The Migration and Entrapment of DNAPLs in Physically and Chemically Heterogeneous Porous Media

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Linda M. Abriola, Avery H. Demond, Scott A. Bradford, and David L. Lord

Department of Civil & Environmental Engineering, University of Michigan, Ann Arbor, Michigan, USA

Abstract

This research is designed to investigate the influence of chemical heterogeneities on the migration of dense nonaqueous phase liquids (DNAPLs) in subsurface formations.

A series of laboratory experiments have been conducted to explore the influence of aqueous and solid phase chemistry on hydraulic properties. Representative surface active agents, dodecylamine (DDA) and octanoic acid (OA), were found to exhibit pH-dependent acid-base speciation in aqueous solution, which resulted in aqueous chemistry-dependent interfacial and hydraulic properties. The measured hydraulic properties for natural (Shale) and synthetic (various combinations of untreated and organosilane treated Ottawa sands) soils were also found to be strongly influenced by the solid surface chemistry characteristics as a result of corresponding changes in solid wettability. Results from these studies will facilitate the development of improved methods to predict and model hydraulic property relations that are required by multiphase flow and transport simulators. An automated apparatus to economically measure the hydraulic property relations on a number of columns in parallel has also been constructed and experimental protocols have been established for its operation.

A two-dimensional multiphase flow simulator was modified to account for wettability effects on the hysteretic hydraulic property relations. Numerical experiments were then conducted to investigate the influence of coupled physical and chemical heterogeneity on DNAPL flow and entrapment. For reasonable estimates of average wettability characteristics, simulations demonstrate that spatial variations in wettability can have a dramatic impact on DNAPL distributions, altering the degree of entrapment and the extent of spreading. Results from this work will facilitate the characterization of DNAPL distributions in the field, and the development and implementation of innovative remediation strategies.

Introduction

Hazardous DNAPLs, such as chlorinated solvents, are slightly water soluble and pose a serious threat to soil and groundwater supplies in many portions of the United States. The migration and entrapment of DNAPLs in aquifer formations is typically believed to be controlled by physical heterogeneities. This belief is based upon the assumption that permeability and capillary properties are determined by the soil texture. Capillarity and relative permeability, however, will also depend on the system wettability; i.e., the pore-scale distribution of immiscible fluids near a solid (cf. Figure 1). This wettability may vary spatially in a formation due to variations in aqueous phase chemistry, contaminant aging, and/or variations in mineralogy and organic matter distributions (cf. Figures 2 and 3). In natural subsurface systems, highly irregular distributions of NAPLs have been observed. These distributions are likely due to the superposition of physical and chemical heterogeneities.

Multiphase flow simulators are commonly employed to predict the spatial and temporal distributions of organic liquids at hazardous waste sites. Numerical studies indicate that the prediction of immiscible flow pathways is extremely sensitive to small scale heterogeneities in permeability and capillary characteristics. All previous numerical multiphase studies have assumed that the simulated porous media were strongly water-wet. Hence, large prediction errors may be encountered when the water-wet assumption does not hold.

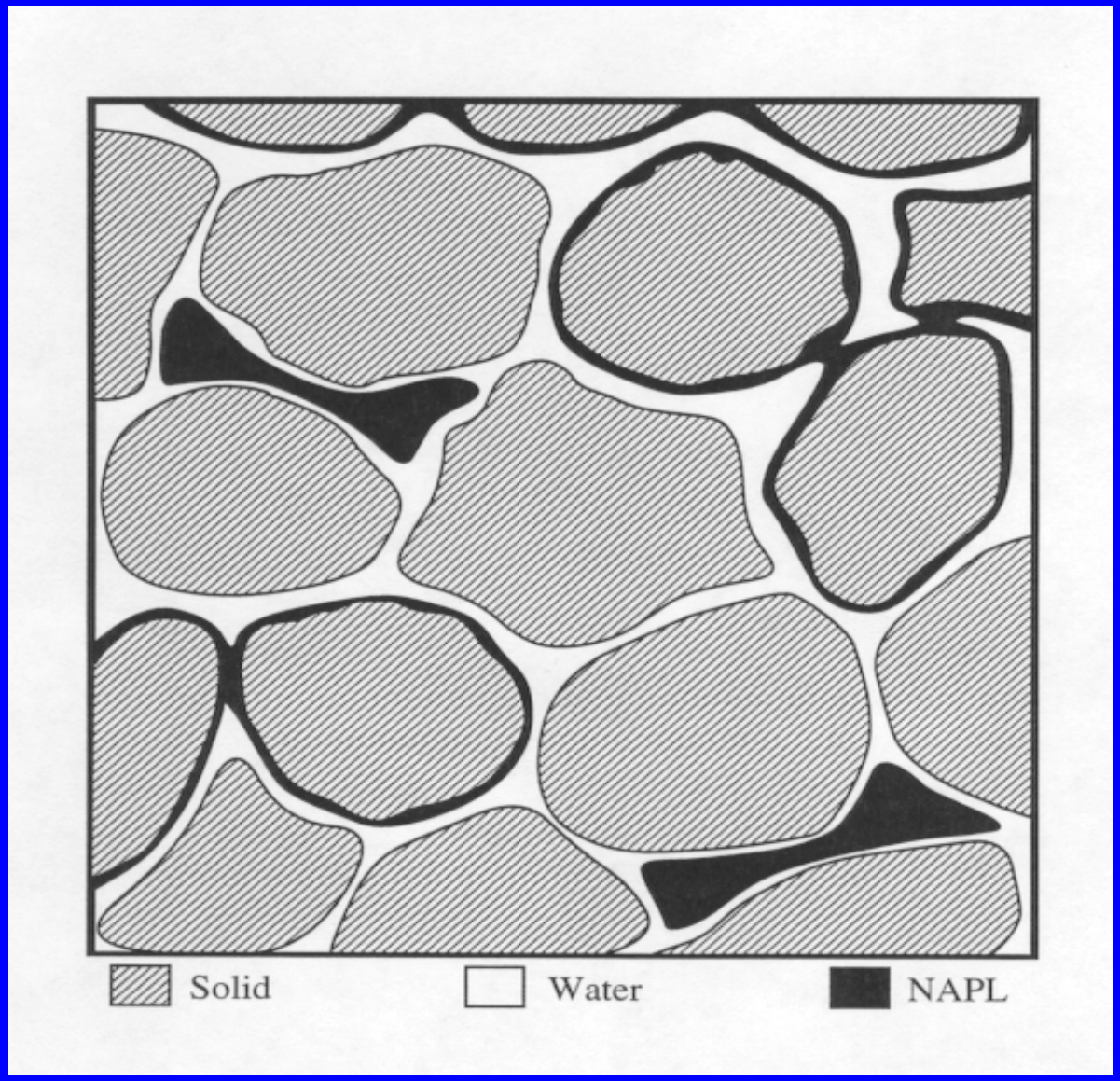

Figure 1: Hypothetical NAPL distribution in fractional wettability media.

Figure 2: The chemically heterogenious Wagner soil is composed of quarts and shale components.

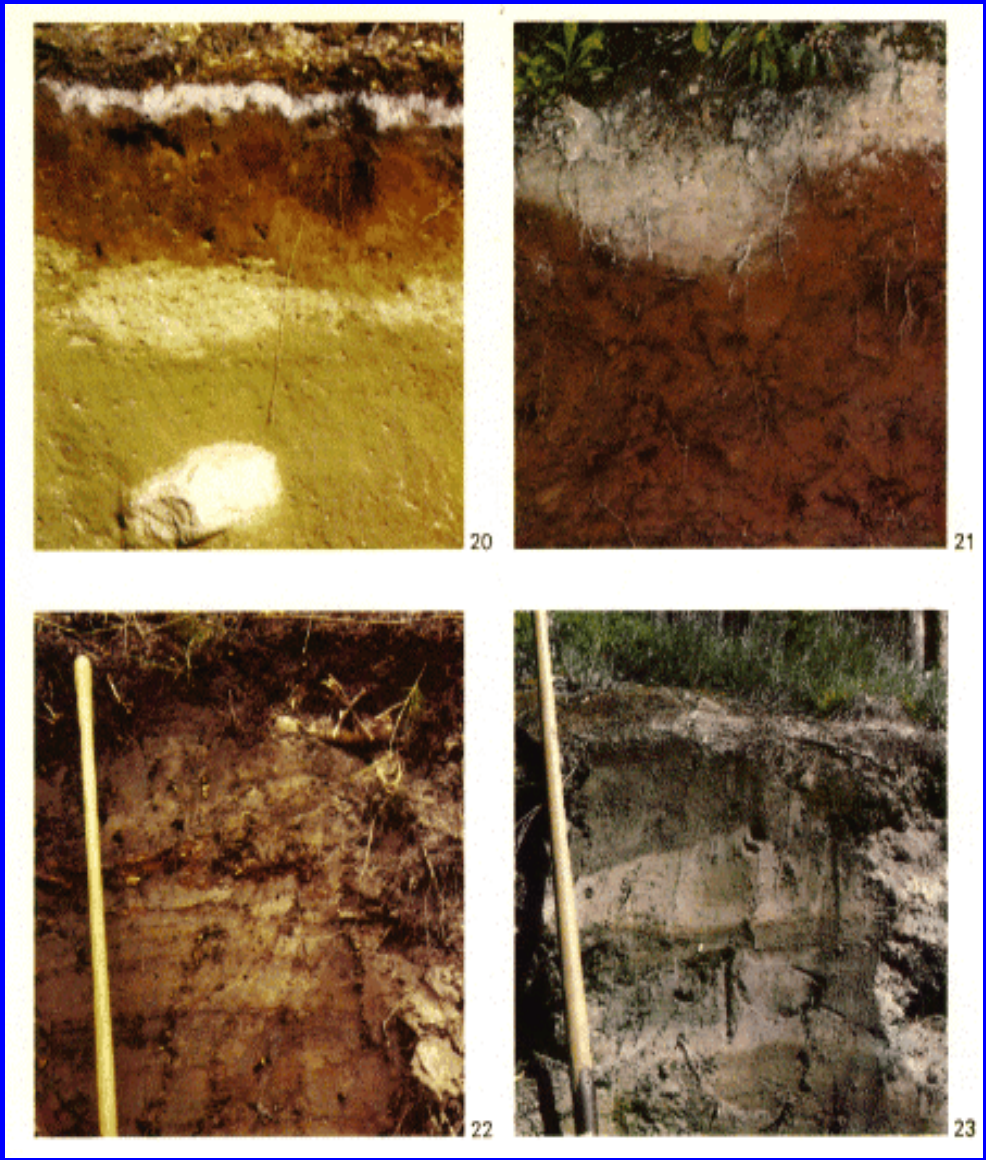

Figure 3: Weathering, variations in mineralogy and organic matter distributions can lead to subsurface chemical heterogeneities.

Objectives

The overall objective of this research is to investigate the influence of coupled physical and chemical heterogeneity on the migration and entrapment of DNAPLs in the saturated zone. This research includes laboratory and numerical investigations for a matrix of fluid and solid properties encompassing a range of wettability characteristics. Specific tasks include:

- Determination and quantification of aqueous phase chemistry influences on medium wettability and interfacial tensions;
- Determination and quantification of hydraulic property relations for organic liquid-water-soil systems having various wettability characteristics;
- Experimental investigation of two-dimensional organic liquid infiltration experiments in coupled physically and chemically heterogeneous media;
- Development of a continuum based multiphase flow simulator to account for physical heterogeneity, saturation independent and saturation dependent wettability, and concentration dependent wettability and interfacial tension;
- Application of this model to explore the potential influence of coupled physical and chemical heterogeneities on the migration of DNAPLs and the development of innovative remediation schemes.
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Research Progress

Aqueous Phase Chemistry

A series of experiments have been conducted for xylene-water-quartz systems using the representative surface active agents, dodecylamine (DDA) and octanoic acid (OA). DDA and OA exhibit pH-dependent acid-base speciation in aqueous solution, which results in aqueous chemistry-dependent interfacial tension and/or wettability in these systems.

Figures 4 and 5 show that when the neutral species of DDA (pH > 10) and OA (pH < 5) prevailed, minimal changes in interfacial tension and wettability were observed because of preferential partitioning of DDA and OA into the NAPL. In contrast, the cationic form of DDA (pH < 10) sorbed both to quartz, which altered the wettability from water-wet to neutral, and to the NAPL-water interface. The anionic form of OA (pH > 5) sorbed only to the NAPL-water interface which lowered the interfacial tension by as much as 50%.

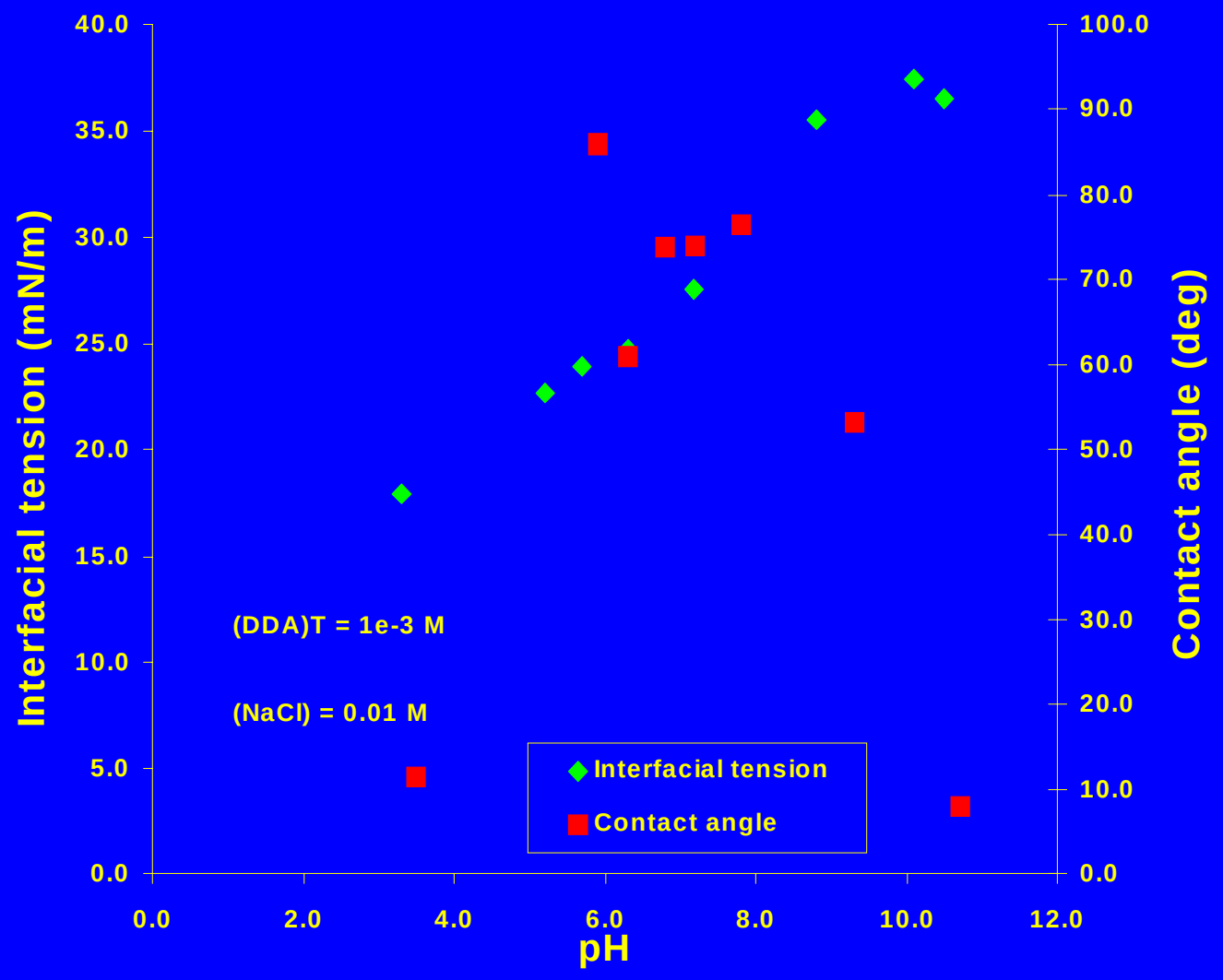


Figure 4: Interfacial tension and contact angle measurements as a function of pH in xylene-water-quartz systems using dodecylamine as the surface active agent in the aqueous phase [Lord et al., 1998].

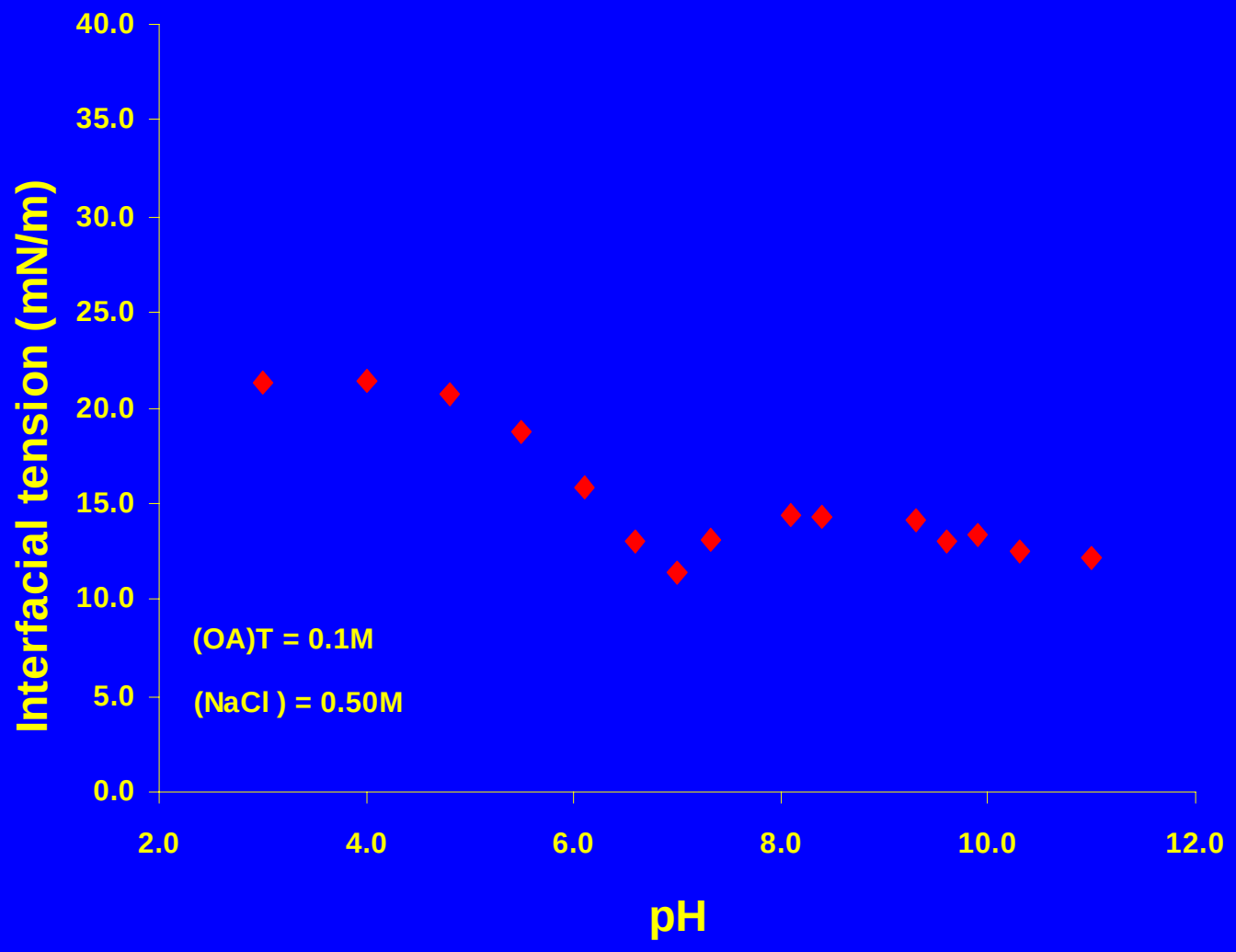


Figure 5: Interfacial tension measure-ments as a function of pH in xylene-water-quartz systems using octanoic acid as the surface active agent in the aqueous phase. Contact angle was approximately 15 degrees. [Lord et al., 1997a].

Changes in the above interfacial properties also influenced the hydraulic property relations as shown below in Figures 6 and 7 .

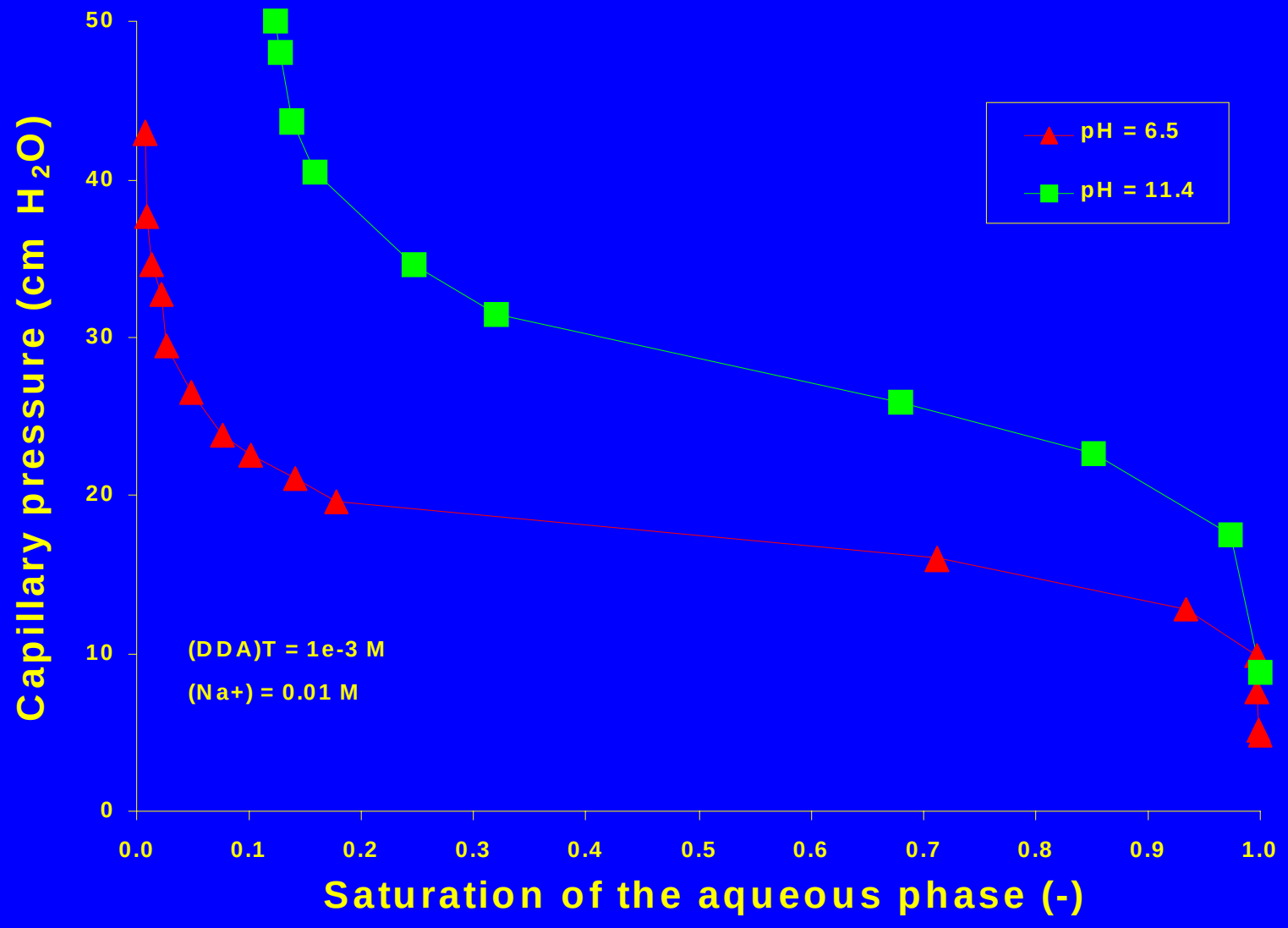


Figure 6: Xylene-water capillary pressure curve for indicated pH and dodecylamine concentration [Lord et al.,1998].

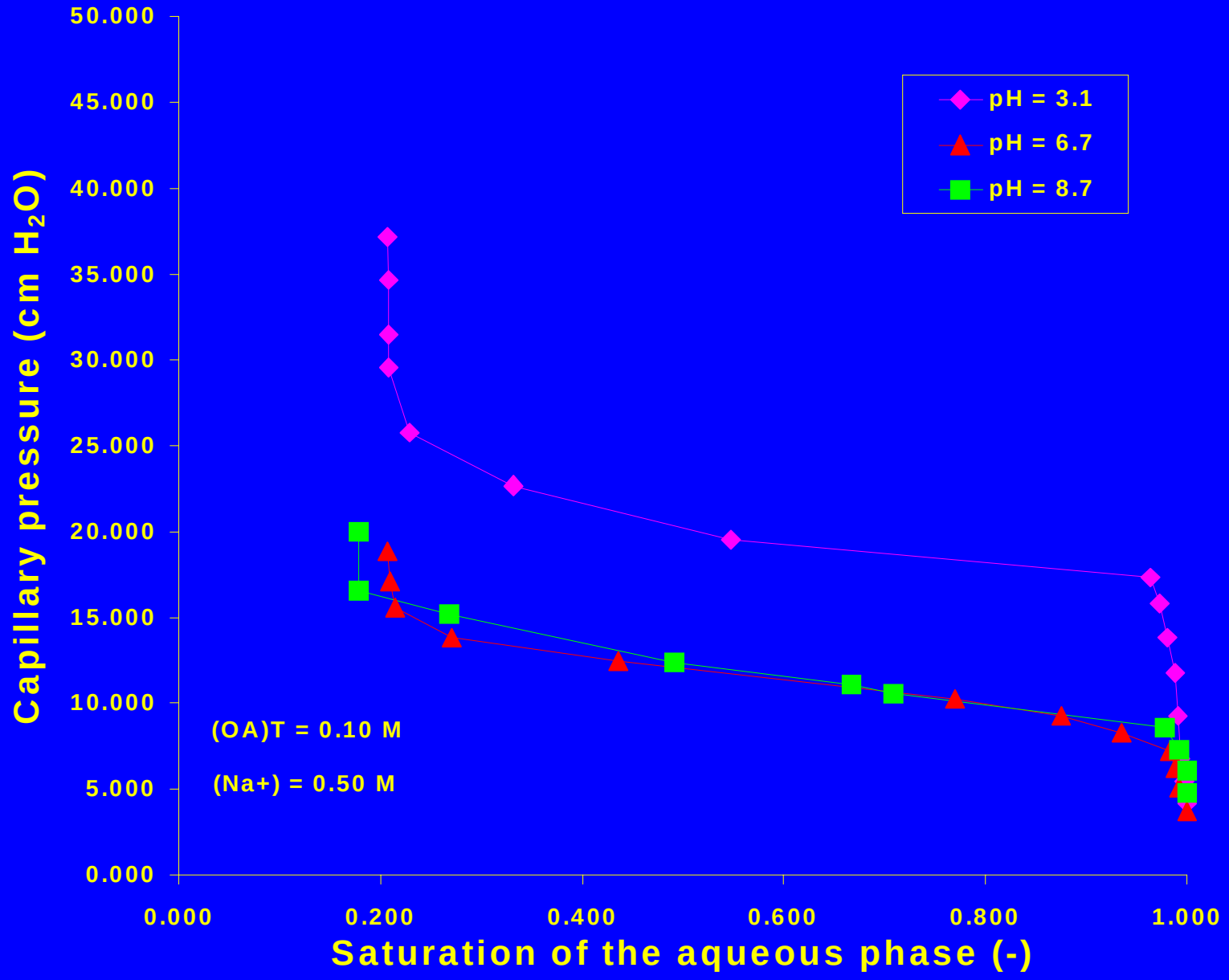


Figure 7: Xylene-water capillary pressure curve for indicated pH and octanoic acid concentration [Lord et al., 1997b].

Solid Phase Chemistry

Capillary pressure relations have also been measured for a representative DNAPL (tetrachloroethylene - PCE), water, and synthetic and natural fractional wettability porous medium systems using a modified pressure cell apparatus.

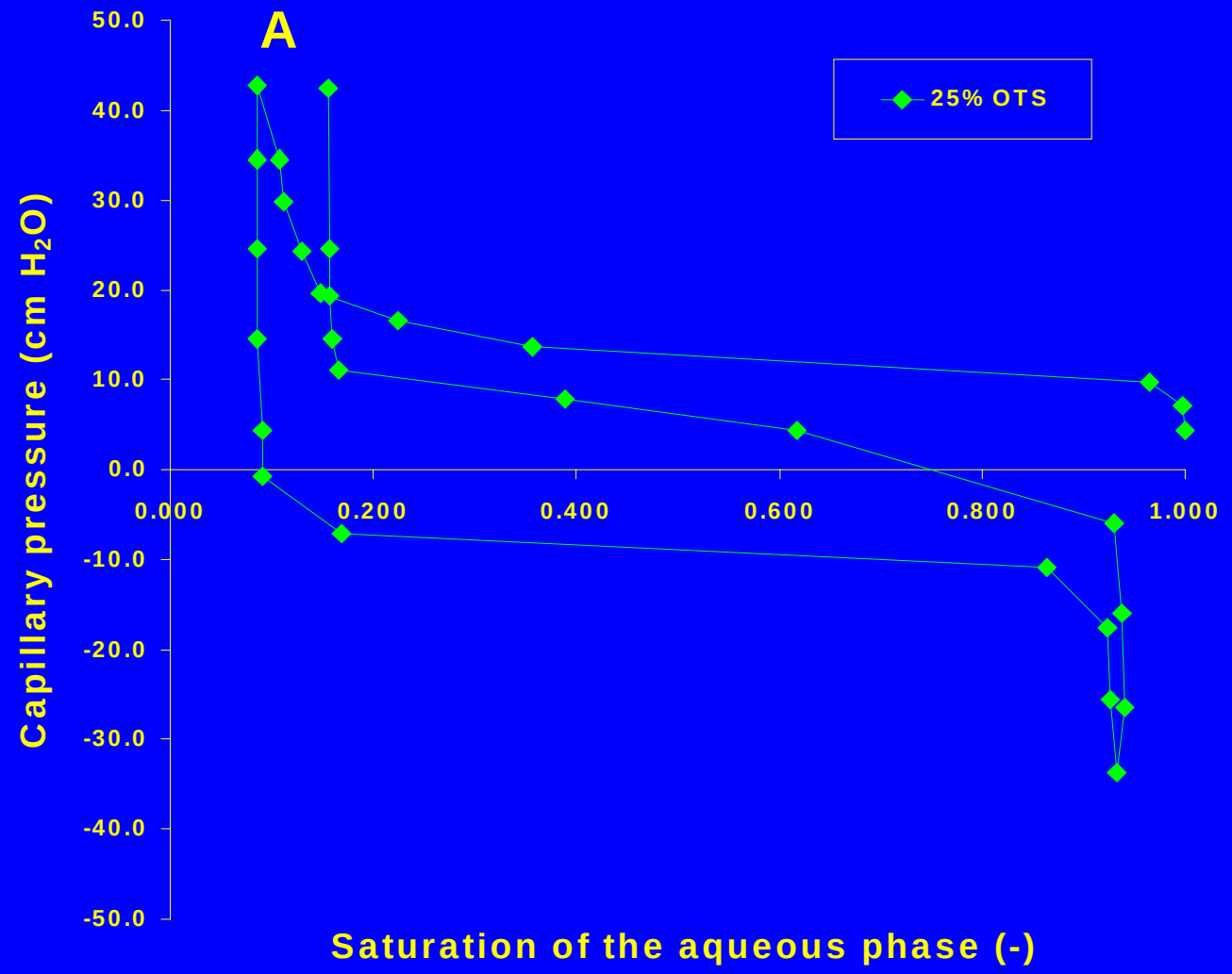


Figure 8A: PCE-water capillary pressure curve for 25% organosilane treated F35-F50 Ottawa sand (OTS).

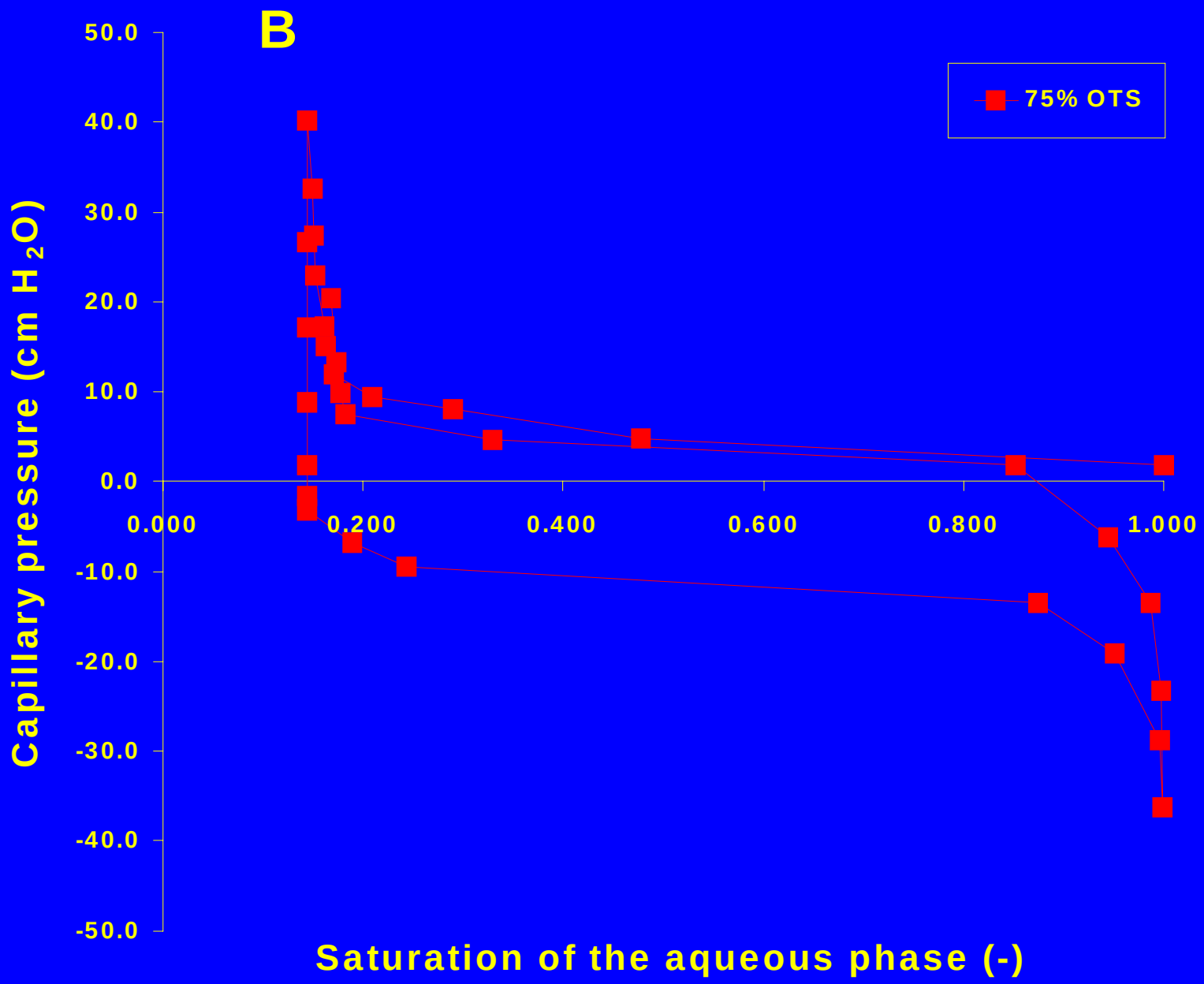


Figure 8B: PCE-water capillary pressure curve for 75% organosilane treated F35-F50 Ottawa sand.

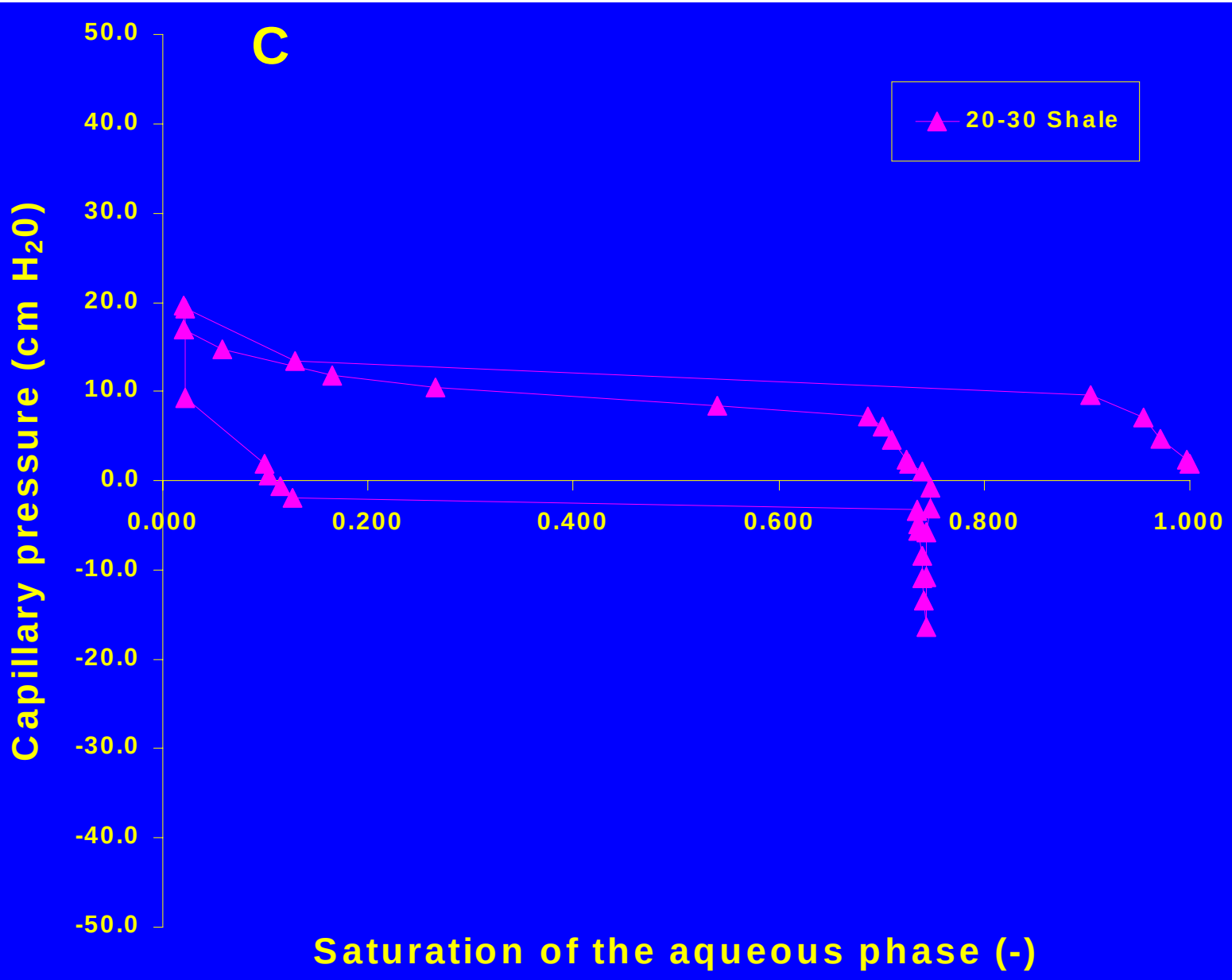


Figure 8C: PCE-water capillary pressure curve for F20-F30 shale.

Figures 8-A and 8-B indicate that, as the organic-wet fraction of a soil increases, for a given saturation and saturation history the residual water saturation increases and the organic liquid-water capillary pressure decreases, becoming negative during imbibition. Figure 8-C demonstrates that natural soil components may also exhibit strong interaction with the organic liquid as demonstrated by the negative capillary pressures during water imbibition.

Work has also been directed towards the design and construction of an automated apparatus to measure the hydraulic property relations on a number of columns in parallel. Construction is now complete and experimental protocols have been established for its operation.

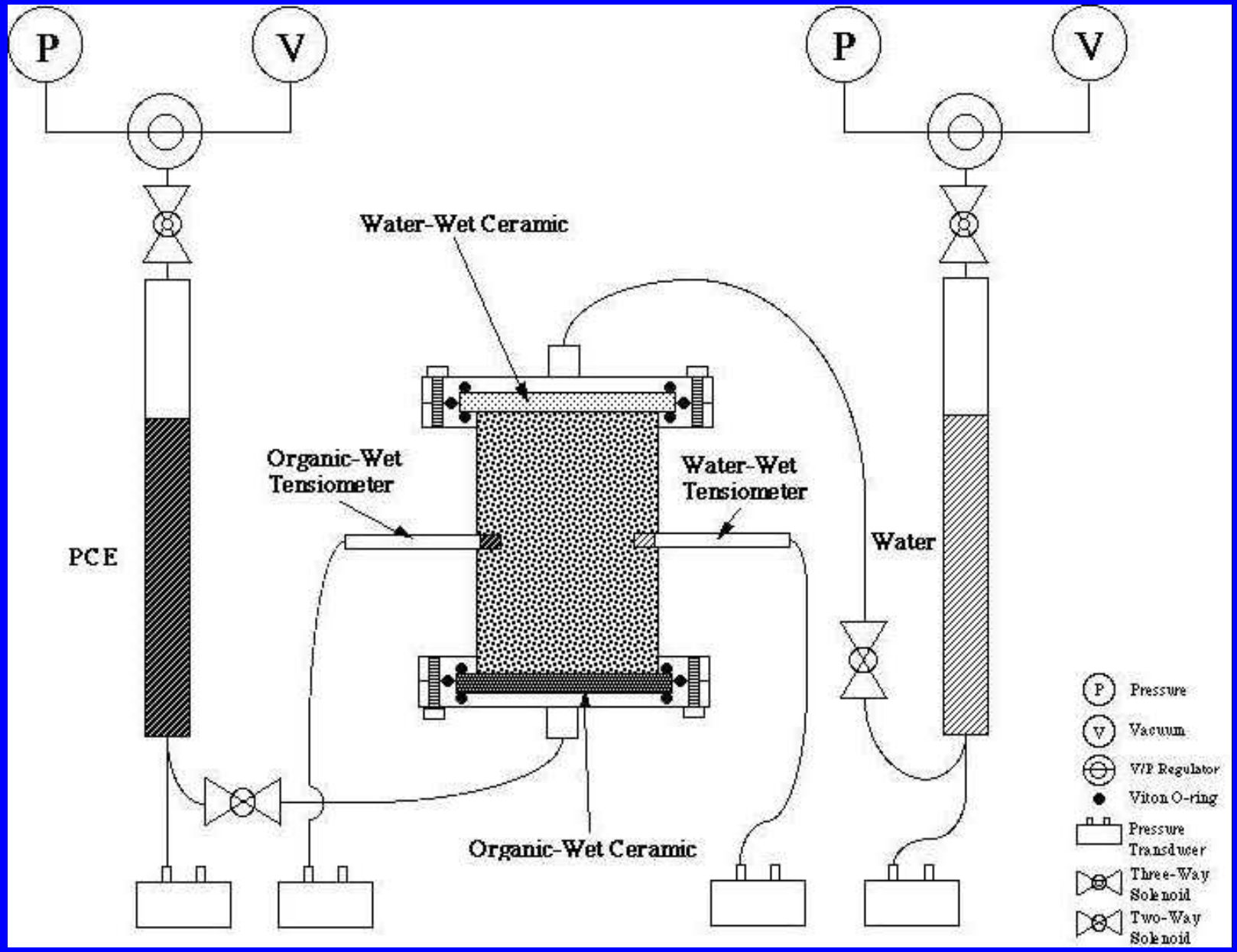


Figure 9: Schematic of automated setup for measuring hydraulic property relations.

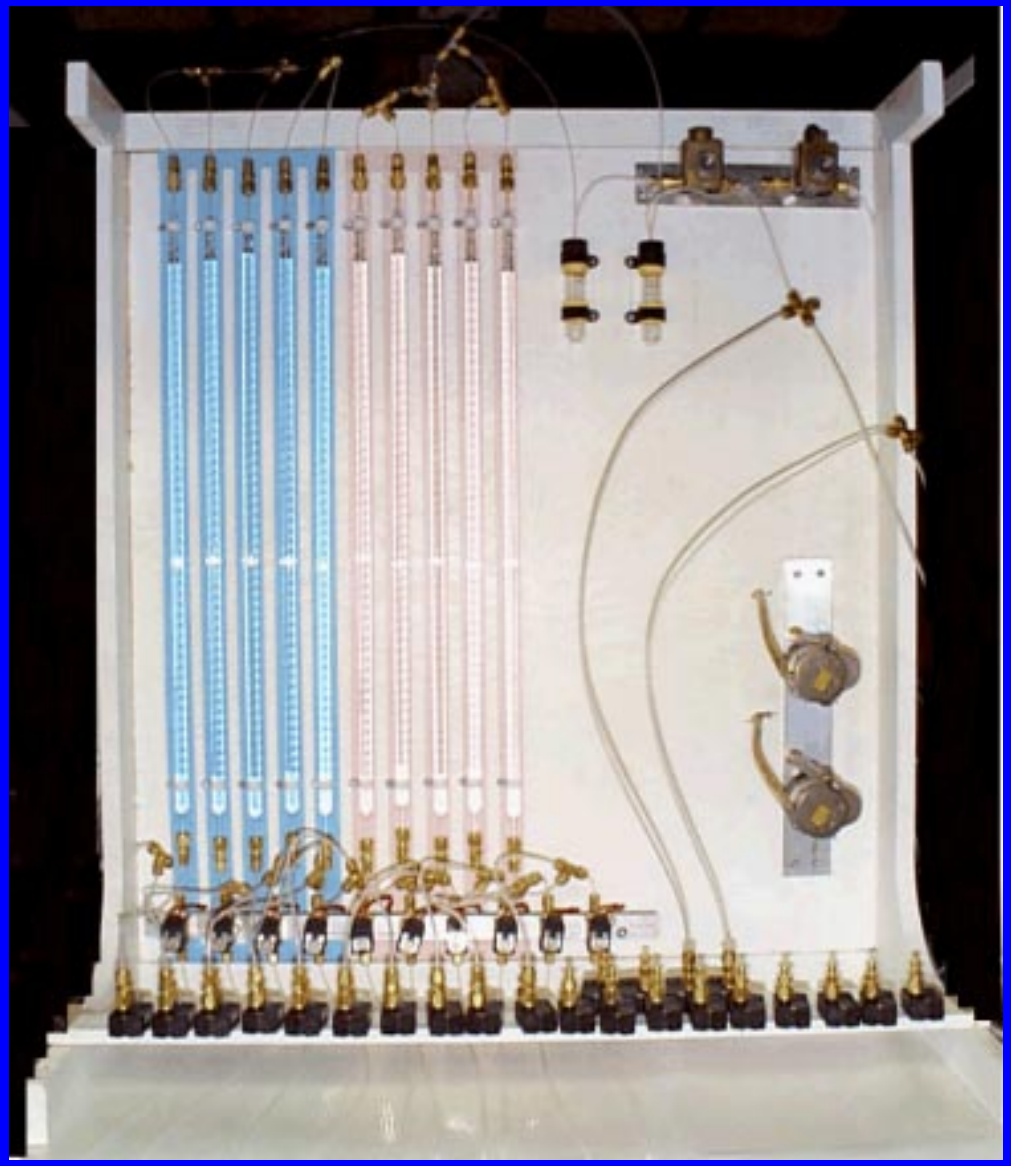


Figure 10: Pictures of automated setup (left) and soil column (below).

Equilibrium liquid pressure and saturations measured with this apparatus will yield capillary pressure relations, whereas transient outflow measurements will be used to determine the relative permeability relations, in conjunction with history matching procedures.

Mathematical Modeling

A two-dimensional multiphase flow simulator has been modified to account for coupled physical and chemical aquifer heterogeneity (cf. Figure 11).

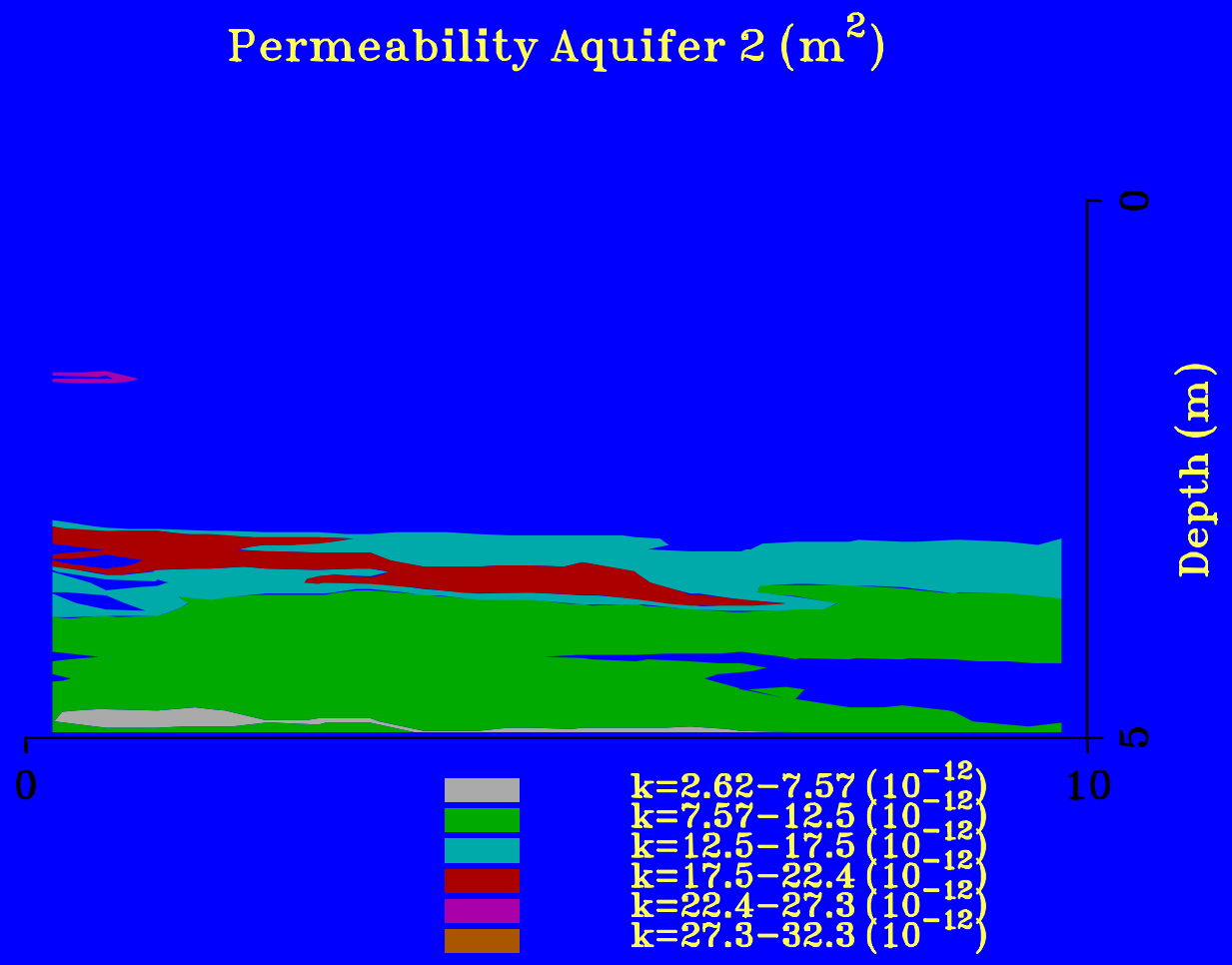


Figure 11A: The turning bands method [Thompson et al., 1986] is used to generate an intrinsic permeability distribution with a specified mean and covariance structure.

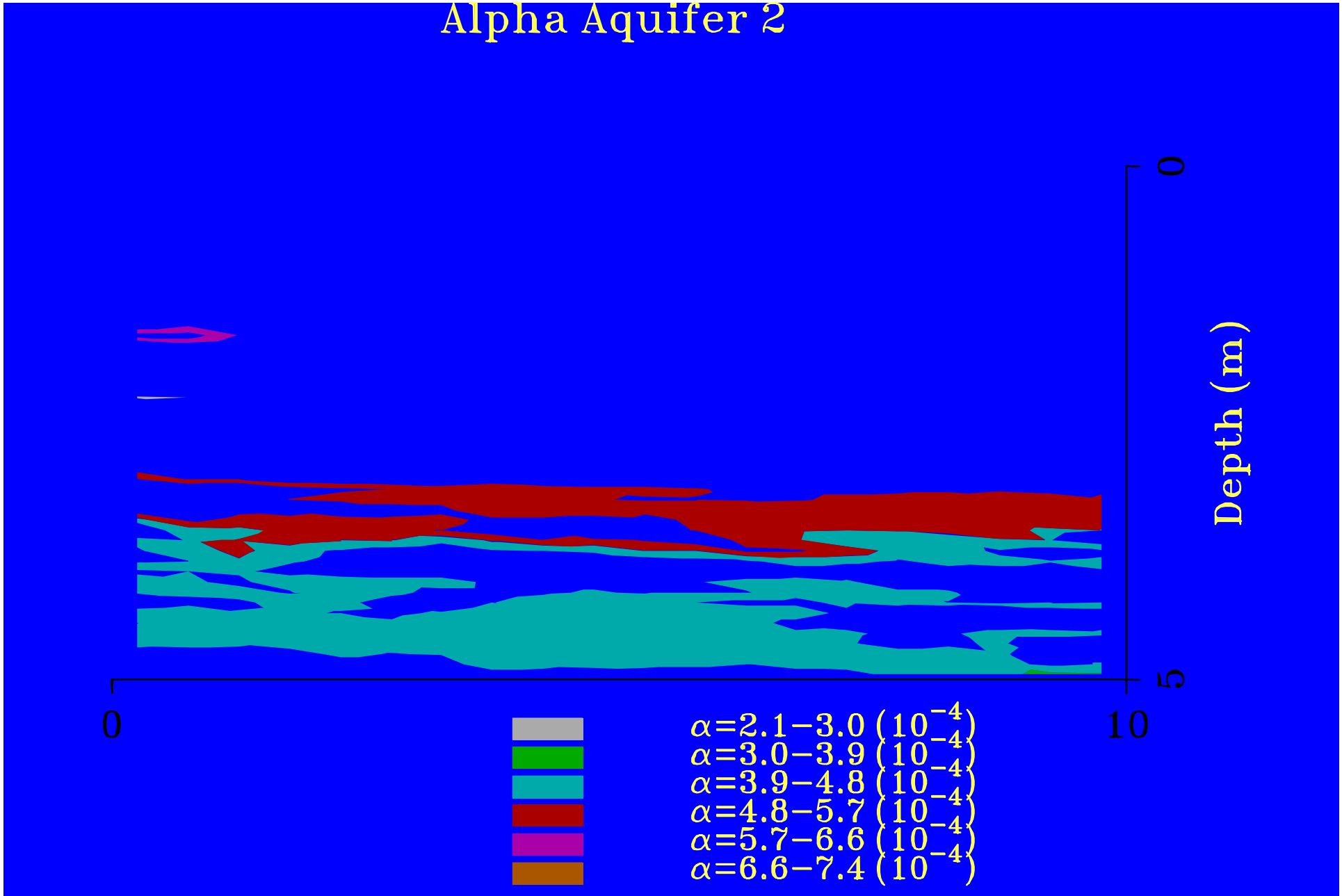


Figure 11B: Leverett scaling [Leverett, 1941] is used to relate capillary properties to the permeability distribution.

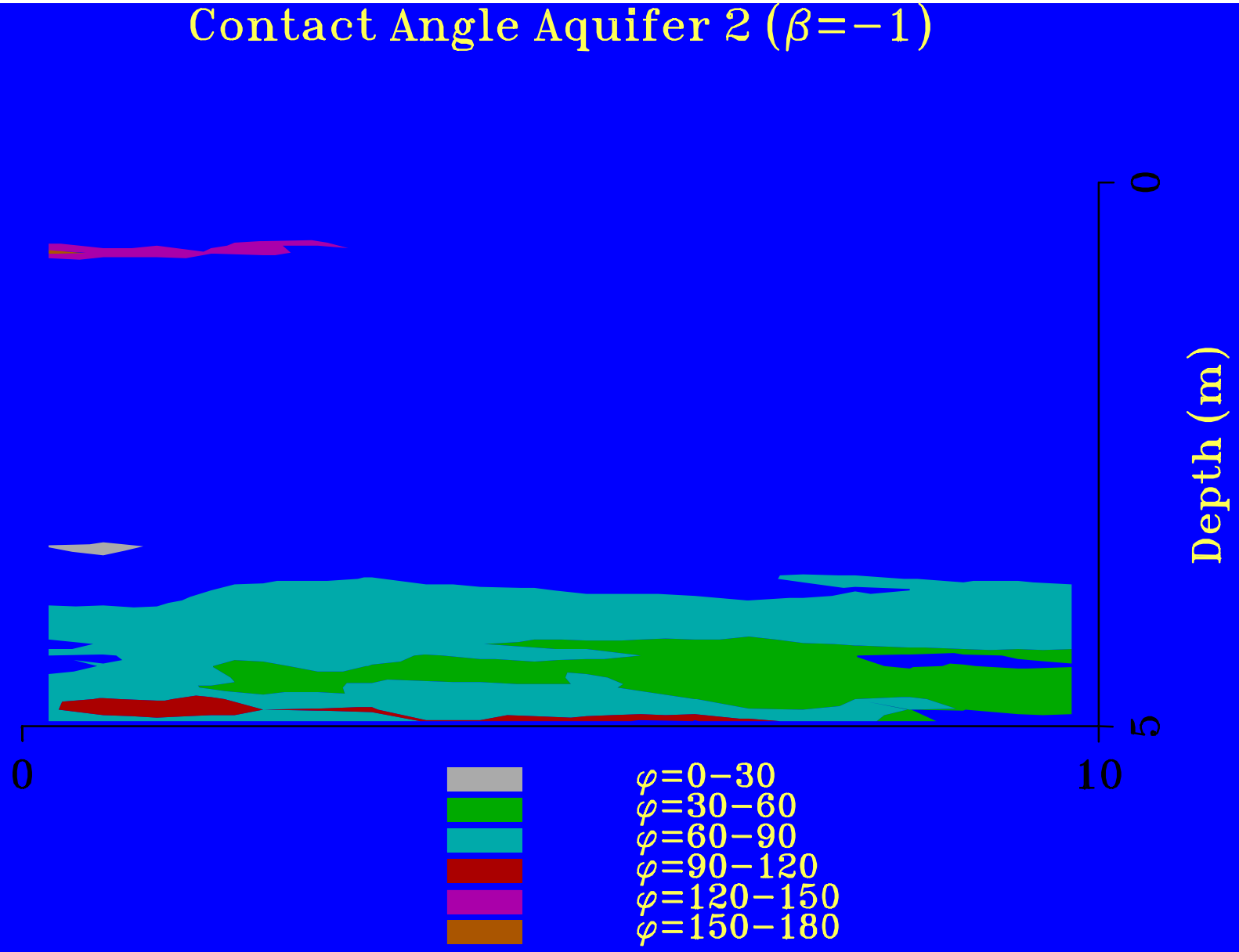


Figure 11C: Spatial distributions of chemical heterogeneity are obtained through correlation to the permeability distribution or by specified input.

Saturation independent and saturation dependent wettability effects on the hysteretic hydraulic property relations are currently included (cf. Figure 12).

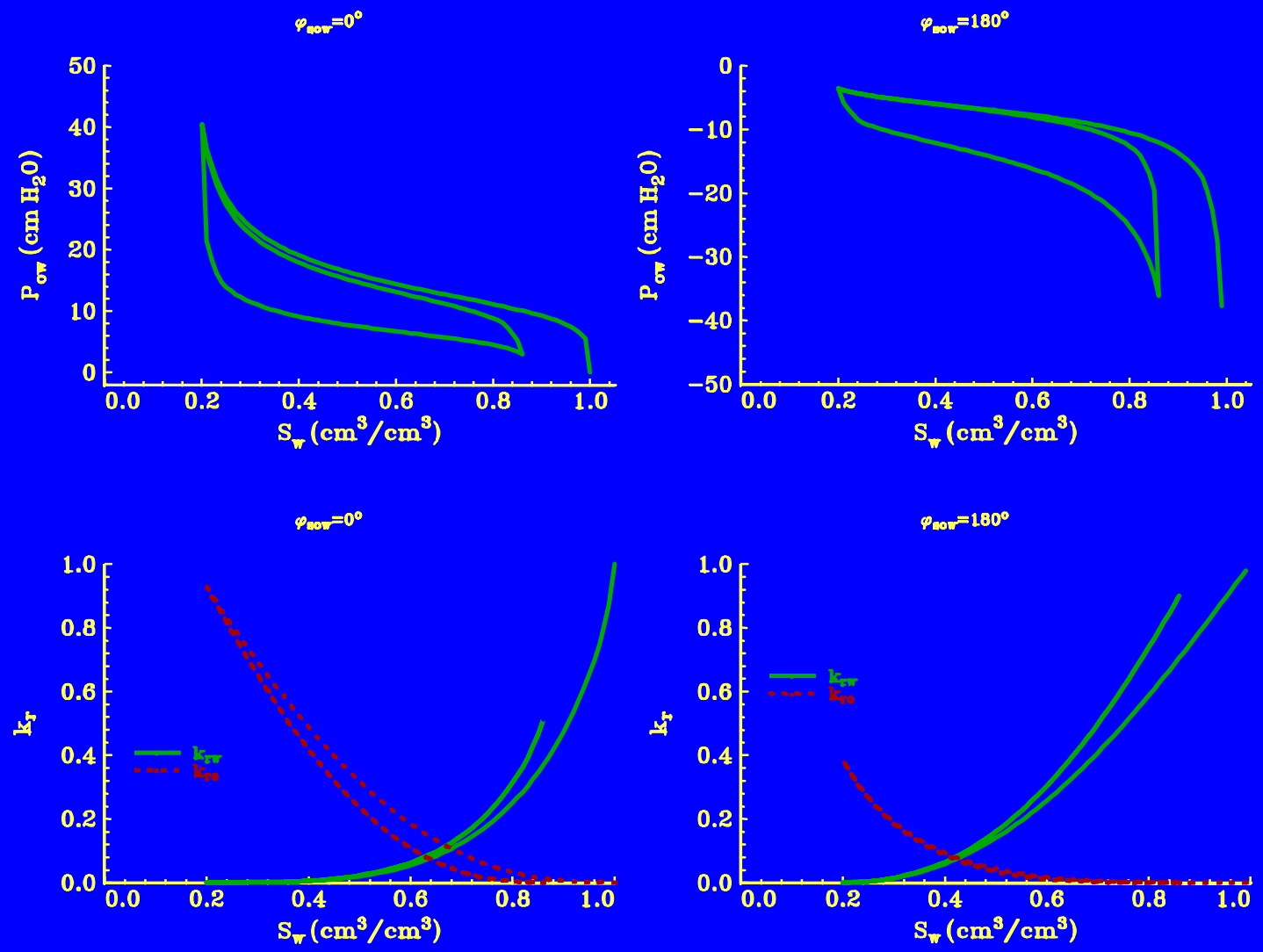


Figure 12 (continued on next slide): Wettability effects on the hydraulic properties are modeled according to the approach of Bradford and Leij [1996], and Bradford et al. [1997].

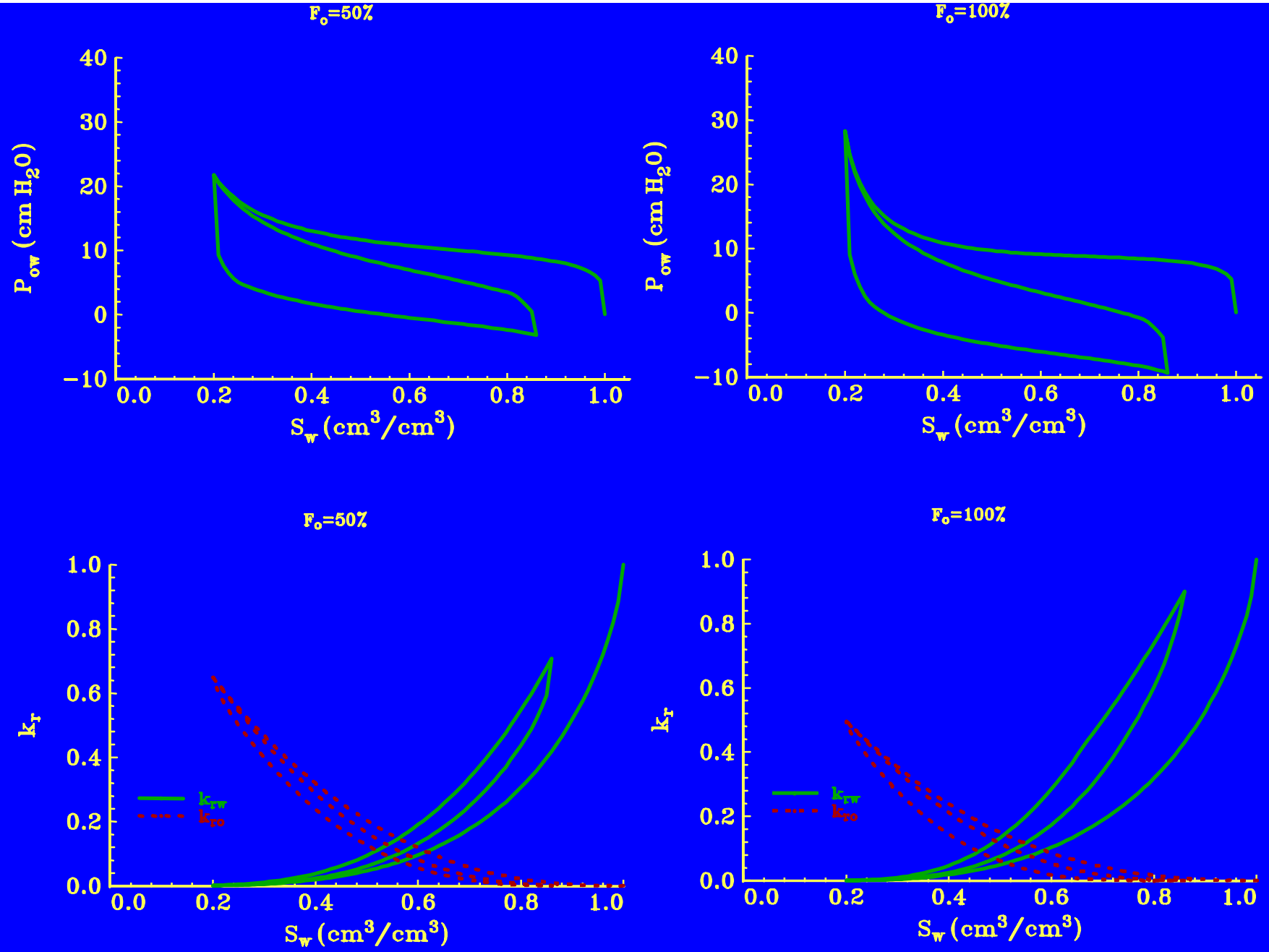


Figure 12 (cont.):

In physically homogeneous systems, increasing the contact angle or organic-wet fraction of a soil produces a prolonged slow migration of the DNAPL creating larger contaminated aquifer regions with lower organic saturations (cf. Figures 13 and 14).

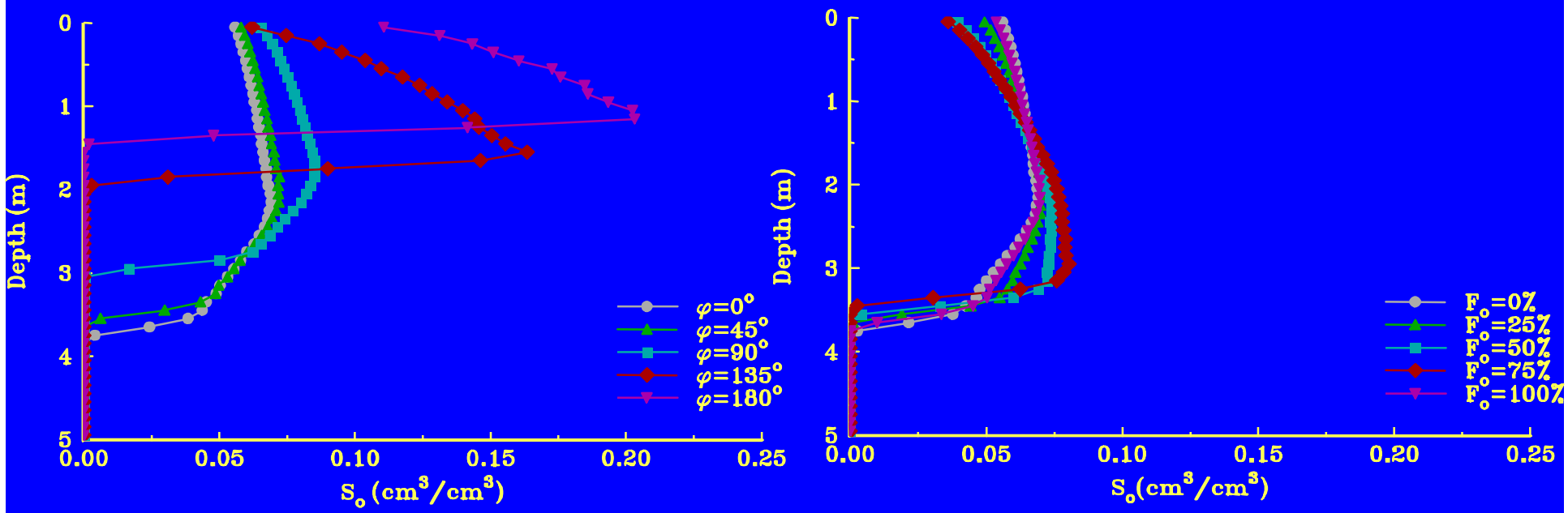


Figure 13: Predicted distribution of PCE after 10 days when 1-D soil column has the indicated wettability properties [Bradford et al., 1998a].

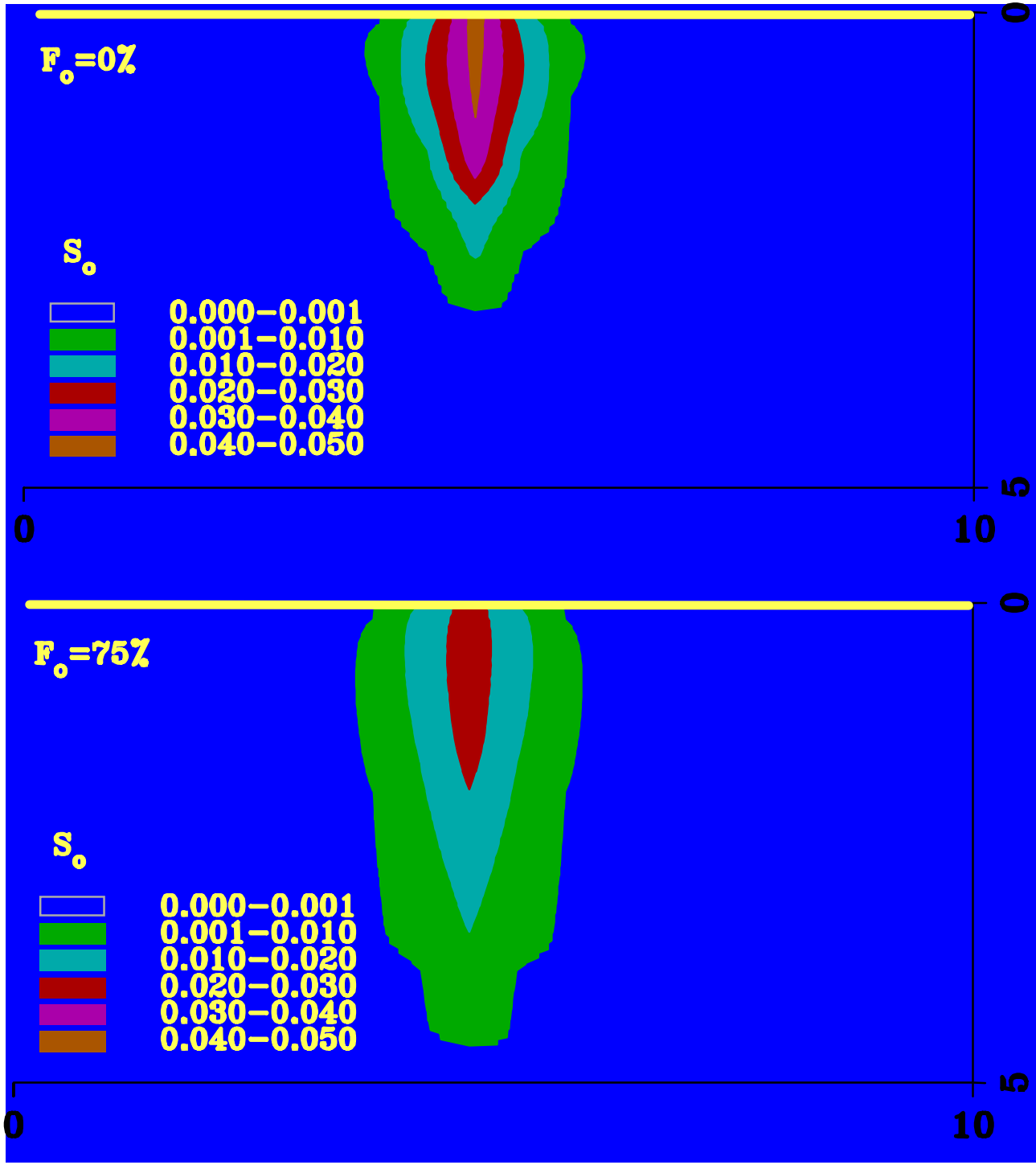


Figure 14: Predicted residual distribution of PCE after 30 days when the 2-D soil profile is completely water-wet and when it has fractional wettability [Bradford et al., 1998b].

This simulator has also been employed to investigate the potential influence of coupled physical and chemical heterogeneity on DNAPL flow and entrapment. For reasonable ranges of wettability characteristics, simulations suggest that spatial variations in wettability can have a dramatic impact on DNAPL distributions. Interfaces of capillary property contrast (soil texture or soil wettabilities) lead to higher organic saturations, increased lateral spreading, and decreased depths of organic liquid infiltration (cf. Figure 15).

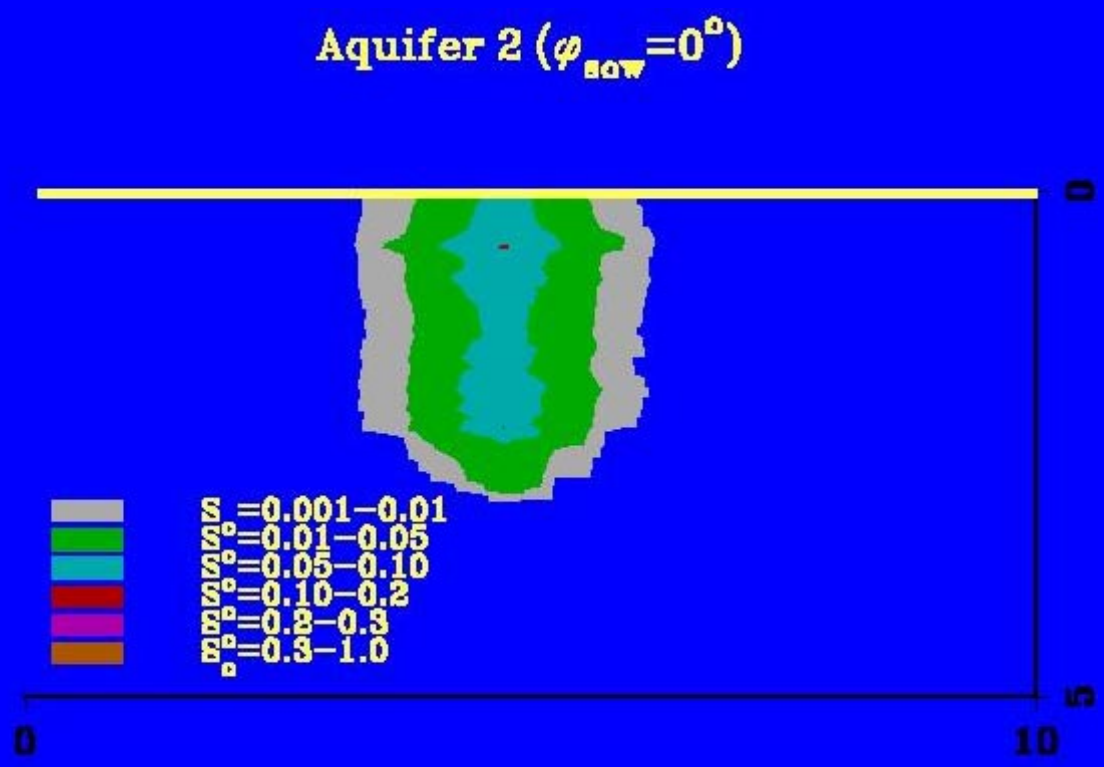
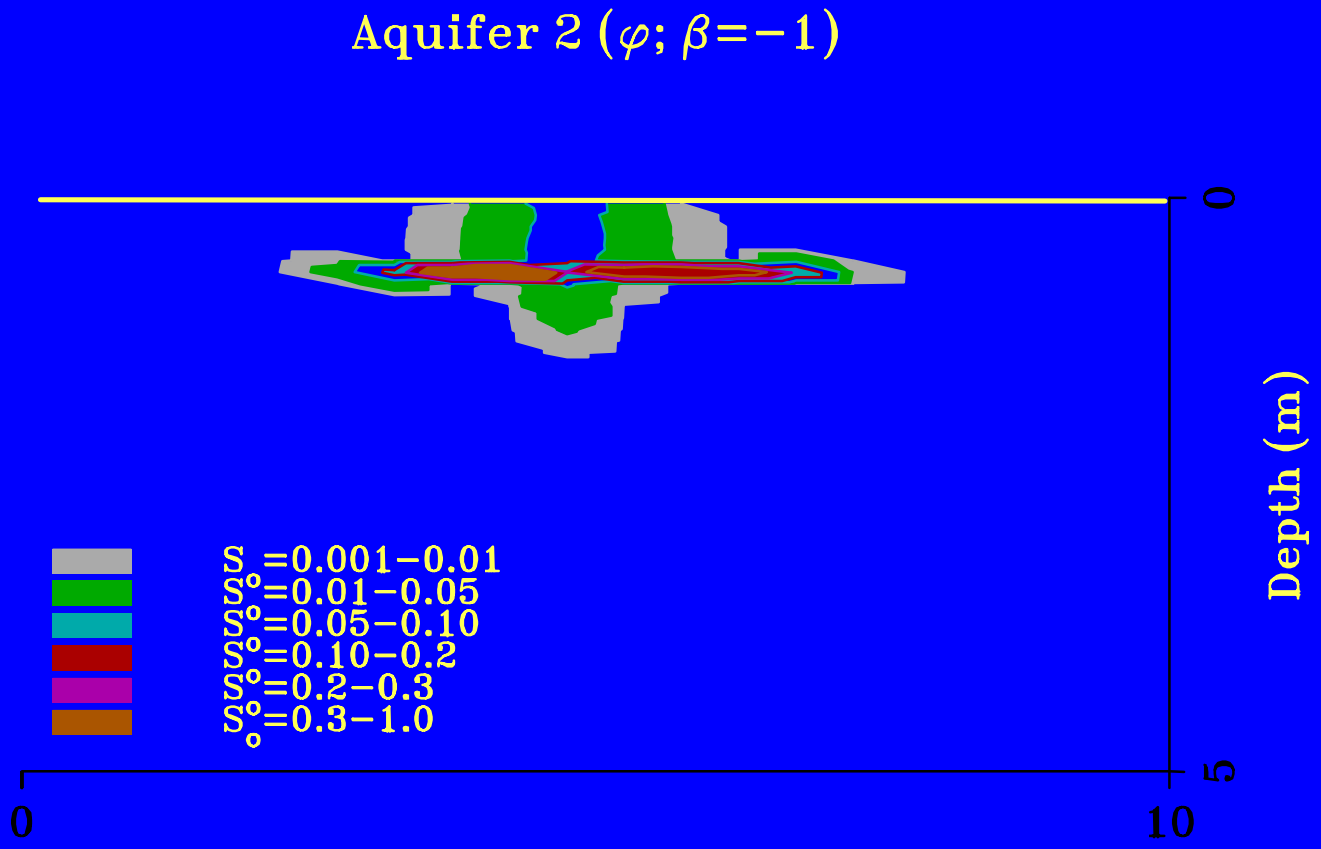


Figure 15 (continues on next 4 slides): Predicted distribution of PCE after 10 days when the physically heterogeneous 2-D soil profile (cf. Figure 11) has various wettability properties [Bradford et al., 1998a].



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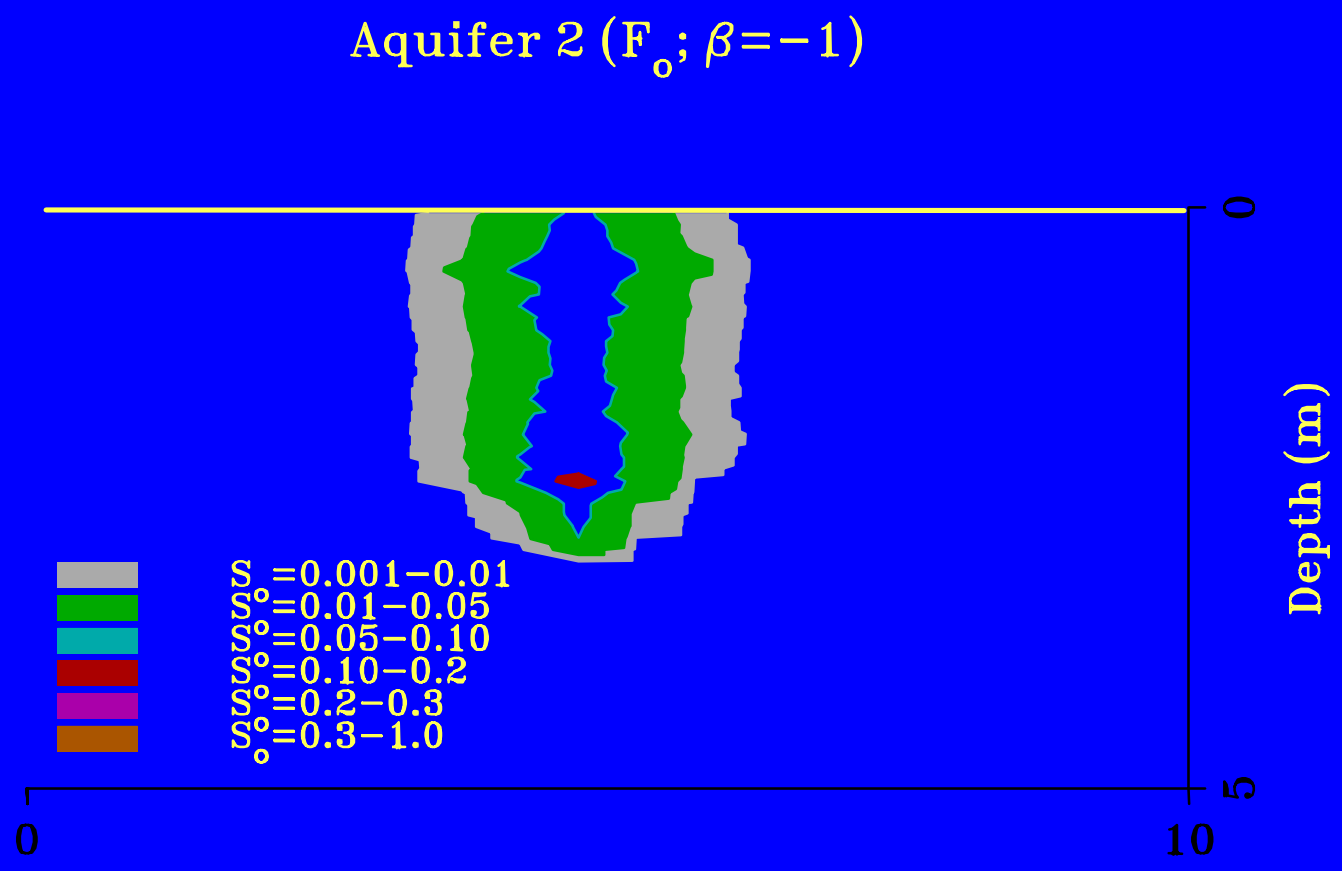

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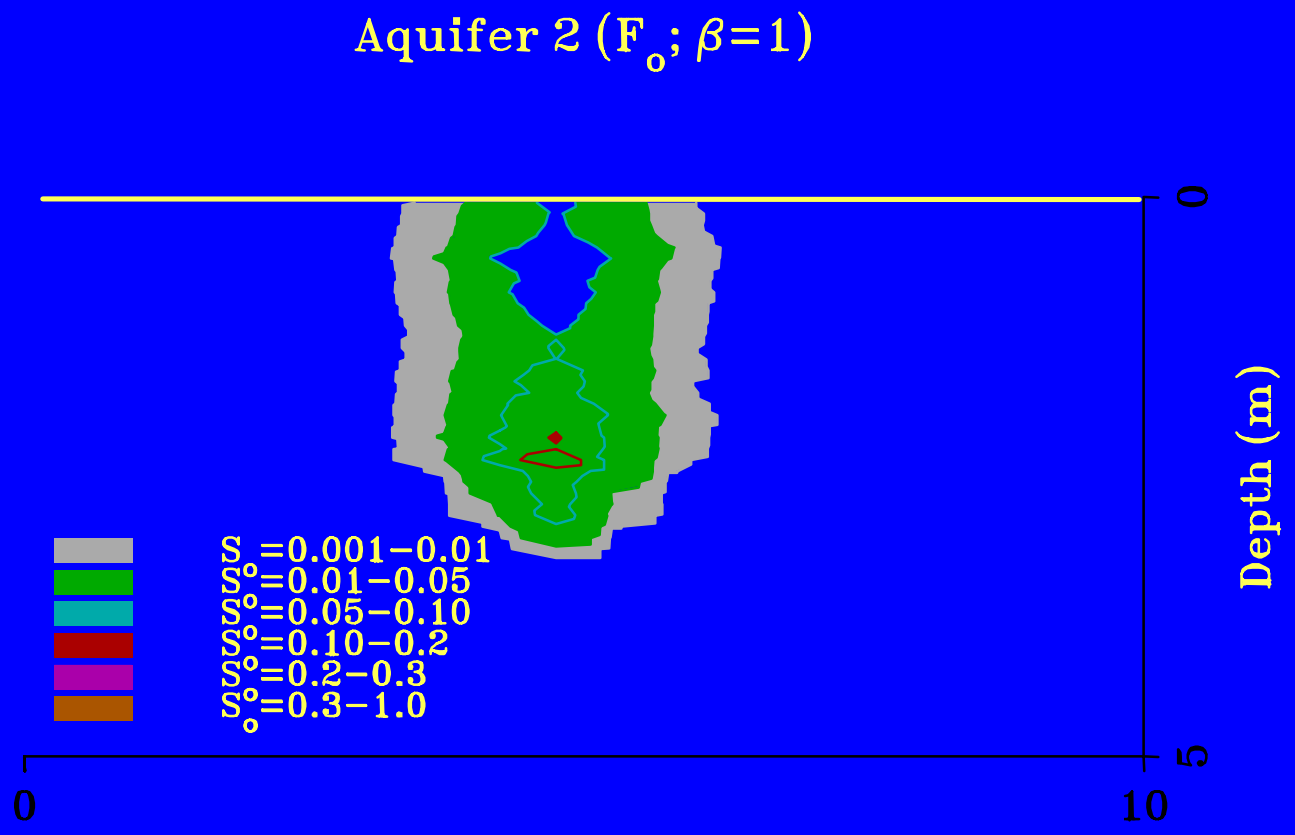

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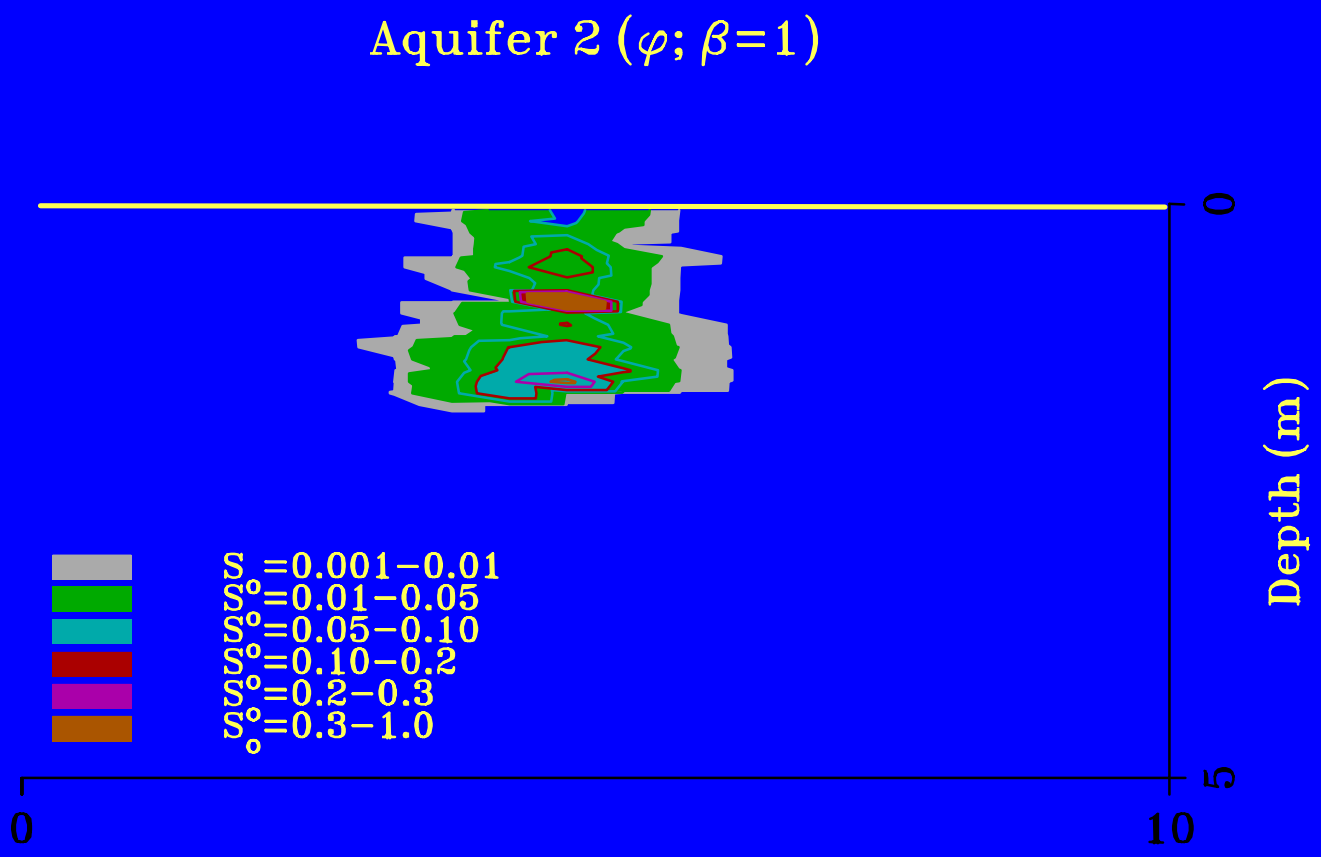

Figure 15 (cont.):

Summary & Conclusions

- Representative surface active agents (DDA and OA) were found to exhibit pH dependent acid-base speciation in aqueous solution which resulted in aqueous chemistry-dependent interfacial tension and/or wettability in these systems. Measured capillary pressure curves for these systems showed a strong dependence on the aqueous phase chemistry.
- Capillary pressure relations have been measured for PCE, water, and synthetic and natural fractional wettability porous medium systems. Results indicate that as the organic-wet fraction of a soil increases, for a given saturation and saturation history, the residual water saturation increases and the organic liquid-water capillary pressure decreases, becoming negative during imbibition.
- An automated apparatus to measure the hydraulic property relations on a number of columns in parallel has been constructed and experimental protocols have been established for its operation.
- A two-dimensional multiphase flow simulator has been modified to account for coupled physical and chemical aquifer heterogeneity. Simulations of DNAPL migration in physically homogeneous systems suggest that an increasing contact angle or organic-wet fraction of a soil will slow migration of the DNAPL, creating larger contaminated aquifer regions with lower organic saturations. In coupled physically and chemically heterogeneous formations, interfaces of capillary property contrast (soil texture or soil wettabilities) will lead to higher organic saturations, increased lateral spreading, and decreased depths of organic liquid infiltration.

Future Work

Future research will investigate the extension of experimental results to other organic liquid-water systems having various aqueous and solid phase chemistries. The determination, quantification, and prediction of interfacial and hydraulic properties will be an area of special focus. Results from these studies will be utilized in the development and design stages of the two-dimensional organic liquid infiltration experiments which will be initiated this year. Numerical modeling efforts will initially be directed towards the simulation of transient outflow experiments (to determine the relative permeability relations), and two-dimensional infiltration experiments. Modifications to the simulator to account for concentration-dependent interfacial tension and wettability will be made as information and insight is gained from the above mentioned experiments.

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