Surfactant effects on unsaturated flow in porous media with hysteresis: horizontal column experiments and numerical modeling

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Abstract

Many organic compounds depress the surface tension of water relative to their aqueous concentration. These surface-active organic solutes have been shown to cause water flow in unsaturated porous media. Flow in these systems typically occurs from contaminated (high concentration) regions toward cleaner (lower concentration) regions. That flow is characterized by significant drainage and rewetting associated with the advance of the solute front. In the literature, modeling of unsaturated flow and transport in systems with solute concentration-dependent surface tensions has been limited to simulations without hysteresis in the hydraulic functions. However, experimental evidence is also presented which shows that hysteresis is a factor. We modified the hysteretic unsaturated flow and transport numerical model HYDRUS 5.0 to include concentration-dependent effects of a mobile organic solute. The moisture content-pressure head and unsaturated hydraulic conductivity functions were scaled for concentration-dependent surface tension and viscosity, respectively. The modified model successfully simulated data from surfactant-induced flow in 1-D horizontal column experiments. The effects of hysteresis were shown to be important to accurately simulate flow in these systems. For example, at final steady state, hysteretic simulations predicted uniform concentration and pressure profiles, but moisture contents that varied with distance. The final simulated moisture contents ranged from 0.12 to 0.25 along the column. In contrast, a non-hysteretic simulation would predict uniform distributions of concentration, pressure and moisture content. Dispersivity also had an effect on flow simulations. Lower dispersivity values caused sharper surfactant concentration gradients, which resulted in larger capillary pressure gradients and higher fluxes near the solute front. The modeling approach used here is expected to be applicable to many organic compounds of environmental interest that depress surface tension and thereby are capable of inducing unsaturated flow in porous media. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is common in conceptual and numerical models of flow and transport through porous media to assume that flow is independent of solute concentration. While this is generally valid, there is mounting evidence and appreciation that the assumption fails when the systems of interest involve unsaturated flow of water contaminated with organic solutes that reduce the surface tension, σ, of water (surfactants). Commercial surfactants and alcohols used for remediation of areas contaminated with non-aqueous phase

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liquids, as well as organic compounds of environmental interest, including both aliphatics and aromatics, can reduce surface tension (Blank and Ottewill, 1964; West and Harwell, 1992; Karkare et al., 1993).

The primary impact of surface-active organic solutes on unsaturated flow is through the dependence of soil water pressure, ψ, on surface tension (Bear, 1972):

$$\psi = -\frac{2\sigma \cos(\gamma)}{\rho g r} \tag{1}$$

where σ is surface tension, ρ the solution density, g the gravitational acceleration, γ the contact angle, and r is the radius of an equivalent circular tube. For a given moisture content and contact angle, Eq. (1) indicates that a decrease in surface tension will result in a proportional decrease in capillary pressure (the negative soil water pressure). Consequently, the hydraulic functions that depend on soil water pressure, as well as the hydraulic gradient, will be affected in the presence of a surface-active solute front.

The effect of surfactant-induced changes in surface tension on the moisture content-pressure head relationship has been demonstrated by numerous researchers (Salehzadeh and Demond, 1994; Lord et al., 1997; Dury et al., 1998; Smith and Gillham, 1999; Lord et al., 2000). In addition, the direct effects of surfactants on unsaturated flow have been observed in experimental systems. It follows from Eq. (1) that differences in surface tension within an unsaturated porous medium can cause gradients in capillary pressure. These capillary pressure gradients can be sufficient to induce water flow. For example, surfactant-induced capillary pressure gradients due to the presence of a sparingly soluble and relatively immobile surfactant, myristyl alcohol (MA), in one half of a homogeneous, uniformly wetted, closed, unsaturated sand column resulted in horizontal flow from the surfactant containing side of the column to the side that contained no surfactant (Tschapek and Boggio, 1981; Karkare and Fort, 1993; Henry et al., 1999). Karkare et al. (1993) also showed that a variety of long-chain alcohols, acids, amines and esters were capable of inducing flow in the unsaturated horizontal column systems.

Smith (1995), Smith and Gillham (1994, 1999)

studied moisture content and pressure changes associated with the advance of a 7% (w/w) butanol solution ($\sigma = 26$ dynes/cm) in unsaturated, vertical, 1-D miscible displacement experiments. They observed a flow perturbation associated with the advancing solute front that was caused by high local capillary pressure gradients due to concentration-dependent surface tension variations. As the solute front neared the water table boundary at the bottom of the column a reduction in the height of the capillary fringe was observed. The reduction in capillary fringe height was proportional to the relative surface tension of the butanol solution vs. that of pure water. That result was consistent with Eq. (1) in that the surfactant-induced reduction in surface tension resulted in a proportional decrease in the air-entry pressure.

Despite the evidence of flow perturbations caused by surface-active organic solutes, modeling of this behavior is limited. Karkare and Fort (1993) used a graphical technique to predict the equilibrium moisture content and pressure in closed, horizontal column experiments using the sparingly soluble surfactant MA. The homogeneous horizontal sand column essentially behaved as a system composed of two media, each wetted with a different surface tension fluid (pure water or water contaminated with MA) and exhibiting different hydraulic functions. Henry et al. (1999) reproduced the experimental results of Karkare and Fort (1993) and successfully modeled the spatial and temporal flow behavior of the MA system using the unsaturated flow and transport code HYDRUS 5.0 (Vogel et al., 1996). They assigned separate non-hysteretic hydraulic functions to the clean and surfactant contaminated zones within the column. The same approach was unsuccessful for modeling similar experiments using the highly soluble surfactant butanol. Because standard unsaturated flow and transport models do not account for concentration-dependent effects of surfactants on hydraulic properties, they are incapable of accurately modeling systems contaminated with mobile surfactants. Smith (1995) and Smith and Gillham (1994, 1999) presented an unsaturated/saturated flow and transport numerical model capable of simulating the effect of concentration-dependent surface tension and viscosity changes on 1-D flow and transport. Their model did not include hysteresis in the hydraulic functions. The differences between experimental and simulated

results were quantitatively attributable to hysteretic behavior that was not accounted for in the model. There are apparently no unsaturated flow models in the peer-reviewed literature that include both hysteresis in hydraulic functions and concentration-dependent surface tension coupling of unsaturated flow and solute transport.

The primary objectives of the research presented here were to produce, test, and evaluate an unsaturated flow and transport model that includes both hysteresis in the hydraulic functions and concentration-dependent surface tension effects on unsaturated flow. We apply that model to simulate unsaturated flow and transport in a 1-D horizontal sand column induced by a mobile surfactant, butanol, by simulating the experimental data of Henry et al. (1999). To accomplish our objectives, we chose to modify the freely available, hysteretic, variably saturated flow and transport numerical model HYDRUS 5.0 (Vogel et al., 1996) to include concentration-dependent surface tension and viscosity effects. An investigation of the sensitivity of the model results to solute dispersivity is presented. In addition, the impact of concentration-dependent surface tension and viscosity changes, as well as the importance of hysteresis in such models, is evaluated.

2. Methods and materials

2.1. Column experiment

The data contained herein is from experiments of flow caused by surfactant-induced capillary pressure gradients in closed, horizontal columns (Henry et al., 1999). The columns were 10.16 cm in diameter and 13.7 cm in length and were made of schedule 80 acrylonitrile-butadiene-styrene (ABS) pipe. The left half of each column was packed with a nominal 120 mesh silica sand prewetted to volumetric moisture content of $\sim 18\%$ with deionized water. The right half of each column was packed with the same silica sand prewetted to the same volumetric moisture content with 7% (w/w) butanol solution. A schematic of the column is shown in Fig. 1. The column was prewetted to a uniform moisture content to eliminate capillary pressure gradients due to moisture content differences. Closed, horizontal columns were used to

generate data from systems in which all the flow was a direct consequence of surfactant-induced surface tension changes. Water movement within the columns was evaluated by destructively sampling replicate columns at 2.5 and 24 h and drying the samples at 100°C for 24 h to determine gravimetric moisture content as a function of longitudinal distance. Full details of the experiments are found in Henry et al. (1999).

2.2. Hydraulic characteristics: pure water retention and hydraulic conductivity

The moisture content-pressure head relationships for the water-wetted sand used in the column experiment were measured in a 2-D flow cell using TDR for moisture content determination and pressure transducer equipped tensiometers for pressure head determination. The measured retention data are shown in Fig. 2. A spreadsheet optimization program (Wraith and Or, 1998) was used to fit the main drainage (MDC) and main wetting curves (MWC) using the van Genuchten moisture content-pressure head relationship (van Genuchten, 1980),

$$\theta = \frac{\theta_s - \theta_r}{(1 + |\alpha\psi|^n)^m} + \theta_r \qquad (2)$$

where θ is the volumetric water content, θ_s the saturated volumetric water content, θ_r the residual volumetric water content, ψ the pressure head, and α, n, and m are the soil-specific curve fitting parameters. The convention that $m = 1 - 1/n$ was used.
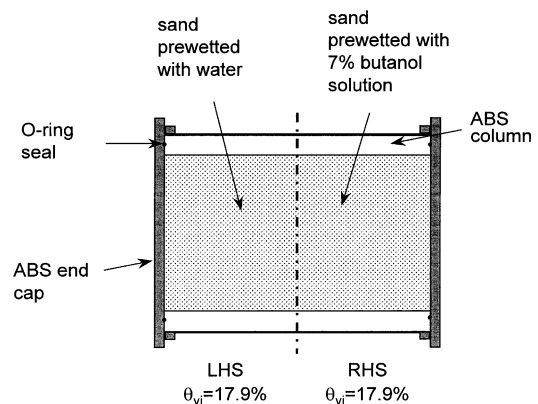

Fig. 1. Apparatus for horizontal flow experiments. θ_{vi} is the initial volumetric moisture content.
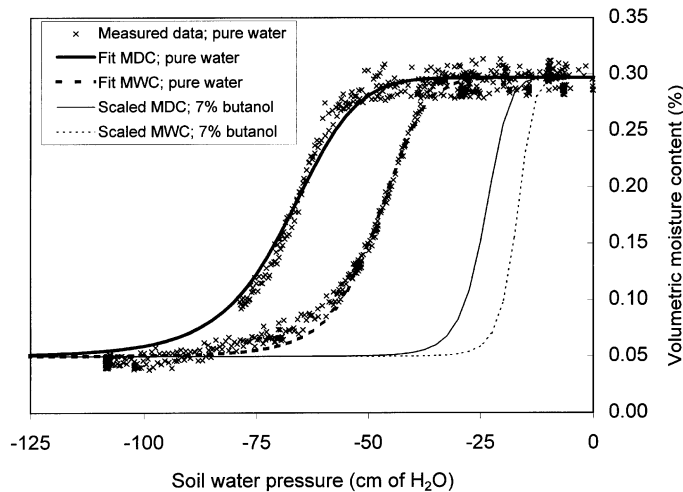
Fig. 2. Retention curves for water and butanol-wetted sand. Pure water MWC and MDC represent van Genuchten fit to measured water retention data. Butanol curves calculated by scaling of water curves.

The porosity of the sand was 0.362. The rewetted moisture contents in Fig. 2 are less than the porosity. That is because the drainage data are for the MDC, rather than the initial drainage curve (i.e. the curve which represents drainage from perfect saturation). From the data in Fig. 2, the saturated and residual moisture contents were determined to be 0.297 and 0.05, respectively. The same values were used for both the MWC and MDC. The hysteresis routine in HYDRUS 5.0 (hereafter referred to simply as HYDRUS, though other versions of the HYDRUS code exist) requires that $n_w = n_d$, where the subscript w refers to the MWC and subscript d refers to the MDC. We fit both the MWC and MDC with a common n value but different α values. The fit parameters for the MWC and MDC were $\alpha_d = 0.01504 \text{ cm}^{-1}$, $\alpha_w = 0.02136 \text{ cm}^{-1}$, and $n_d = n_w = 9.0$. The fit MWC and MDC for the silica sand wetted with pure water are shown in Fig. 2. One of the limitations of the HYDRUS model is that the hysteresis routine does not incorporate scanning curves. Rather, the technique of Scott et al. (1983) is used to calculate a new moisture characteristic curve that passes through the reversal point and either the saturated moisture content (for a reversal from drying to wetting) or the residual moisture content (for a reversal from wetting to drying).

Unsaturated hydraulic conductivity was predicted using Mualem's function (Mualem, 1986) based on the van Genuchten retention function

$$K(\Theta) = K_s \Theta^l (1 - (1 - \Theta^{1/m})^m)^2 \qquad (3)$$

where $K(\Theta)$ is the unsaturated hydraulic conductivity, K_s the saturated hydraulic conductivity, l and m the curve fitting parameters, and Θ is the effective saturation

$$\Theta = \frac{\theta - \theta_r}{\theta_s - \theta_r} \qquad (4)$$

The measured saturated hydraulic conductivity of the sand was 14.58 cm/h. Unsaturated hydraulic conductivity was not measured, instead we chose to adjust l in the conductivity function to obtain a reasonable match between our measured and simulated moisture contents within the column at 2.5 and 24 h. The fitting parameter, l, in the unsaturated hydraulic conductivity function is commonly assumed to be equal to 0.5. This value led to an over-prediction of water flow in our simulations. Through a trial-and-error process involving the comparison of 2.5 and 24 h simulation results to experiment results (after Henry et al., 1999), we selected an l value of 3.75 and used it in all simulations.

The experimental data of Henry et al. (1999) was from vertical slices of soil core that had experienced 1-D horizontal flow. The uniform initial moisture content within their 10.16 cm diameter columns was 17.9%. Under static conditions, the vertical distance

of ±5 cm from the midpoint in the horizontal column would be expected to generate ±5 cm of pressure head. It can be seen from Fig. 2 that at a volumetric water content of 17.9%, ±5 cm of pressure head could generate a vertical water content difference of a few percent. The butanol system has the potential to have a slightly larger change due to its steeper moisture retention curve. Such a system would be expected to behave one-dimensionally, with the lower section of the core slightly wetter than the upper section. To directly address a concern raised by a reviewer that substantial 3-D flow effects may have existed in the experimental columns of Henry et al. (1999), we analyzed data from a preliminary experiment of surfactant-induced flow in the same closed columns but instrumented with closely spaced horizontal and vertical time domain reflectometry (TDR) probes for the determination of moisture content. A horizontal set of probes was placed between two sets of vertical TDR probes 1.3 cm apart. The differences between the moisture contents measured with the horizontal TDR probes and the average of those measured with the two sets of adjacent vertical TDR probes during the surfactant induced flow events were continuously less than 1% over the 24 h duration. The 24 h results are directly comparable to the Henry et al. (1999) data used in this paper. The moisture content measurements at adjacent vertical and horizontal TDR probes indicate that an insignificant amount of vertical flow occurred (i.e. the system behaved as a 1-D horizontal system). Consequently, the 1-D model used here for the simulations is applicable to the data from Henry et al. (1999).

2.3. Concentration dependence of surface tension and viscosity

In order to understand the effect of butanol-induced surface tension and viscosity variations on the moisture content-pressure head relationship and hydraulic conductivity, respectively, the influence of butanol concentration on surface tension and viscosity must be known. The dependence of surface tension on butanol concentration has been described by Bikerman (1970) and Smith and Gillham (1994, 1999). Smith and Gillham (1994, 1999) fit surface tension data as a function of butanol concentration with the expression of Adamson (1990) for the concentration dependence of non-ionized organics

$$\frac{\sigma}{\sigma_0} = 1 - b \ln\left(\frac{c}{a} + 1\right) \tag{5}$$

where a and b are constants for the compound of interest, σ the surface tension at concentration c, and σ_0 is the surface tension at the reference concentration, c_0 ($\sigma_0 = 72$ dynes/cm at $c_0 = 0.0\%$). For butanol at 25°C, the constants a and b are 0.365% wt butanol and 0.215, respectively (Smith, 1999).

Smith (1995) used a similar expression to fit viscosity data as a function of butanol concentration

$$\frac{v}{v_0} = \left(1 - e \ln\left(\frac{c}{d} + 1\right)\right)^{-1} \tag{6}$$

where d and e are the compound specific constants, v the kinematic viscosity at concentration c, and v_0 is the viscosity at the reference concentration, c_0 ($v_0 = .9017$ cSat $c_0 = 0.0\%$). For butanol at 25°C, the constants d and e are 34.49% wt butanol and 1.366, respectively (Smith, 1999). The concentration-dependent behavior of both surface tension and viscosity is shown in Fig. 3.

2.4. Hydraulic characteristics: butanol system retention and conductivity functions

The retention curves for a water-wetted porous medium can be used to represent the retention curves for a system with a surfactant-modified surface tension but constant contact angle by scaling the pressure term by the ratio of the concentration-dependent surface tension of the pore water of interest over the surface tension of pure water (after Leverett, 1941). Scaling of the pressure head term by the relative surface tension can be expressed as

$$\Psi(\theta, c) = \frac{\sigma}{\sigma_0} \psi(\theta, c_0) \tag{7}$$

where ψ is the measured pressure head at water content θ and reference concentration c_0 ($c_0 = 0$ when pure water is the reference solution), and Ψ is the calculated scaled pressure head at the same water content and at concentration c. This approach has been applied to the scaling of retention curves for silica sand wetted with butanol solution (Smith, 1995; Dury et al., 1998; Smith and Gillham, 1994, 1999). They also noted that dissolved butanol had
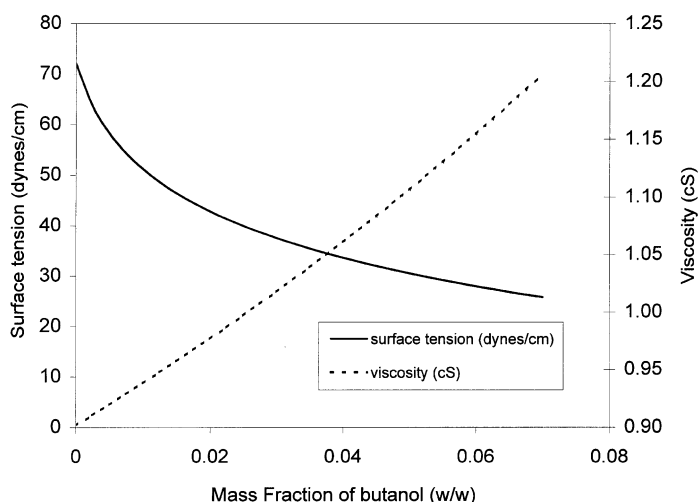
Fig. 3. Dependence of surface tension and viscosity on butanol concentration. Curves calculated after Smith (1999), Smith and Gillham (1994, 1999).

no significant effect on the maximum wetting fluid saturation or residual wetting fluid saturation. For 7% butanol solution, the scaling factor calculated using Eq. (5) is 0.354. The scaled retention curves for the 7% butanol-wetted sand are shown in Fig. 2 along with the measured and fitted water-wetted retention curves. As shown in Fig. 2, at all moisture contents less than θ_s the pressures that are characteristic of the 7% butanol system are greater (less negative) than those for the pure water system. Thus, in these types of systems flow will tend to occur from contaminated regions toward clean or less contaminated regions.

Based on the dependence of hydraulic conductivity on viscosity, a similar scaling approach can be applied to determine the concentration-dependent hydraulic conductivity, $K(\theta,c)$, based on the relative viscosities of butanol solution and pure water (Smith, 1995; Dury et al., 1998; Smith and Gillham, 1999)

$$K(\theta, c) = \frac{v_0}{v} K(\theta, c_0) \qquad (8)$$

Here, the concentration-dependent unsaturated hydraulic conductivity, $K(\theta,c)$, is determined by scaling the pure water-wetted conductivity at the same moisture content, $K(\theta,c_0)$, by the ratio of the viscosity of pure water over that of butanol solution. The calculated hydraulic conductivity scaling factor

for 7% butanol solution is 0.748 (i.e. the calculated K_s for the 7% butanol system is 10.91, compared to 14.58 cm/h for the water system).

2.5. Implementation of concentration dependent effects in HYDRUS

Smith and Gillham (1994, 1999), Smith (1995) modeled the effects of butanol on flow and transport in 1-D miscible displacement experiments. Their model included the effects of concentration dependent surface tension and viscosity changes, but did not include hysteresis in the hydraulic functions. Smith and Gillham (1999) showed quantitatively that disagreement between their experimental and modeled results was attributable to hysteresis and was a direct consequence of the substantial drainage and rewetting events in such systems. Thus, a numerical model that incorporates hysteresis is necessary for accurately simulating the flow and transport of surface-active solutes in unsaturated porous media. In order to improve the state of modeling of these systems and improve our understanding of the underlying phenomena, we modified the flow and transport code HYDRUS 5.0 to incorporate concentration-dependent surface tension and viscosity effects, using the relationships described by Eqs. (5)–(8). In addition to modeling flow and transport in variably

saturated porous media, HYDRUS is capable of simulating hysteretic behavior in the hydraulic functions. HYDRUS is a widely used, proven code that is public domain and user-friendly.

No analytical solution for concentration-dependent flow perturbations exists. For model verification, the modified HYDRUS model was used to reproduce the non-hysteretic simulations of Smith (1995). The two models showed extremely good agreement. This occurred despite the fact that our model uses an upwind weighting of the concentration-dependent hydraulic functions calculated using the concentration profile during the previous time step, whereas, Smith (1995) modeled the butanol system by solving flow and transport within the iterative loop during each time step.

2.6. Model parameters

For the first time step the half of the column wetted with 7% butanol solution was assigned the retention properties and hydraulic conductivity calculated for the 7% butanol-wetted sand. After the first time step the hydraulic properties throughout the column were scaled as a function of solute concentration using Eqs. (5)–(8). The initial conditions were specified to be uniform volumetric moisture content of 17.94% throughout the column, with a butanol concentration of zero in the left hand side (LHS) of the column and a butanol concentration of 7% in the right hand side (RHS) of the column. Zero-flux water and solute boundary conditions were assigned at the ends of the closed column.

Because hysteresis was considered, it was necessary to specify whether the initial condition corresponded to the MWC or MDC. The experimental method of packing the column may have generated an initial condition such that the column was on a moisture retention-scanning curve. However, HYDRUS does not allow initial conditions to be specified on a scanning curve. Because the premixing procedure involved adding liquid to dry sand and then packing the wet sand into the column, we decided that the average state of the wetted sand was better represented as initially on the MWC. Consequently, the initial condition for the entire model domain was set on the MWC for either pure water or 7% butanol-wetted sand.

The initial time step size was 10^{-8} h. HYDRUS provides an option for updating the time step size based on the number of iterations required for convergence. The adaptive time step size multiplier was set at 1.2 and the maximum allowable time step size was 50 h.

The model was found to be sensitive to nodal spacing. For the results presented here, a spacing of 0.1 cm was used for the first interval on the left end of the column and a uniform spacing of 0.2 cm was used for the remainder of the domain, resulting in a total domain length of 13.7 cm. Model results were also found to be sensitive to convergence criteria. For the results given here, moisture content and pressure convergence criteria were specified as 0.000005 (dimensionless) and 0.0000005 cm, respectively.

A time-centered scheme with upwind weighting was used for transport calculations. The aqueous molecular diffusion coefficient for butanol was specified as 0.036 cm^2/h (Yaws, 1995). A dispersivity of 2 cm was used for our modeling of the experimental data. This value was chosen through a trial-and-error fitting of simulated moisture contents to experimental data. In contrast to most flow and transport models, the hydraulic properties in a system contaminated with a surface-active solute like butanol are a function of solute concentration. Thus, dispersivity has an effect on flow and transport calculations (Smith and Gillham, 1999). The sensitivity of simulation results to dispersivity is presented in Section 3.

3. Results and discussion

3.1. Experimental results

Fig. 4 shows the 2.5 and 24 h moisture content profiles from the butanol column experiments of Henry et al. (1999) presented as the change in volumetric moisture content vs. longitudinal distance. A bulk density of 1.64 g/cm^3 was used to convert measured gravimetric moisture contents to volumetric moisture contents (Henry et al., 1999). Tests A and B indicate replicate column experiments run for each time. A detailed description of the system behavior was given by Henry et al. (1999) but will be briefly summarized here.
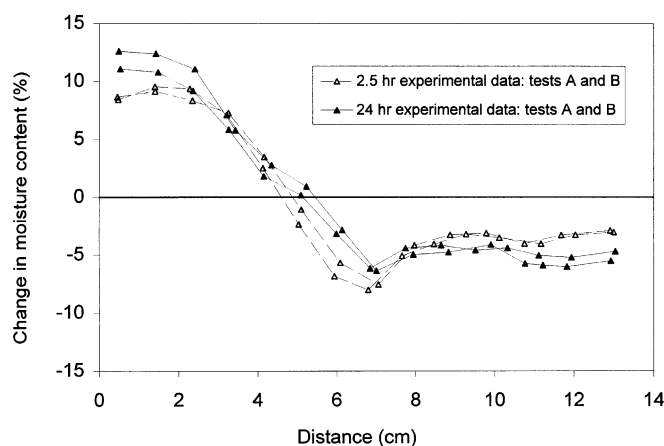
Initially, the surfactant-induced surface tension

Fig. 4. Change in moisture content in experimental column at 2.5 and 24 h. Tests A and B are replicate experiments at each time.

gradient between the two halves of the column causes a large capillary pressure gradient at the interface between the surfactant-free left half (LHS) and surfactant-containing right half (RHS). This pressure gradient causes a flux of butanol solution from the contaminated region toward the clean region (i.e. to the left). The flux results in drainage of the contaminated region (RHS) near the center of the column and wetting of the previously clean region (LHS). As butanol solution moves into the LHS of the column due to the surfactant-induced drainage of the RHS of the column, pure water is displaced. However, a large concentration gradient remains in the vicinity of the solute front and further surfactant-induced drainage occurs behind the solute front, with concurrent wetting ahead of the solute front; the solute front continues to move to the left due to the high local surface tension-induced fluxes in the vicinity of the solute front. This process results in wetting from 0 to 5 cm and drainage from 5 to 13.7 cm by 2.5 h, as shown in Fig. 4.

From 0 to 3 cm, the moisture content at 2.5 h is approximately uniform. This region has been wetted primarily by pure water displaced by the advancing drainage front. Within this region surfactant-induced capillary pressure gradients are small and flow is dominated by pressure gradients due to non-uniform moisture content distributions. The relatively high moisture content in this region results in relatively high hydraulic conductivities and thus pressure gradient changes are rapidly manifested as changes in moisture content within this region.

The gradual change in moisture content observed between 3 and 7 cm is due to the dispersed nature of the solute front and the coincident wetting/drying processes that accompany movement of the solute front to the left. Within this zone, capillary pressures are a function of both moisture content and butanol concentration. However, surfactant-induced capillary pressure gradients dominate those due to non-uniform moisture content distributions and flow occurs from right to left.

The moisture content profile in the RHS of the column (7–13.7 cm) at 2.5 h is primarily influenced by the reduction in the hydraulic conductivity at the center of the column caused by the initial drainage. Because the concentration within the RHS is essentially uniform (~7% butanol solution), concentration-dependent capillary pressure gradients in that region are small and cannot compensate for the reduction in hydraulic conductivity. Thus, additional drainage from the RHS, driven primarily by capillary pressure gradients caused by the non-uniform moisture content distribution, is slow.

At 24 h, flow within the column is still from right to left but the magnitude of the fluxes decreases as concentration gradients within the column decrease and capillary pressure gradients caused by non-uniform moisture content distributions in the LHS balance those due to surfactant-induced surface tension variations. As shown in Fig. 4, the fluid that continues to drain out of the RHS from 2.5 to 24 h partially rewets the drained region in the center of the

column and produces additional wetting between 1 and 3 cm (Henry et al., 1999).

3.2. Modeling of butanol experiments

Though the use of a standard unsaturated flow and transport modeling technique was successfully applied by Henry et al. (1999) for simulating flow induced within a closed horizontal column by an immobile surfactant, the same technique could not adequately simulate flow in a column contaminated with a mobile surfactant such as butanol. That was because the model did not account for concentra-

tion-dependent changes in the hydraulic functions. The modified HYDRUS model that we present here incorporates concentration-dependent effects on both the moisture content-pressure head relationship and hydraulic conductivity, as discussed above. Simulation results produced using the modified HYDRUS model are plotted in Fig. 5a and b for 2.5 and 24 h, respectively, along with the corresponding experimental data of Henry et al. (1999). The 2.5 and 24 h data are plotted on separate graphs for clarity. The modified HYDRUS model simulates the experimental results well.

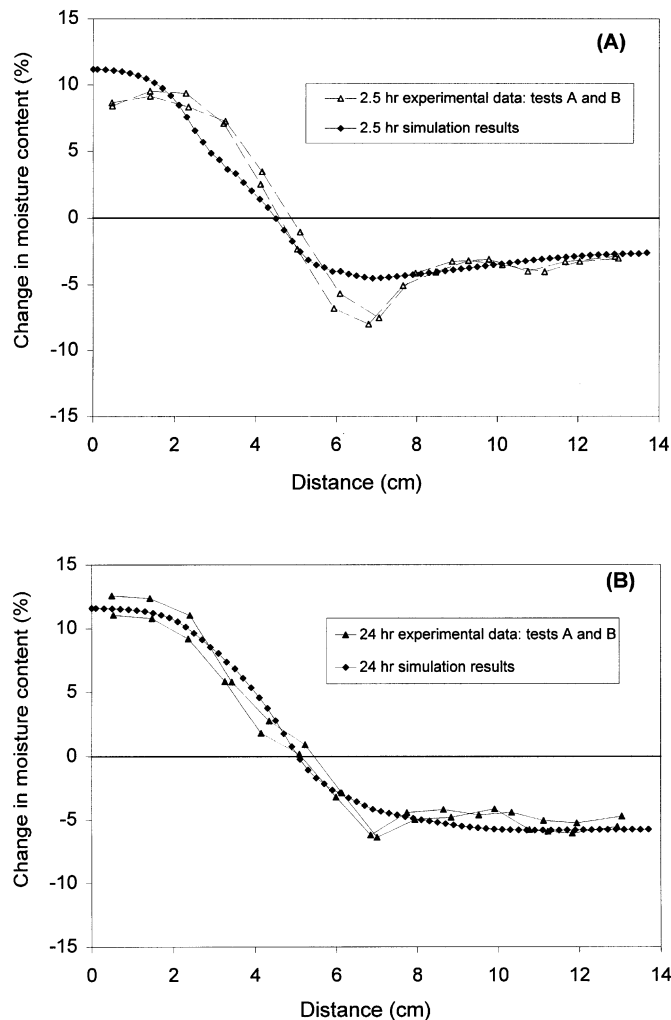The simulated change in moisture content in the

Fig. 5. Experimental and simulated change in moisture content at (A) 2.5 h and (B) 24 h. Simulations conducted using modified HYDRUS 5.0 model that accounts for concentration-dependent hydraulic functions.

RHS of the column provides a good match to experimental results at both 2.5 and 24 h. The simulations also capture the gradual change in moisture content with distance between 3 and 7 cm at both times. At 2.5 h the model slightly over-predicts water movement at the left end of the column and under-predicts drainage at the center of the column. The differences between experimental and simulated results are likely due to inaccuracies in the hydraulic functions used for modeling. Early in the experiment, the rate of change of moisture content in the column is fast. Inaccuracies in the hydraulic functions, particularly the unsaturated hydraulic conductivity function, which was estimated by Mualem's method rather than measured, would be expected to cause differences between simulated and experimental moisture contents at early times. As fluxes in the column decrease over time, the moisture content profile changes more slowly and slight over- or under-predictions of water flow are reduced. By 24 h, as shown in Fig. 5b, the simulation results match the experimental data well throughout the column.

Another source of discrepancy between the simulated results and the experimental data may be the assumption that the initial condition of the column was characteristic of the MWC for either the pure water or 7% butanol wetted silica sand. It is probable that the actual initial condition in each half of the column fell on a scanning curve. However, HYDRUS does not provide the option of setting initial conditions on scanning curves. Additional differences between the experimental and simulated results may stem from the fact that the majority of the experiment proceeded along scanning curves but the hysteresis routine in HYDRUS uses scaled versions of the MWC and MDC, rather than actual scanning curves, to simulate hysteresis. Kool and Parker (1987) noted the potential for error when this scaling technique is used because it does not predict closed scanning loops. Therefore, the predicted scanning curves may have been steeper than the actual experimental conditions.

The shapes of the moisture content profiles in Fig. 5a and b are not intuitive and merit further discussion. To describe the evolution of the moisture content profiles, simulation results were examined for several times less than 24 h, as shown in Fig. 6a. In addition to the moisture content profiles of Fig. 6a and b,

simulated moisture content, pressure head, concentration, gradient, conductivity, and flux values were plotted for various times in Fig. 7 to aid in interpretation of the moisture content profiles. At $t = 0$ h, the change in moisture content is zero throughout the column. By 0.001 h the high fluxes at the interface between the clean and contaminated halves of the column result in drainage within the RHS and wetting of the LHS near the center of the column, as shown in Fig. 6a. The areas of both the wetted and drained regions increase and the boundary between the wetted and drained regions continues to move to the left from 0.001 to 0.075 h. As concentration gradients within the solute front decrease due to dispersion, solute-induced capillary pressure gradients also decrease, as shown in Fig. 7. Thus the advance of the boundary between the wetted and drained regions slows. From 0.075 to 0.25 h the moisture content at 2.5 cm (Fig. 6a) remains approximately constant while the region to the left of this point wets and the region to the right drains. The wetting and drainage centered around 2.5 cm causes a 'hump' in the moisture content profile in the LHS of the column at 0.25 h. Drainage from the RHS of the column from 0.25 to 24 h causes additional wetting between 0.0 and 2.5 cm and rewetting of regions that had previously experienced drainage between 2.5 cm and the center of the column. After 24 h, this wetting effectively damps out the hump that was seen in the moisture content profile at 0.25 h.

Though data were not collected for $t > 24$ h, the modified HYDRUS model is useful for investigating the long term behavior of the closed column system. Henry et al. (1999) speculated that, "After the hydraulic gradient is near zero with the water content and surfactant-induced components essentially balancing one another, diffusion of butanol will become the primary mechanism of solute transport." As butanol diffuses out of a contaminated region, the concentration-dependent surface tension of the region increases and causes a decrease in the soil water pressure. Similarly, diffusion of butanol into less contaminated regions results in an increase in the soil water pressure. We expected this diffusion process to result in backflow within the column and used the model to evaluate the importance of the process and to predict the final steady-state condition of the system.

Though the simulated moisture content profile was essentially constant after 25 000 h, simulation results
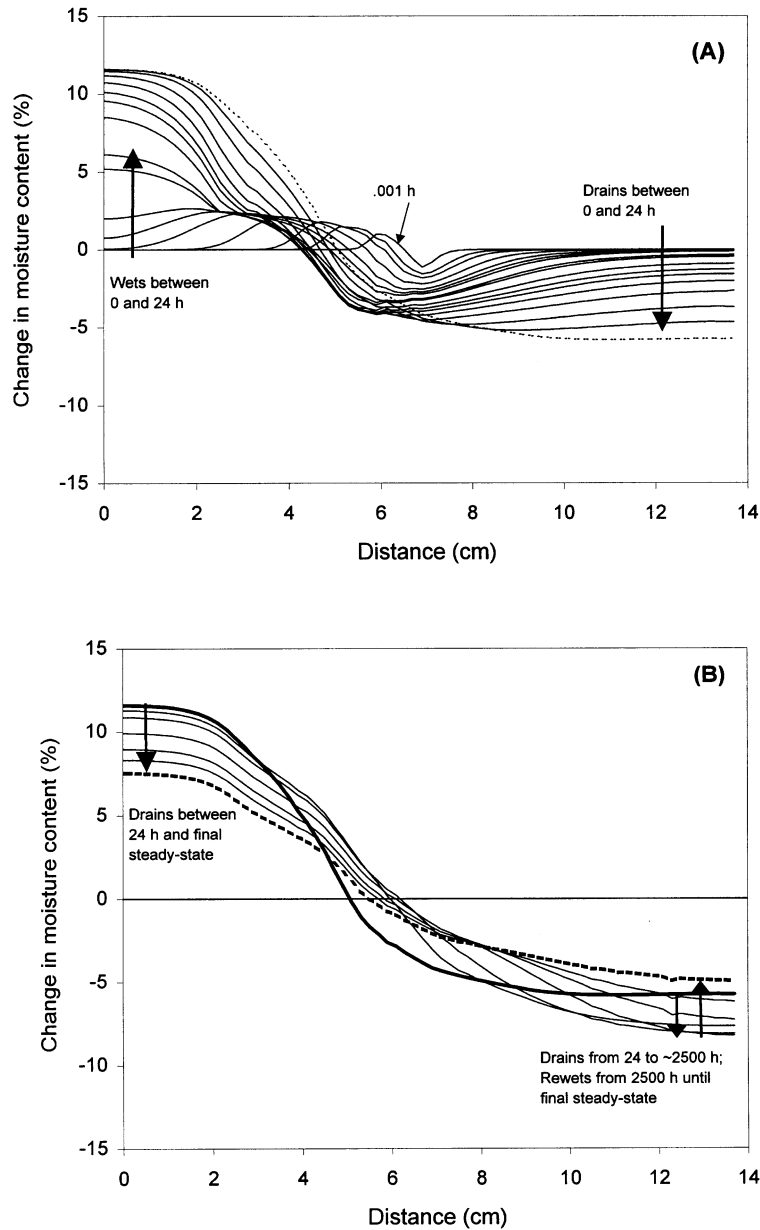
Fig. 6. Simulated change in moisture content for (A) $t < 24$ h and for (B) $t > 24$ h. Progressive values of curves in (A) are 0.001, 0.005, 0.01, 0.025, 0.05, 0.075, 0.1, 0.2, 0.25, 0.5, 0.75, 1, 1.5, 2.5, 5, 10, and 24 h. Progressive values of curves in (B) are 24, 500, 1000, 2500, 7500, and 200 000 h.

indicated that pressures in the system continued to change slightly (~1 cm) until 200 000 h. Fig. 6b shows the simulated moisture content profiles for selected times between 24 and 200 000 h (final steady-state). Water and solute mass balance errors

were less than 0.102 and 0.000%, respectively, for all times shown in Fig. 6. The selected profiles in Fig. 6b illustrate the major flow processes in the system. After ~24 h, there is negligible additional wetting between 0 and 3 cm. Thus, leftward flow in
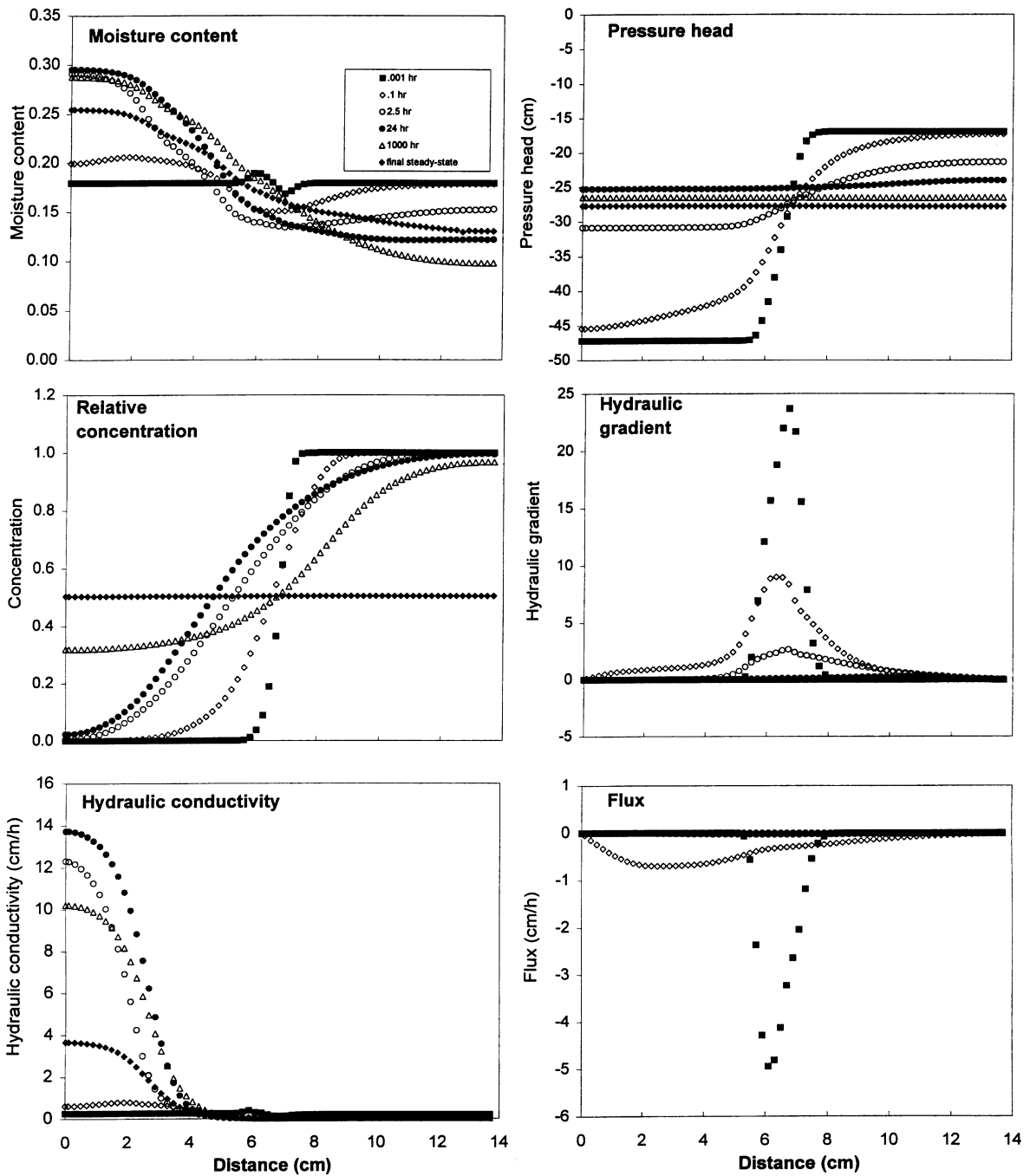
Fig. 7. Simulated moisture content, pressure head, relative concentration, hydraulic gradient, hydraulic conductivity, and flux. Symbols in all graphs correspond to legend shown in moisture content graph.

this region has ceased but continues in the rest of the column. By 500 h, drainage from between 0 and 3 cm indicates that backflow (flow from left to right) is occurring. This is confirmed by positive fluxes in the model output. Wetting/rewetting is seen between 3 and 12 cm due to additional drainage from the far right end of the column (12–13.7 cm) and backflow from the region between 0 and 3 cm. By approximately 2500 h, drainage at the far right end of the column has reached a maximum. Subsequent backflow from 2500 to 200 000 h, caused by surface tension gradients resulting from the slow diffusion of butanol to the left, causes drainage in the region between 0 and 8 cm and rewets the section between 8 and 13.7 cm. The occurrence of backflow, as indicated by comparison of the 24 and 200 000 h profiles of Fig. 6b, demonstrates that butanol diffusion can indeed have a significant effect on flow within the column.

3.3. Effect of hysteresis on simulation results

The observed processes of draining and rewetting within the column are consistent with those observed by others due to concentration-dependent surface tension variations within a solute front. The importance of hysteresis in these types of systems is exhibited by the non-uniform steady-state moisture content profile in the horizontal column (Fig. 6b). At steady state, the concentration at all locations within the column is equal to one half of the initial concentration within the RHS of the column (Fig. 7). The hydraulic gradient is zero everywhere within the column and thus the pressure in the column must be uniform. The hydraulic properties of the column at steady-state are those for the silica sand wetted with 3.5% butanol solution. If hysteresis were not considered, the uniform pressure distribution within the column at steady state would be associated with a uniform moisture content profile. Because the column is closed, a mass balance on water is required and the final moisture content would necessarily be equal to the initial moisture content. The apparent change in moisture content at steady state would be zero throughout the column. However, because hysteresis is considered in our simulations, the moisture content-pressure head relationship within the column may be indicative of the MWC, MDC, or any of the

intermediate wetting and draining curves for the 3.5% butanol system and will vary spatially. Thus, as shown in Fig. 6b, the final steady-state moisture content in the column is non-uniform and is a function of wetting/drying history. This supports the conclusion of Smith and Gillham (1999) that hysteresis in the hydraulic functions is required to accurately simulate concentration-dependent surface tension effects on unsaturated flow.

3.4. Effect of dispersivity on simulated moisture content profile

Since the hydraulic functions for an unsaturated system contaminated with a surface-active organic solute like butanol depend on solute concentration, transport parameters such as the aqueous molecular diffusion coefficient and dispersivity can significantly affect simulation results. Smith and Gillham (1999) showed that adjusting the dispersivity had a substantial effect on the magnitude and velocity of the flow perturbation associated with the surface tension changes in the solute front. The butanol molecular diffusion coefficient for all modeling presented here was taken from the literature (Yaws, 1995), but dispersivity was adjusted to determine a value that resulted in a good fit of simulation results to experimental data. The dispersivity chosen for modeling the experimental data was 2 cm.

Additional simulations were run using dispersivities 1/2 and 2 times the value used for modeling of the experimental data. The goal of these simulations was to systematically evaluate the effect of dispersivity on the induced flow phenomena by examining the simulated moisture content profiles within the column at 2.5 and 24 h. Decreasing dispersivity results in a steeper solute front and larger concentration gradient within the front. Thus dispersivity has a direct effect on the surfactant-induced capillary pressure gradients and surfactant-induced fluxes associated with the solute front.

Fig. 8a and b shows the 2.5 and 24 h simulated moisture content profiles, respectively, for dispersivity values of 1, 2, and 4 cm. At 2.5 h (Fig. 8a) large surfactant-induced fluxes result in more drainage near the center of the column when the dispersivity is 1 cm than when dispersivity is 2 or 4 cm. This enhanced drainage results in a decrease in the hydraulic conductivity near the center of the column. The
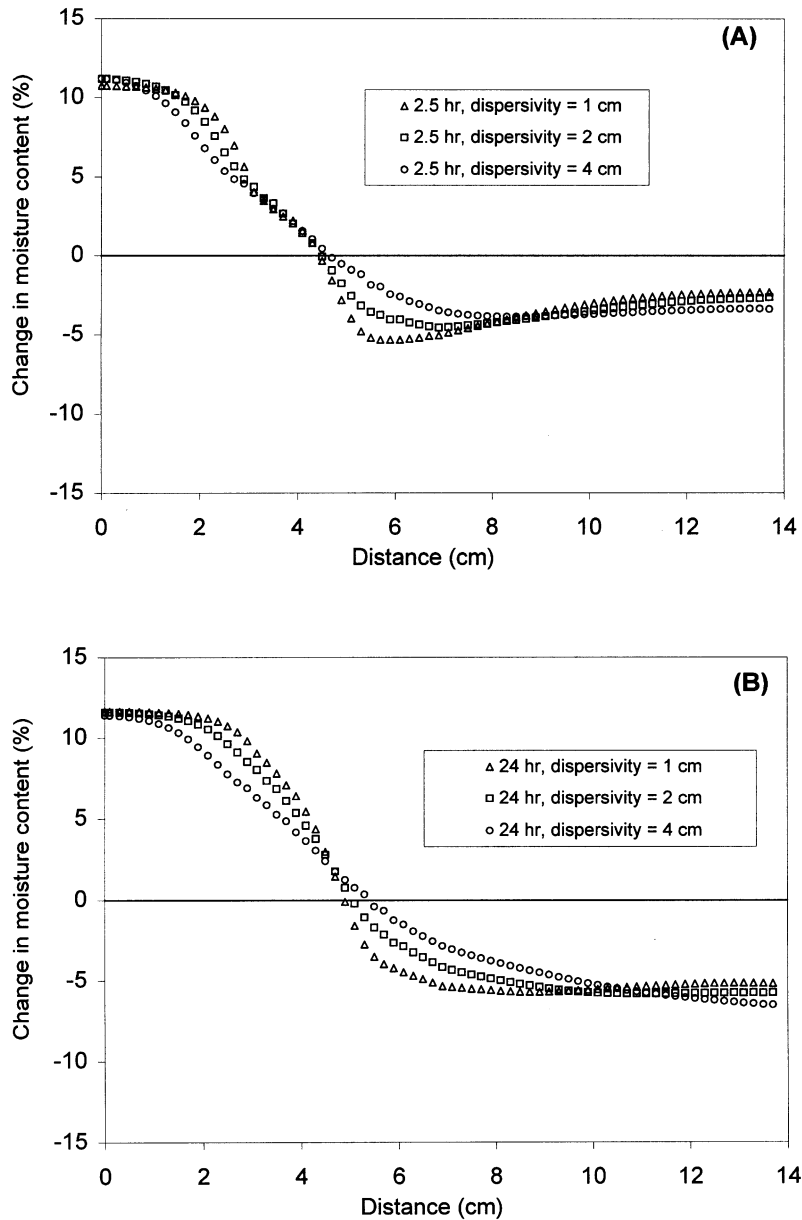
Fig. 8. Effect of dispersivity on simulated (A) 2.5 h and (B) 24 h change in moisture content.

reduction in hydraulic conductivity slows additional drainage from the RHS that occurs between 8 and 13.7 cm, thus the amount of drainage observed within this region at 2.5 h decreases with decreasing dispersivity. Though less water drains from the RHS by 2.5 h when dispersivity = 1, more water is moved to the region between 0 and 4.5 cm because of the

enhanced drainage near the center of the column. Despite the fact that more water has moved into the region between 0 and 4.5 cm, the maximum change in moisture content at the far left end of the column at 2.5 h is less because the wetting front is sharper. In addition to affecting the amount of flow at the left and right ends of the column, a dispersivity of 1 cm also

leads to a steeper change in moisture content between 2 and 6 cm at 2.5 h, relative to the more gradual change in moisture content observed as dispersivity increases to 2 and 4 cm. The 24 h moisture content profile (Fig. 8b) displays some of the same general trends noted at 2.5 h that are associated with decreasing dispersivity: (1) drainage at the far right end of the column decreases; (2) drainage at the center of the column increases; (3) the change in moisture content is steeper between 2 and 6 cm; and (4) more water accumulates between 0 and 5 cm. In contrast to the 2.5 h profiles, by 24 h, the maximum change in moisture content at the far left end of the column is associated with the smallest dispersivity value and varies inversely with dispersivity.

4. Conclusions

Surface-active solutes can have a significant effect on flow and transport in unsaturated porous media. Because of the nature of these types of systems, hysteresis in the hydraulic functions must be considered if flow and transport are to be accurately simulated by numerical models. We have apparently presented the first numerical model of unsaturated flow and transport to include both hysteresis and concentration-dependent changes in the hydraulic functions due to the presence of surface-active organic contaminants. Additionally, we have shown that concentration-dependent effects on unsaturated flow can be readily incorporated into standard numerical models. In this study we have limited our investigation to modeling flow and transport in a system contaminated with butanol, however, the same technique could be applied to any surface-active contaminant for which the concentration-dependence of surface tension and viscosity is known. As shown by Karkare et al. (1993), surface-active organic compounds, including alcohols, amines, acids and esters, can induce flow in unsaturated porous media. The ability of a range of surface-active compounds to induce unsaturated flow should provide further motivation for measuring concentration-dependent surface tension and viscosity for water contaminated with surface-active organic compounds of environmental interest.

Numerical models that incorporate contaminant-induced flow perturbations can serve as a useful tool for contaminant hydrogeologists, modelers, and regulatory agencies. The magnitude of the observed flow perturbations will be a function of both the surface-active behavior of the contaminant of interest and the geology of the site under consideration. Thus, numerical models such as the one presented here provide a method for evaluating the importance of these effects on a site-specific and contaminant-specific basis. Depending on the contaminant and site of interest, the use of standard numerical models that do not incorporate concentration-dependent hydraulic functions to simulate flow and transport in systems contaminated with surfactants may result in considerable differences between predicted and observed flow and transport. Further, without a thorough understanding of surfactant-induced flow perturbations, the application of standard methods for determining transport parameters, such as fitting breakthrough curves, would give incorrect results in these types of systems because flow within the system is not steady. Standard methods for determining transport parameters would predict a higher dispersivity than is actually characteristic of the system. Accounting for the effect of surfactant-induced flow perturbations is necessary for determining transport parameters in these systems. Other desirable improvements to the state of modeling these types of systems would include partitioning of the solute to the gas and solid phases, as well as dissolution from the organic phase. These features would be of the greatest interest for simulating contaminant transport and remediation in systems contaminated with volatile organic compounds of environmental concern.

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