess	0	8.08^{a}	85.6^{a}	NA	NA
	25	4.09^{b}	87.8^{b}	NA	NA
	50	4.97^{b}	87.3^{b}	NA	NA

*Assuming the capillary rise is fully controlled by the Young-Laplace model, an assumption that is probably not valid for the loess where clay particles may swell, clog pores and therefore significantly change the capillary rise. The letters a, b indicate statistical significance ($p<0.05$).

The effect of surfactant on capillary rise was more noticeable in the sand over a narrow range of concentrations; a surfactant concentration of 20 mg kg^{-1} or more virtually prevented any capillary rise in the soil, while in the loess soil, only a surfactant concentration of 1000 mg L^{-1} in the rising solution prevented any capillary rise. Interestingly, when the sand was wetted with freshwater and different concentrations of laundry detergent solution were used in the reservoir, the capillary rise was only slightly affected, whereas in the loess soil increasing concentrations of surfactant in the rising solution resulted in smaller capillary rise (Figures 3B and 4B). It is possible that the differences between the two soils is due to the smaller pore size and lower homogeneity of the loess matrix, which result in significantly longer contact time between the rising solution and the matrix, enhancing the surfactant adsorption and consequently reducing the capillarity. Analyzing the capillary rise results in loess by the Young-Laplace model reveals a contact angle of 85 degrees when the surfactant concentration is zero, suggesting that the loess soil used is hydrophobic. This may be misleading, however, as the capillary rise in the loess is likely to be affected by partial clogging and clay swell and not only by the contact angle of the rising solution and the capillary radius, as suggested by the model. Moreover, this may explain the smaller capillary rise in loess (Table 4) in spite of the higher porosity and smaller pore radii (as compared to sand). Therefore, it may not be appropriate to analyze the capillary rise results of the loess using only the suggested models.

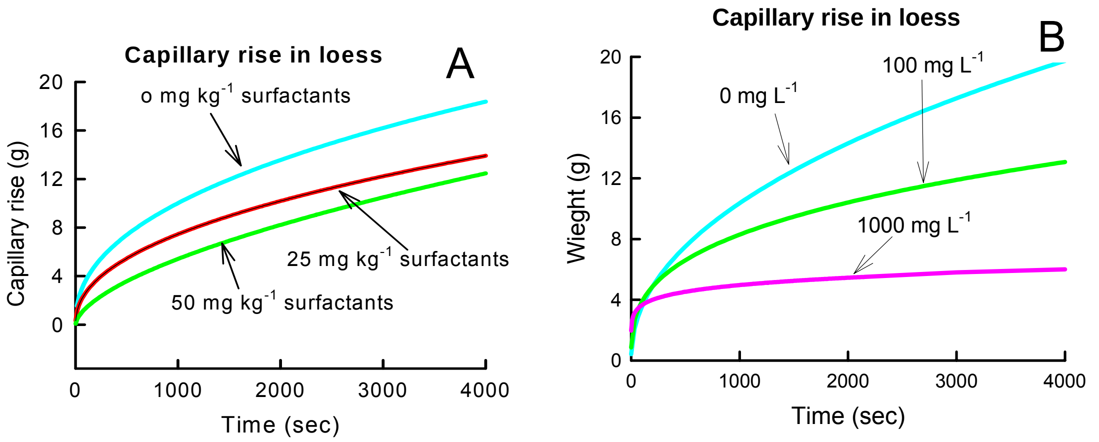

Figure 4. A. The effect of laundry detergent solution in the loess (final moisture content 10% w/w) on the capillary rise of freshwater. B. The effect of different concentrations of laundry solutions on capillary rise in loess that was pre-wetted with freshwater to give 10% (w/w) moisture content.

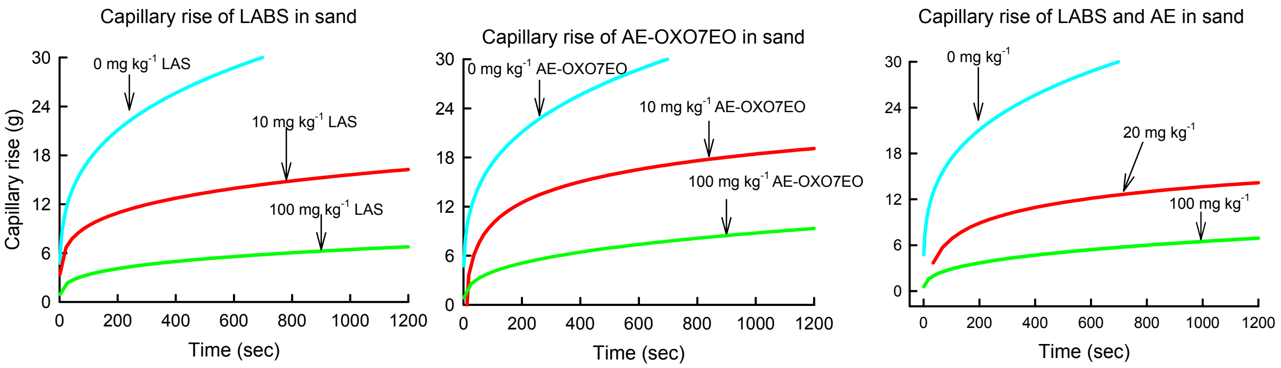

Figure 5. The effect of anionic surfactant (LABS), nonionic surfactant (AE-OXO7EO), and a mixture of the two pre-wetted in sand (final moisture content 10% w/w) on the capillary rise of freshwater.

CONCLUSIONS

Long-term irrigation with GW rich in surfactants might cause their accumulation in the soil and may result in the formation of water repellent soils, as well as enhanced environmental pollution. Although the subject of water repellent soils has been studied by researchers in different parts of the world (e.g. DeBano, 2000), the literature is lacking in quantitative explanations of its causes and characteristics, as well as its actual extent, and effective management practices to reduce it. Consequently, current soil and water management practices in water repellent regions are insufficient. The magnitude of surfactant accumulation in soils and its contribution to the development of water repellent soils should be further explored and modelled in order to determine safe levels for the sustainable use of GW and other surfactant rich effluents.

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