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Research and Development

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Project Summary

Determination of Capillary Pressure-Saturation Curves Involving TCE, Water and Air for a Sand and a Sandy Clay Loam

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The contamination of aquifers and other groundwater by Non-Aqueous Phase Liquids (NAPLs) such as chlorinated solvents, has become a major concern in many areas of the U.S. Characterization and modeling of these contaminants require accurate and realistic data for the fluids and media involved. Most capillary pressure (P_c) - saturation (S) curves are determined with a pressure or tension apparatus that often contains a porous medium sample of more than 5 cm in height. If the porous medium sample consists of a rather coarse material and the interfacial tension between the wetting and non-wetting fluid is sufficiently low, it is not inconceivable that large changes in S occur over the height of the sample. Using the standard procedure of measuring the outflow volume of one of the fluids, from which average values of S are calculated, can therefore result in substantial errors. In this study, a method is proposed to measure P_c-S drainage and imbibition relationships for TCE/air and TCE/water systems at points along a 0.94-m long sand column and a 0.94-m long sandy clay loam column with the help of a gamma radiation system and from knowledge of the fluid pressure distributions in the porous media at hydraulic equilibrium. The results showed that the S-values of the fluids present in the sand, either TCE and air or TCE and water, changed from complete saturation to their residual values, and vice versa, over P_c changes ranging from 2.5 to 10 cm of water pressure. For the sandy clay loam the changes in S of the fluids were less dramatic with changes in P_c, making the use of a pressure cell more acceptable, although the P_c-S curves will still not be as accurate as for the method used in this study.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Dense non-aqueous phase liquids (DNAPLs), such as trichloroethylene (TCE) are the cause of many current ground-water contamination problems. An essential component in understanding and simulating multiphase fluid flow is the accurate determination of the hydraulic properties of the different fluids involved. It has been standard procedure to use pressure cells to determine capillary pressure (P_c)-saturation (S) curves, where $P_c = P_{nw} - P_w = 2\sigma/r$ (P_{nw} = pressure of the non-wetting fluid; P_w = pressure of the wetting fluid; σ is the interfacial tension; and r is the radius of curvature at the interface of the two fluids). The interfacial tension at 20ºC between TCE and air is only 30 mN/m, and 38 mN/m between TCE and water, as compared to 72 mN/m between water and air. The height of the pressure cell may therefore be critical during the displacement of one fluid by another if S changes rapidly with small changes in P_c, as is the case for coarser materials (the density of TCE is 1.456 g/cm^3 and its viscosity ratio with respect to water 0.52, both at 20°C). The main objective of this study was therefore to explore an improved way to determine P_c-S curves for TCE/air and TCE/water during wetting and drainage of the wetting fluid (hysteresis loops) in a sand and a sandy clay loam. Two additional factors of importance for simulation and cleanup purposes are the P_c-values at which the non-wetting fluid starts to displace the wetting fluid and the values for the residual saturation of TCE. These values were determined as well.

Materials and Methods

A 1.0-m long glass column experiment was designed to allow accurate P_c-S information to be collected at any given point along the column. The column (i.d. = 7.5 cm), with Teflon end caps, was first filled uniformly to a height of 0.94 m with Flintshot 2.8 Ottawa (medium) sand and later with a sandy clay loam (25% non-swelling clay, 20% silt and 55% sand). The outlet at the bottom of the column was connected to a TCE supply (or drainage) bottle by Teflon tubing. This bottle was also used to adjust the fluid pressures in the column by lowering or raising it.

For the TCE/air combination, the initially air-saturated column was subjected to the following cycles:

- Saturation from the bottom, by slowly raising the bottle, until TCE was ponded on the surface. It was not possible to displace all of the air in this manner, so a certain amount of air should be considered trapped.
- TCE displaced by air by stepwise lowering the bottle.
- Air displaced by TCE by stepwise raising the bottle.
- Upon reaching equilibrium after each step change (no more flow from or into the supply bottle), dual-energy gamma radiation measurements were taken at the desired locations to determine the volumetric TCE content, θ_{TCE}.

P_c-values were obtained from knowledge of the height of the TCE-level in the supply/drainage bottle. Corresponding S-values were calculated from S = θ_{TCE}/porosity. By matching the corresponding P_c and S-values, P_c-S data points were obtained.

Upon completion of the TCE/air experiments, a 2-cm layer of water (top of water at 96 cm above reference level) was maintained on the soil surface to displace the TCE by water, or vice versa, and P_c-S curves were determined for TCE/water in a similar manner as described for TCE/air. The dual-energy gamma radiation system now determined both θ_{TCE} and the volumetric water content, θ_w. An example of the P_c determination for a TCE/water system is shown in Figure 1. The TCE-level in the supply/drainage bottle for this example was at 85.7 cm.

The P_c-S data were fitted with the van Genuchten curve fitting procedure. The P_c entry value for the non-wetting fluid was taken as 1/α.

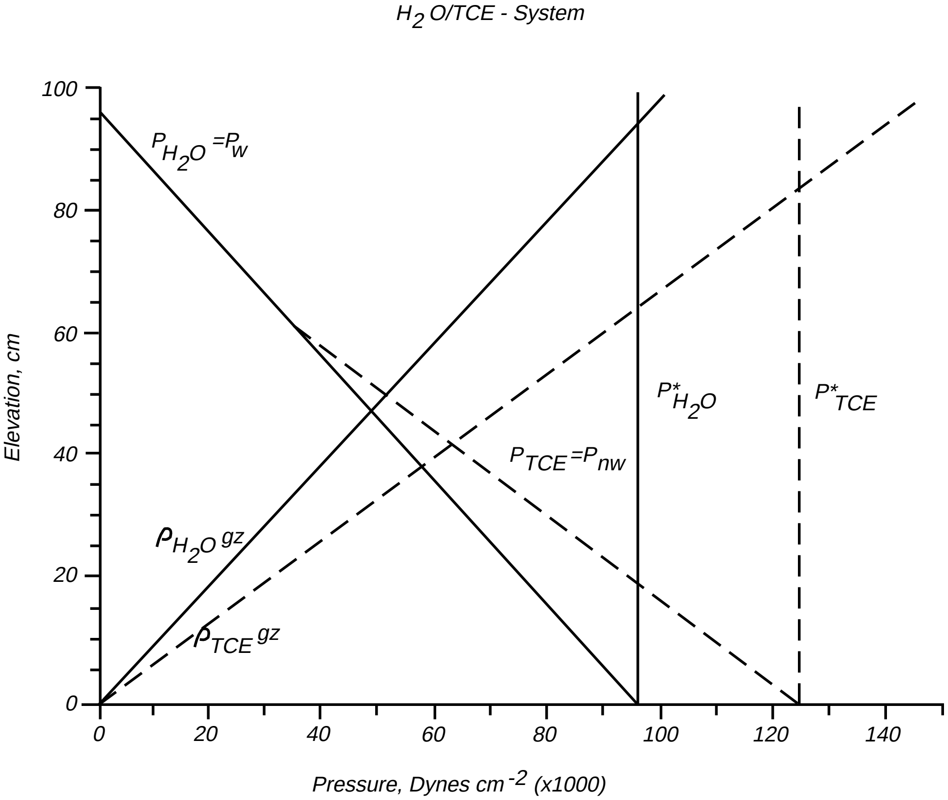

Figure 1. *Graphical display of fluid pressures in a TCE/water system when the TCE level in the supply/drainage bottle is 85.7 cm above the reference level. At 51.5 cm above the reference level the pressure in the TCE is* $P_{TCE} = P_{nw} = (85.7 - 51.5) \times 1.456 \times 1000 =$ *49,800 dynes/cm*^{2}*, while the water pressure* $P_{H2O} = P_w = (96 - 51.5) \times 1 \times 1000 =$ *44,500 dynes/cm*^{2}*. Therefore,* $P_c = P_{nw} - P_w =$ *5,300 dynes/cm*^{2} *or 5.3 cm of equivalent water pressure.*

Results and Discussion

The full explanation of this research is reported in the full report. It contains extensive data tables and parameter values for the van Genuchten function obtained for many different imbibition and drainage cycles, plus graphical representations of both the acquired and fitted data.

Average values for the bulk density, porosity, θ_{TCE}, and S as measured at nine locations along the TCE-saturated column are listed in Table 1 for both the sand and sandy clay loam.

Flintshot 2.8 Ottawa Sand

An example set of TCE saturation data during the displacement of TCE by air (TCE drainage) is given in Table 2 and graphically displayed in Figure 2. An example of similar results, obtained during the displacement of air by TCE (TCE wetting), is illustrated in Figure 3. The solid lines in Figures 2 and 3 represent the curves as fitted by the van Genuchten procedure. It should be noted that the fitted curves look somewhat awkward at times, because they only connect points calculated from measured P_c-values. To appreciate the amount of hysteresis, the fitted van Genuchten functions are shown without values. Based on actual measurements, these values were the data points in Figure 4. The sets of data evaluated in the full report showed that S changes from its maximum to its minimum value, and vice versa, over a capillary pressure difference of about 5.5 cm of equivalent water pressure. The data also show that ignoring hysteresis can have a major effect on S.

A similar presentation is given for the results obtained during the displacement of TCE by water (Figure 5) and for the displacement of water by TCE (Figure 6). Representation of hysteresis is shown again using the fitted van Genuchten functions in Figure 7. The change in S with capillary pressure is again very rapid, especially for the (water) wetting curve. The amount of hysteresis in this case is even more pronounced than for the TCE/air system.

The average value for the van Genuchten parameter α during the displacement of TCE by air was 0.155 (st. dev. = 0.020), which means that the average air entry value into a TCE saturated system is 6.5 cm of equivalent water pressure (st. dev. = 0.7 cm).

For the TCE/water system the pressure in the TCE must, on average, be at least 12.0 cm higher (st. dev. 0.6 cm) than in the water before it will displace the water.

Table 1. *Average values for the bulk density (ρ_b), the corresponding porosity ($\in$) based on a particle density of 2.65 g/cm^3, and the average volumetric TCE content (θ-TCE) during TCE saturated conditions (upon TCE wetting into dry soil). N is the number of observations for each location, z is the distance to the reference level, and S is the degree of TCE saturation.*

Location	z cm	ρ_b g/cm^3	N	$\in$ cm^3/cm^3	θ-TCE cm^3/cm^3	N	S
				Flintshot Sand			
1	91.5	1.52	92	0.426	0.332	5	0.78
2	81.5	1.48	92	0.440	0.360	9	0.82
3	71.5	1.47	92	0.446	0.376	11	0.84
4	61.5	1.45	92	0.454	0.371	13	0.82
5	51.5	1.51	92	0.431	0.353	17	0.82
6	41.5	1.50	92	0.433	0.359	17	0.83
7	31.5	1.49	92	0.438	0.356	19	0.81
8	21.5	1.48	92	0.442	0.365	21	0.83
9	11.5	1.48	92	0.443	0.361	21	0.82
				Sandy Clay Loam			
1	91.5	1.25	253	0.528	0.443	48	0.84
2	81.5	1.24	253	0.531	0.445	48	0.84
3	71.5	1.22	253	0.538	0.454	48	0.84
4	61.5	1.23	253	0.535	0.439	48	0.82
5	51.5	1.24	253	0.531	0.446	48	0.84
6	41.5	1.23	253	0.536	0.453	48	0.84
7	31.5	1.23	253	0.537	0.462	48	0.86
8	21.5	1.22	253	0.539	0.446	48	0.83
9	11.5	1.27	253	0.521	0.444	48	0.85

Table 2. *Volumetric TCE content (θ-TCE) as a function of capillary pressure (P_c), expressed in cm of equivalent water pressure, during displacement of TCE with air in a 1-m long column filled with Flintshot 2.8 Ottawa sand. Location #3.*

θ-TCE cm^3/cm^3	P_c cm	θ-TCE cm^3/cm^3	P_c cm	θ-TCE cm^3/cm^3	P_c cm
0.376	0.0	0.040	20.5	0.038	39.5
0.380	0.9	0.044	21.3	0.042	40.9
0.369	2.3	0.045	22.0	0.036	42.4
0.371	3.8	0.046	22.7	0.033	43.8
0.374	4.5	0.038	23.4	0.042	45.3
0.320	5.2	0.043	24.9	0.044	46.7
0.230	6.0	0.044	26.4	0.038	47.5
0.150	6.7	0.037	27.8	0.042	48.2
0.113	7.4	0.041	29.3	0.040	48.9
0.092	8.2	0.044	30.7	0.041	49.7
0.066	8.9	0.044	32.2	0.038	50.4
0.060	10.3	0.038	32.9	0.041	51.1
0.055	11.8	0.043	33.6	0.033	51.8
0.049	13.2	0.038	34.4	0.033	52.6
0.045	14.7	0.037	35.1	0.039	53.3
0.045	16.2	0.039	35.8	0.047	54.0
0.042	17.6	0.040	36.5	0.041	55.5
0.045	18.3	0.044	37.3	0.027	56.9
0.038	19.1	0.046	38.0		
0.039	19.8	0.042	38.7		

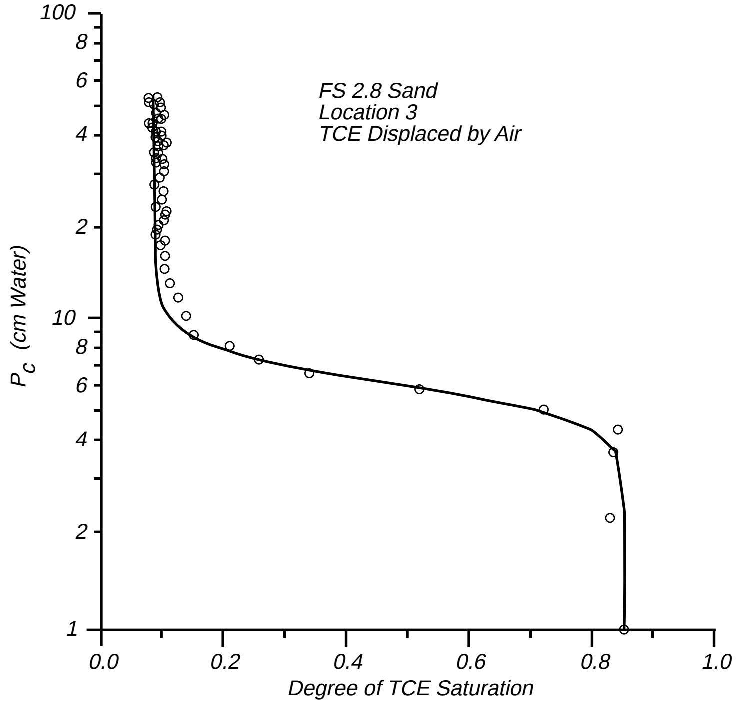

Figure 2. *TCE drainage curve at location 3 for a Flintshot 2.8 Ottawa sand containing TCE and air.*

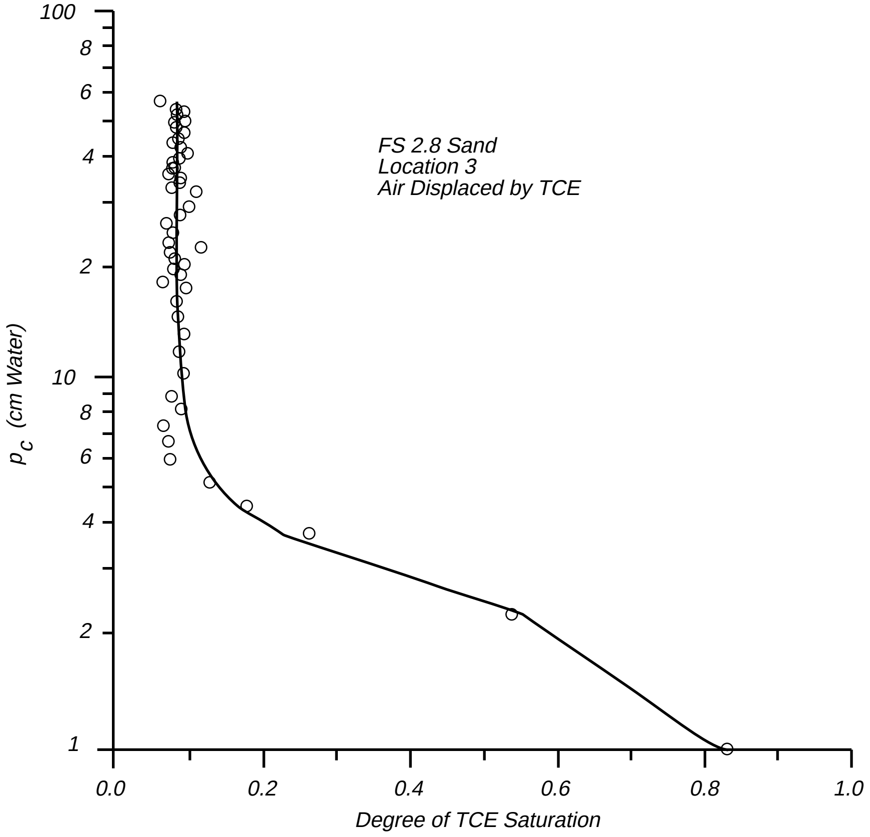

Figure 3. *TCE imbibition curve at location 3 for a Flintshot 2.8 Ottawa sand containing TCE and air.*

During the displacement of TCE by air and of TCE by water, the degree of TCE saturation had rapidly attained their residual values. Based on actual measurements, these values were 0.085 (number of measurements = 150) and 0.050 (number of measurements = 506) for the TCE/air and TCE/water, respectively. Subsequent flushing of the column with water had no measurable impact on the residual S-value of 0.050.

Sandy Clay Loam

The experimental setup and procedure for the sandy clay loam soil was the same as for the Flintshot 2.8 sand. Example graphs for the TCE saturation data during the displacement of TCE by air (TCE drainage) and for the displacement of air by TCE (TCE wetting) are shown in Figures 8 and 9, respectively. The amount of hysteresis becomes obvious from the fitted curves (Figure 10). It is obvious that changes in S with P_c are much more gradual and that hysteresis is less profound than for the sand (Figures 4 and 7).

Example graphs of the results obtained during the displacement of TCE by water and the displacement of water by TCE are presented in Figures 11 and 12, respectively. Due to the similarity in data and the limited range in S-values, several measurement locations were combined into one graph and the P_c-S wetting and drainage curve for the combined data sets was used to demonstrate the amount of hysteresis (Figure 13).

The average value for α during the displacement of TCE by air was 0.055 (st. dev. = 0.012), which means that the average air entry value into this TCE-saturated system was 18.3 cm of equivalent water pressure (st. dev. = 3.4 cm).

For the TCE/water system, the pressure in the TCE was, on average, at least 24.0 cm higher (st. dev. 1.4 cm) than in the water before displacement of the water occurred.

In considering the two porous medium systems used in this study, the data show very rapid changes in saturation with only very small changes in capillary pressure in the medium sand for both the TCE/air and TCE/water systems. The use of alternative procedures, such as the use of pressure cells, should therefore be avoided for coarser materials. The changes in saturation with capillary pressure were more gradual for the sandy clay loam, which would result in smaller differences between the P_c-S curve determined with a pressure cell and the "true" curve. Although both media exhibited considerable hysteresis, it was most pronounced for the medium sand containing TCE and water. The average air

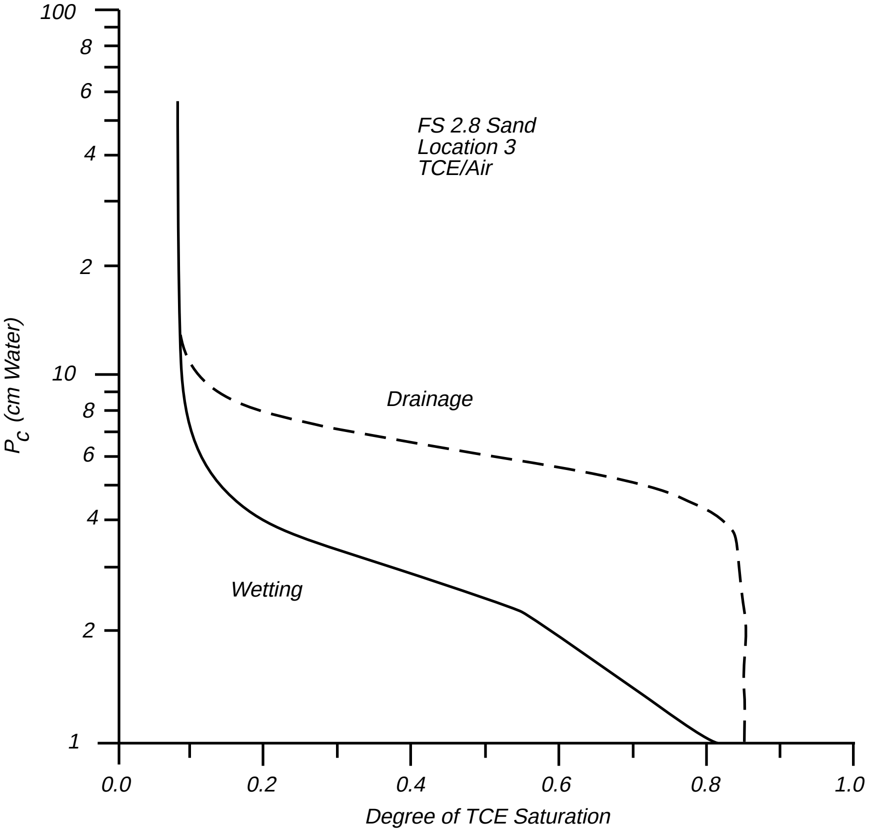

Figure 4. *TCE drainage and imbibition curve at location 3 for a Flintshot 2.8 Ottawa sand containing TCE and air.*

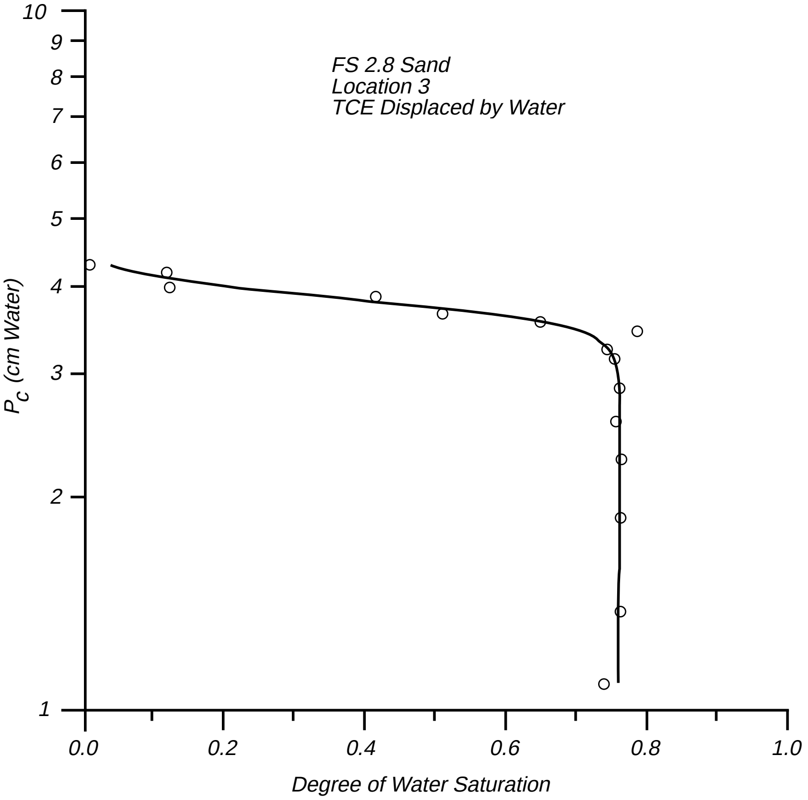

Figure 5. *Water imbibition curve at location 3 for a Flintshot 2.8 Ottawa sand containing TCE and water.*

entry value for the TCE/air systems was 6.5 cm for the medium sand and 18.3 cm for the sandy clay loam. For the TCE/water systems the average TCE entry value was 12.0 cm for the medium sand and 24 cm for the sandy clay loam. The average measured TCE residual saturation for the sand was 0.085 when TCE was displaced by air and 0.050 when it was displaced by water.

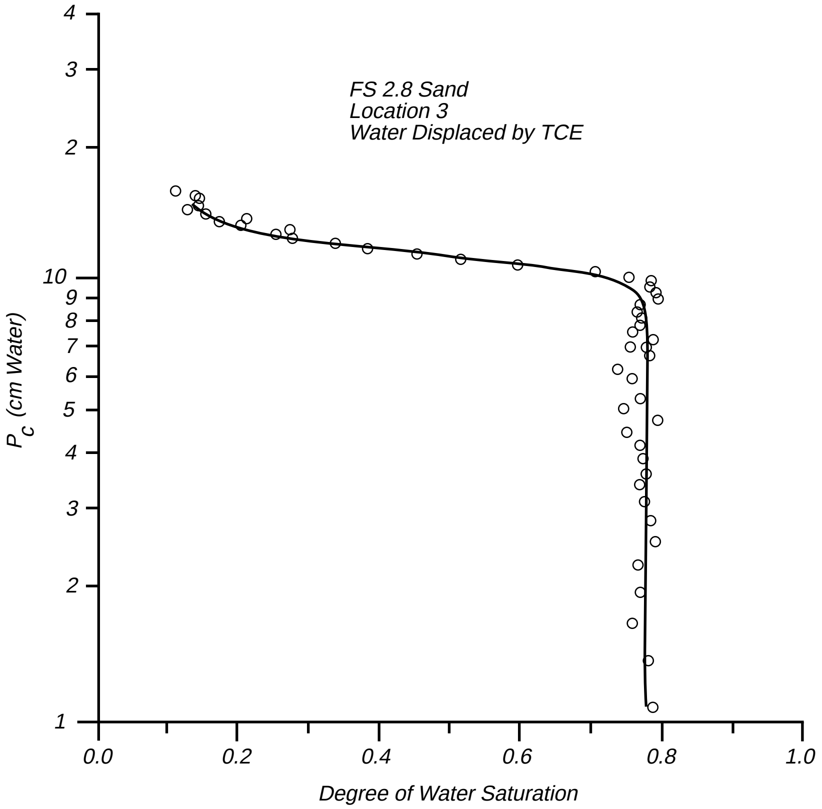

Figure 6. *Water drainage curve at location 3 for a Flintshot 2.8 Ottawa sand containing TCE and water.*

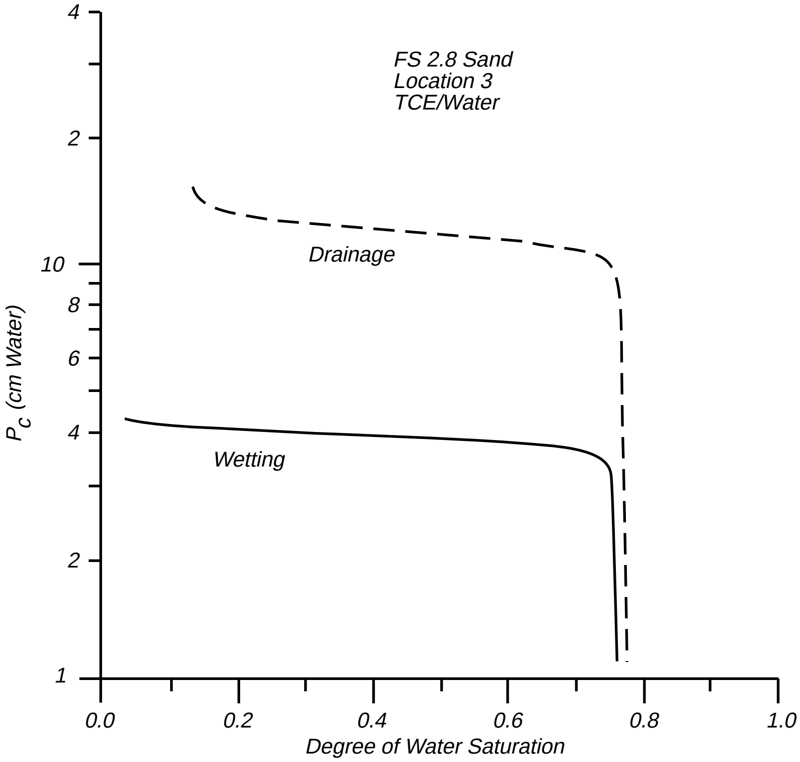

Figure 7. Water imbibition and drainage curve at location 3 for a Flintshot 2.8 Ottawa sand containing water and TCE.

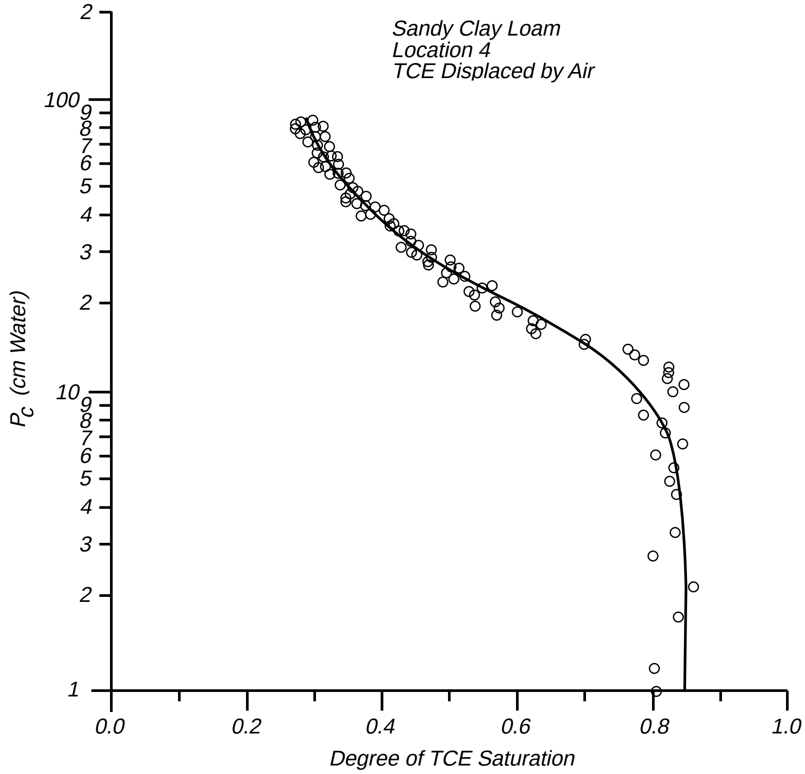

Figure 8. TCE drainage curve at location 4 for a sandy clay loam containing TCE and air.

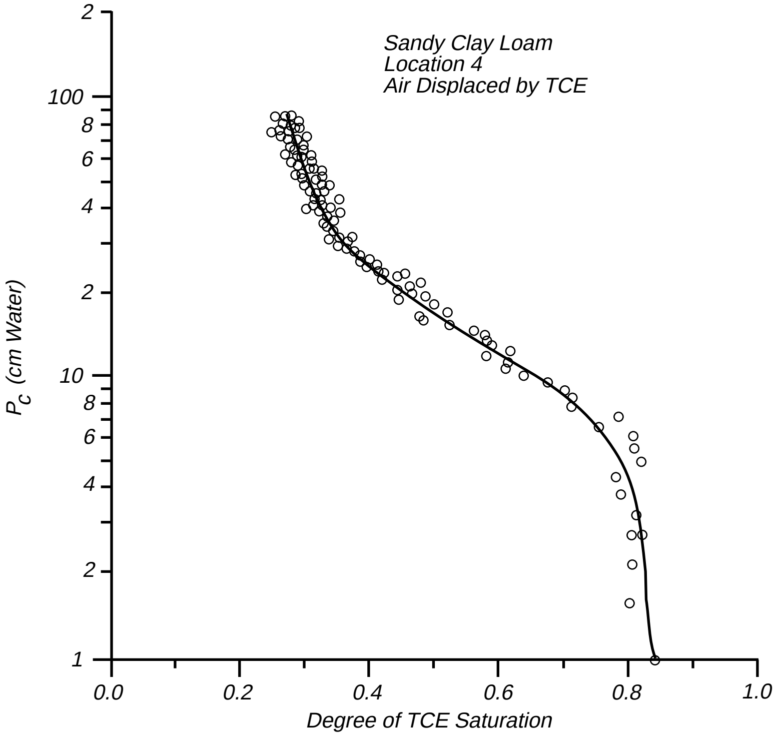

Figure 9. TCE imbibition curve at location 4 for a sandy clay loam containing TCE and air.

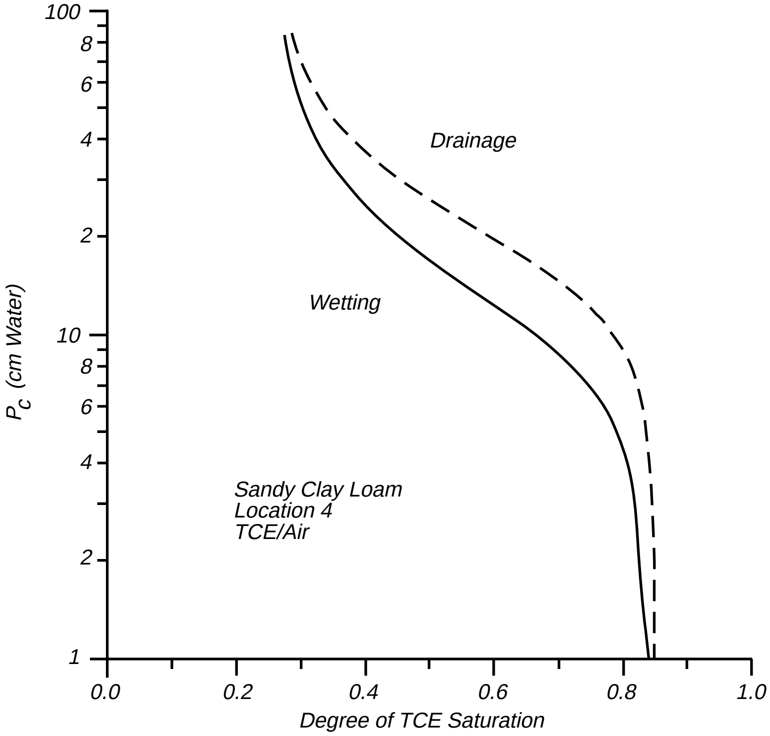

Figure 10. *TCE drainage and imbibition curve at location 4 for a sandy clay loam containing TCE and air.*

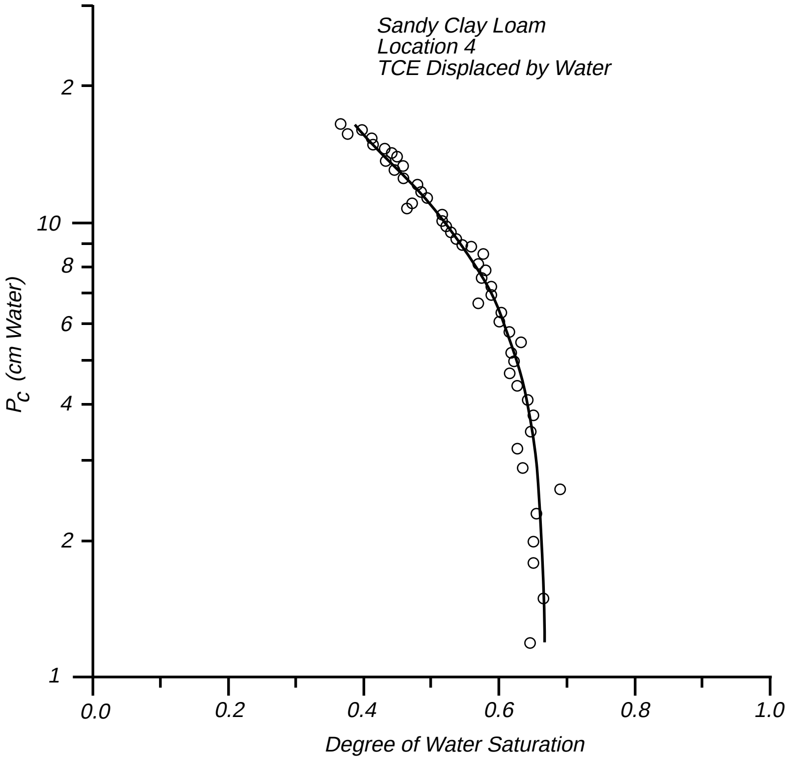

Figure 11. *Water imbibition curve at location 4 for a sandy clay loam containing TCE and water.*

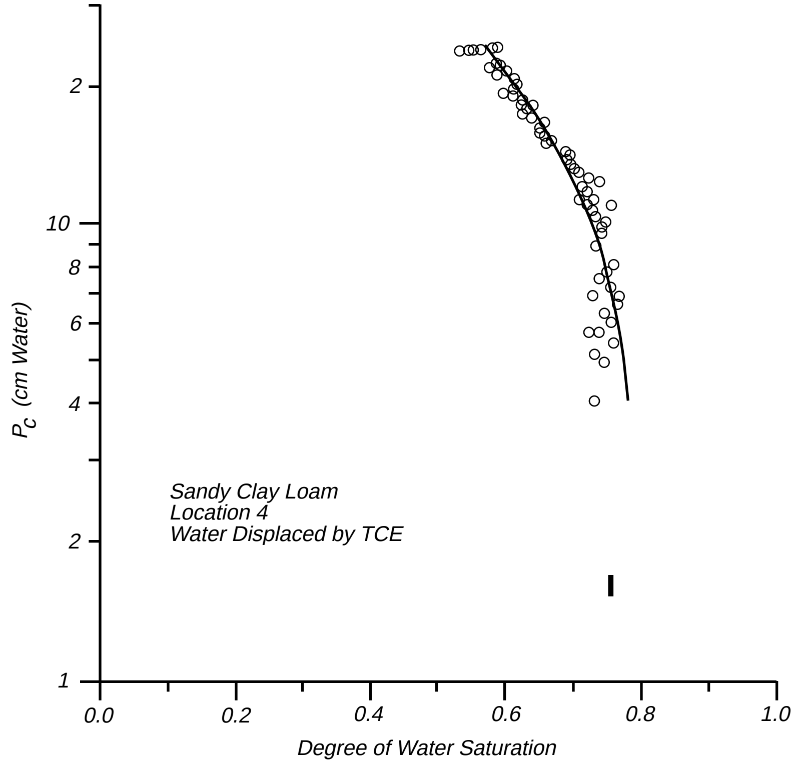

Figure 12. *Water drainage curve at location 4 for a sandy clay loam containing TCE and water.*

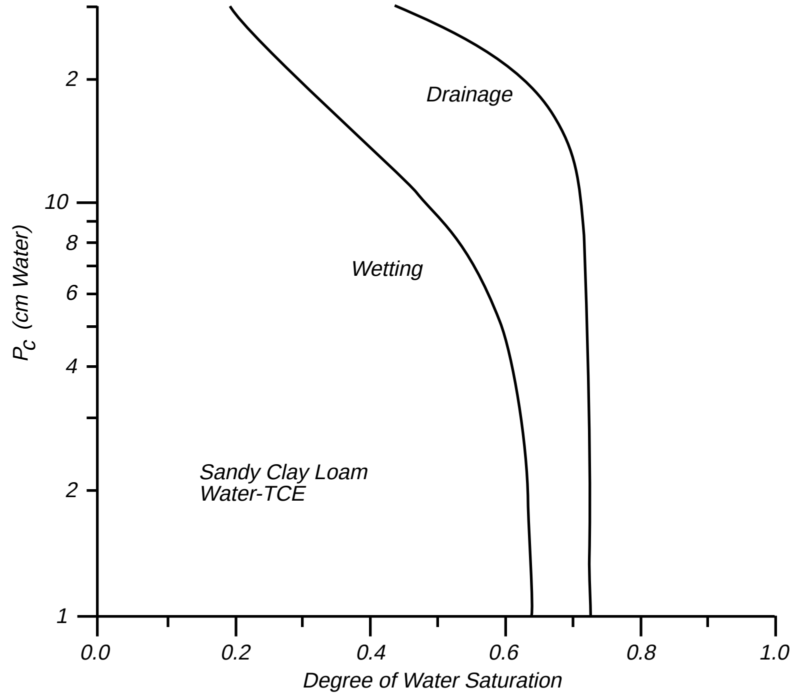

Figure 13. Water imbibition curve (combined data of locations 5, 6, and 7) and drainage curve (combined data of locations 3 and 4) for a sandy clay loam containing TCE and water.

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James W. Weaver *is the EPA Project Officer (see below).*

The complete report, entitled "Determination of Capillary Pressure - Saturation Curves Involving TCE, Water and Air for a Sand and a Sandy Clay Loam," (Order No. PB94-130 754/AS; Cost: $27.00, subject to change) will be available only from
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