Residual saturation of packed columns with chlorinated solvents

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Abstract

Sparingly soluble organic contaminants (non-aqueous phase liquids or NAPLs) spread laterally at the interface between layers of differing permeability, in porous media, due to capillary forces. Less dense (than water) substances infiltrate and become trapped at the capillary fringe. More dense substances (dense non-aqueous phase liquids or DNAPLs) penetrate to and through the saturated zone after passing through the unsaturated zone. However, residual DNAPL remains trapped as discrete pendular, funicular and capillary bodies. A Model has been developed to estimate residual retentions in two-phase (DNAPL–water) systems under unsaturated (vadose zone) conditions, in the presence of air. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The characterization of a soil containing very poorly soluble organic contaminants (non-aqueous phase liquids or NAPLs), as separate phases, presents a formidable challenge. Infiltrating NAPLs migrate downward through the unsaturated zone as a mobile liquid phase. Lateral spreading occurs at interfaces between layers of the solid matrix with different organic and/or water permeabilities, due primarily to capillary forces. As the organic phase flows through interparticle voids, a residual volume of NAPL is trapped by interfacial forces at air–water interfaces in the unsaturated zone.

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NAPLs are classed as 'less dense', i.e. less-dense non-aqueous phase liquids (LNA-PLs) or 'dense', i.e. dense non-aqueous phase liquids (DNAPLs). Benzene and other hydrocarbons found in fuels derived from petroleum are LNAPLs; Per(tetra)chloroethylene (PCE) and related chlorinated aliphatic hydrocarbons are DNAPLs. LNAPLs are trapped in the capillary fringe; DNAPLs can penetrate the saturated zone but may be trapped in the unsaturated zone, also. Residual NAPLs in the unsaturated zone persist for long periods as sources of contamination via diffusion, convection and dissolution.

Residual NAPL in unsaturated porous media may be present as pendular, funicular or capillary liquid. Pendular refers to discrete rings of liquid at interparticle contact points. With reference to aquifers, liquids are retained in the pendular configuration in regions of unsaturated soil at heights well above the water table. Closer to the water table, the total liquid content of soil increases and air tends to be excluded from interparticle voids, allowing formation of larger fluid bodies that encompass several interparticle contact points, i.e. funicular liquids. At the interface between saturated and unsaturated zone, funicular fluid bodies can merge to form a continuous capillary fluid. Capillary fluids occur in intraparticle voids, i.e. pores also. Hoag and Marley [1] reported that nearly 80% of organic liquid trapped in gravity-drained packed beds was retained as pendular fluid. Thus, the capacity of unsaturated porous media to serve as NAPL sinks may be approximated closely in terms of pendular fluid retention.

The potential for NAPL contamination of ground water, due to surface spillage or leakage from storage vessels, is dictated by retention in the unsaturated zone. Several investigators have observed NAPL retention in unsaturated porous media. Hoag and Marley [1] examined gasoline retention in columns packed with uniform Connecticut sand. Gasoline residual saturation, i.e. the fraction of available void volume occupied by gasoline, increased with increasing packing density or decreasing particle diameter. By assuming gasoline spreads over the entire surface of wet and dry sand particles, these authors postulated that specific gasoline retention (g gasoline per cm^2 of soil surface area) is linearly related to effective particle diameter.

McBride et al. [2] observed propagation of a NAPL front under the influence of capillary forces in water-wetted glass beads. The rate and extent of capillary rise and residual NAPL saturation was a function of the sign and magnitude of the spreading coefficient, C_{sp}. The sheading coefficient is a linear combination of air, water and NAPL interfacial tensions that quantifies the behaviour of a NAPL at an air–water interface, as follows:

$$C_{sp} = \gamma_{aw} - (\gamma_{nw} + \gamma_{an})$$

where γ is interfacial tension and the subscripts a, n and w refer to air, NAPL and water, respectively.

For compounds with negative spreading coefficients $\{C_{sp} \ll 0\}$, equilibrium capillary rise and retention are less than the same quantities for compounds with a C_{sp} of approximately zero. Chlorinated aliphatic hydrocarbons have negative spreading coefficients; contact angles are generally between 0° and 90°, leading to the formation of stable NAPL lenses at the leading edge of an advancing front.

The objectives of the research discussed in this paper were to: (i) observe the effects of media dimensions and fluid properties on water and NAPL retention in unsaturated

porous media, consisting of water-wet glass beads, and (ii) modify an existing predictive retention model. Residual saturations for 1,2-dichloroethane (DCA), 1,1,1-trichloroethane (TCA) and chloroform (trichloromethane or TCM) were measured in packed columns.

2. Model development

A model developed by Rugge [3] was modified to more precisely represent retention of water and DNAPLs in unsaturated porous media. As in the initial model, residual saturations are related to a dimensionless parameter, dependent on solid medium and fluid properties. A force balance is derived in terms of capillary and gravitational forces acting on the liquid(s), in the vertical plane, rather than on the cohesive forces acting between the solid matrix by the liquid(s).

2.1. Estimating bed properties

The properties of a bed of homogenous spherical particles can be estimated from purely geometric considerations; see Ref. [4]. Coordination number, porosity, average capillary diameter, and related bed properties fall somewhere between values for ideal cubic and hexagonal packing arrangements; see Table 1. Coordination number is the number of contact points between individual bed units. Porosity is determined relatively easily. Other parameters can be related to porosity by linear interpolation between limit values of cubic and hexagonal configurations.

2.2. Single-phase pendular liquid retention in porous media

A long column of beads with pores filled initially with water, then drained for a long period, retains water predominantly as pendular rings; see Ref. [5]. Retention of water is described in terms of wetting angle (ϕ) and particle radius (r_p); see Ref. [6] and Fig. 1a. The retention or wetting angle is defined by Fisher [6] as the angle between the line connecting the particle centers (through the interparticle contact point) and the line orthogonal to the surface at the point of water–particle contact.

Assuming a zero-degree contact angle between liquid and solid at air–water–solid contact points, the volume of fluid trapped in a single-phase pendular ring can be

Table 1
Packed bed properties for homogeneous spherical packing

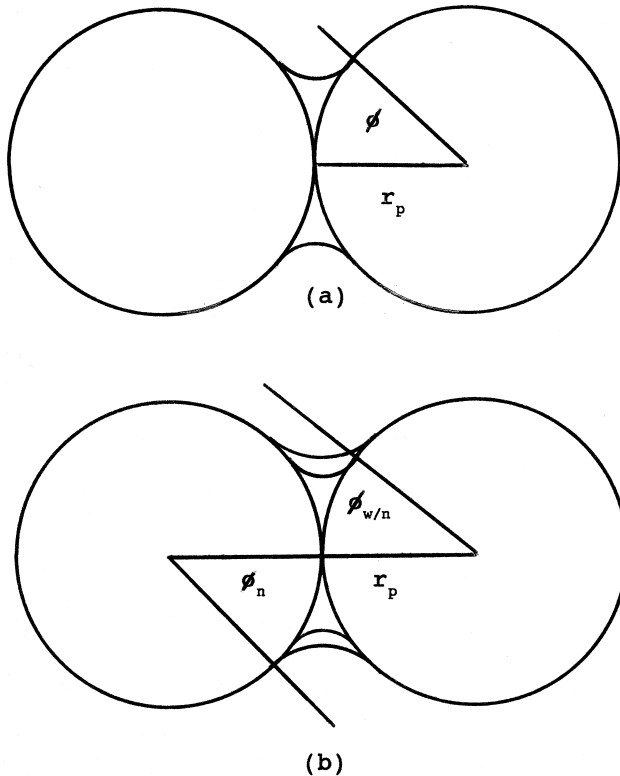| Packing arrangement	Coordination number	Porosity (percent)	Narrowest capillary	Widest capillary	Packing angle
Cubic	6	47.6	$0.41r_p$	$0.73r_p$	90°
Random	6–12	47.6–25.9	$0.41r_p$–$0.16r_p$	$0.73r_p$–$0.29r_p$	60°–90°
Hexagonal	12	25.9	$0.16r_p$	$0.29r_p$	60°

Fig. 1. Representations of pendular fluids in homogeneous porous media. (a) One-phase (water); (b) Two-phase liquid cup. ϕ_n is the angle at the air–NAPL–water interface and $\phi_{w/n}$ is the angle at the NAPL–water–solid interface.

calculated directly from geometric considerations. Total liquid retention is the sum of pendular ring volumes over the entire column. The number of contact points is determined from packing geometry assuming a linear relationship between coordination number and porosity. A linear function, $f(e)$, relates coordination number to porosity. Haughey and Beveridge [7] determined $f(e)$ experimentally for randomly packed glass beads; the resulting relation is given by

$$f(e) = 22.47 - 39.39e$$

where e is superficial porosity or interparticle void fraction.

The average specific retention can be determined by means of a force balance on trapped liquid rings. Assuming that suction force created by movement of air above the packed bed is negligible, gravitational force equals capillary force. Fisher [6] derived an expression to describe the cohesive forces for water trapped in soil. To separate two identical spherical particles held together by pendular water, both capillary and interfacial forces must be overcome. In addition, the vector on which these forces must act is

oriented through the centers of mass of the particles. However, when liquid retention is balanced by surface and gravity forces, the force vector is orthogonal to the line through the centers of the particles. Further, it is assumed that pendular drops are not sheared by displacement and only capillary forces are required to balance gravitational forces.

The ratio of gravitational to surface forces is given by a dimensionless parameter, the bond number (Bo):

$$\text{Bo} = \rho g r_p^2 / \gamma$$

where ρ is the density of a pure fluid, r_p is the average radius of particles constituting a packed bed, and γ is surface tension or the interfacial tension of the fluid in air. The bond number is specific to each combination of liquid and packing configuration.

The volume retained in an individual pendular ring can be expressed as a function of bond number and contact angle. Total retention is the integral of average individual ring retention over the entire packed bed. Specific and total retentions are proportional to (r_p^3 / Bo); the contact angle may be determined by linear regression of experimental measurements of residual saturation. For solid packing, fractional saturation of the porous medium by infiltrating liquid (water) is the volume of retained liquid divided by volume of interparticle void space.

2.3. Two-phase liquid retention

Infiltration of a NAPL through a porous medium containing water as a pendular fluid will cause the wetting phase to be redistributed, leading to the formation of two-phase liquid cups; see Fig. 1b. Retention of NAPL depends on the configuration of the water–NAPL interface and the NAPL spreading coefficient. Typically, NAPLs have spreading coefficients greater than zero and tend to form thin films on relatively flat air–water interfaces. DNAPLs do not penetrate an air–water interface until a critical mass of organic liquid accumulates and gravitational forces exceed interfacial forces. However, at curved interfaces with concave menisci, as found in porous media and capillaries, water surface tension is greater than at a flat interface. Therefore, NAPLs will be retained in a configuration resembling that shown in Fig. 1b. The approaches suggested by Fisher [6] yield comparable results.

Wetting phase retention is a function of water–NAPL interfacial tension and NAPL density. Analysis of wetting-phase retention in the presence of a NAPL must consider the effect of redistribution during infiltration and/or drainage; see Ref. [3]. In a manner similar to that described for one-phase liquid cups, water retention can be related to $\text{Bo}_{w/n}$ for the two-phase system, i.e.,

$$\text{Bo}_{w/n} = (\Delta \rho) g r_p^2 / \gamma_{w/n}$$

where $(\gamma_{w/n})$ is interfacial tension and $(\Delta \rho)$ is the difference in densities between the two pure or mutually saturated phases. Rugge [3] observed that DNAPL retention is related to $\text{Bo}_{w/n}$ after modification to account for surface forces; the latter utilizes a function of Bo_n. Contact angles for both water and DNAPL can be estimated from experimental retention data.

3. Materials and methods

3.1. Columns and packing

NAPL and water retention were measured in packed glass columns (Lab Glass, Vineland, NJ). Columns of two column sizes were used: 152 mm I.D. × 610 mm long and 76.2 mm I.D. × 610 mm long. Columns were packed with borosilicate glass beads with six average diameters, i.e. 0.5, 0.8, 0.925, 1.084, 1.334, and 2.0 mm (Glenn Mills, Maywood, NJ). Note, the smallest ratio of column diameter (I.D.) to particle diameter $(2r_p)$ was greater than 38; thus, wall effects were deemed to be minimal. Reducing sections, filled with 10 mm glass beads, were placed at the bottoms of the columns to avoid channelling and air entrapment during filling and draining of liquids. Columns were fitted with Teflon tubing and valves; columns were vented via a 'pig-tail' tube in the top plate, to strictly limit diffusion losses. Fig. 2 is a schematic diagram for a typical column.

3.2. Liquids

Distilled water, made 0.005 N in $CaCl_2$, was used in all experiments; reagent grade DNAPLs, i.e. TCA, DCA and TCM, were used without additional purification (Fisher
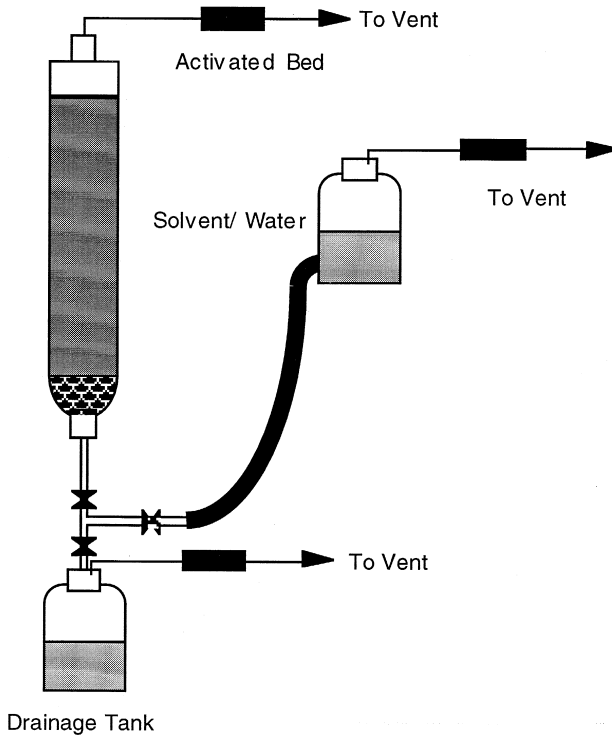

Fig. 2. Apparatus for residual saturation experiments.

Scientific, Springfield, NJ). The DNAPL phase was dyed with Sudan Oil Red to permit detection of hydraulic bypass during experiments. Prior to all experiments, DNAPLs and water were saturated with each other to prevent any effect of dissolution on experimental observations. Volumes of liquids added to, or drained from, columns were determined by physical separation of phases in a separatory funnel and weighing on a Mettler Balance with an accuracy of 1 mg. Liquids were passed through Whatman AH-970 glass

Table 2
Equilibrium water and DNAPL residual saturations in columns with homogeneous glass bead packing

DNAPL	Packing diameter (mm)	Porosity	Initial water saturation, v/o	Final water saturation, v/o	Final DNAPL saturation, v/o
TCA	0.500	0.399	10.39	8.96	1.26
TCA	0.500	0.399	12.31	11.68	3.15
TCA	0.800	0.390	15.89	18.47	7.99
TCA	0.800	0.390	16.65	27.24	8.37
TCA	0.925	0.389	12.63	9.71	2.91
TCA	0.925	0.389	12.09	10.25	2.37
TCA	1.084	0.380	18.93	15.09	3.16
TCA	1.084	0.380	16.27	16.74	6.83
TCA	1.334	0.377	11.52	12.26	5.09
TCA	1.334	0.377	9.75	10.50	5.80
TCA	2.000	0.374	10.60	9.92	2.62
TCA	2.000	0.374	15.11	14.83	2.12
DCA	0.500	0.399	12.90	14.30	3.48
DCA	0.500	0.399	13.33	12.48	3.93
DCA	0.800	0.390	19.01	16.19	8.51
DCA	0.800	0.390	20.97	18.64	9.78
DCA	0.925	0.389	15.90	15.36	3.94
DCA	0.925	0.389	13.74	14.19	3.52
DCA	1.084	0.380	16.90	17.99	6.23
DCA	1.084	0.380	18.82	17.30	4.82
DCA	1.334	0.377	5.84	7.40	4.20
DCA	1.334	0.377	11.25	9.66	5.10
DCA	2.000	0.374	11.18	9.45	3.34
DCA	2.000	0.374	10.45	9.86	3.57
TCM	0.500	0.399	15.06	15.94	2.77
TCM	0.500	0.399	13.76	11.70	3.90
TCM	0.800	0.390	18.85	15.41	5.49
TCM	0.800	0.390	25.98	25.40	6.08
TCM	0.925	0.389	26.10	25.44	3.96
TCM	0.925	0.389	11.96	11.46	5.22
TCM	1.084	0.380	16.64	18.47	5.82
TCM	1.084	0.380	18.01	16.05	5.27
TCM	1.334	0.377	12.27	17.51	3.48
TCM	1.334	0.377	12.56	11.64	3.36
TCM	2.000	0.374	6.73	6.38	3.58
TCM	2.000	0.374	11.74	10.81	3.13

microfiber filters, between experiments, to remove microbial and abiotic suspended solids.

3.3. Retention measurements

Packing porosity was determined by (i) slowly back-filling with derated water and, (ii) subsequently, draining water through the bottom valve until water ceased to exit. Reducer porosity was determined in the same manner. In two-phase retention experiments, columns were brought to stable residual saturation with water; water was drained and DNAPL was filled from bottom to top of packing. Columns were drained of water and DNAPL phases; liquid was separated in a separatory funnel and the residual mass of each phase determined by mass measurement. Drainage volume was measured every 24 h for at least 1 week following initial draining; no further draining occurred after 72 h. To simulate rainfall events in natural aquifers, columns were flooded twice (again) with distilled water to evaluate potential for secondary displacement of DNAPLs by infiltrating water. Two determinations were carried out for each DNAPL, at each packing size.
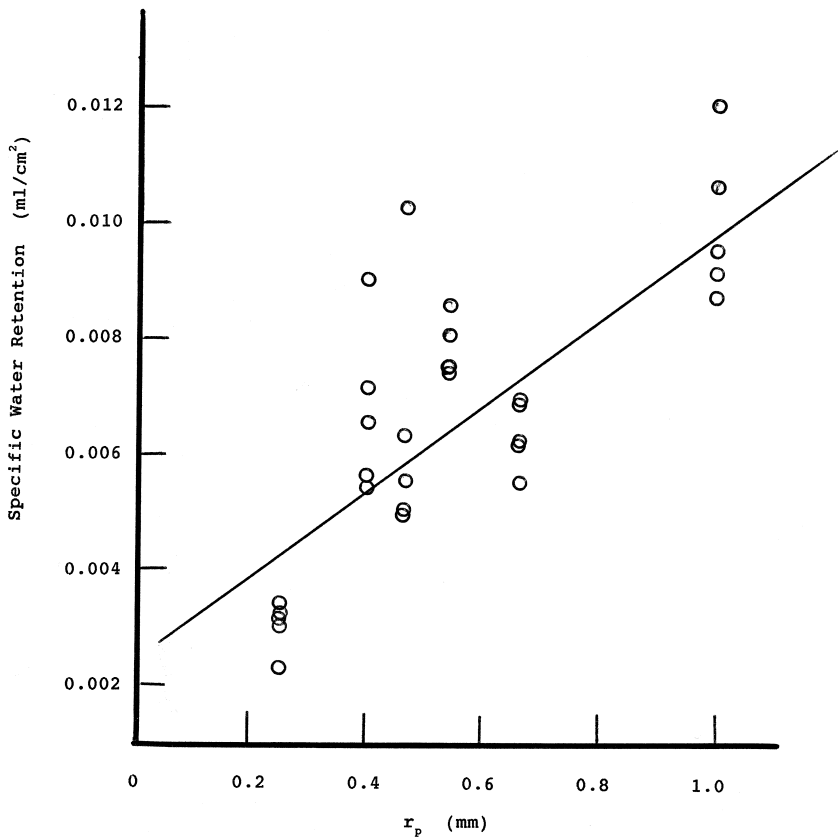

Fig. 3. Correlation of initial specific water retention with bead surface area [$R^2 = 0.56$].

Between experiments, columns were cleaned by repetitive heating and treatment with 30% nitric acid. Clean, dry air was passed through the columns, during heating with electrical heating tape; heating was continued until no liquid was observed to exit the column. Columns and packing were soaked in 30% nitric acid for 24 h. After acid solution was drained, columns were flushed seven times with distilled water or until drainage pH was neutral, i.e. between 6.9 and 7.1. Finally, columns were dried in the same manner as the heating step.

4. Results and discussion

In 36 experiments, equilibrium water and DNAPL residual saturations were measured at specific points along the imbibition-drainage curve. Initial water retention was measured (i) as an indication of 'field capacity' moisture content and (ii) to determine water displaced by infiltrating DNAPL. Results are summarized in Table 2.

Hoag and Marley [1] reported that water and gasoline retentions in unsaturated sands, expressed as volumetric retention per unit available surface area, correlated well with
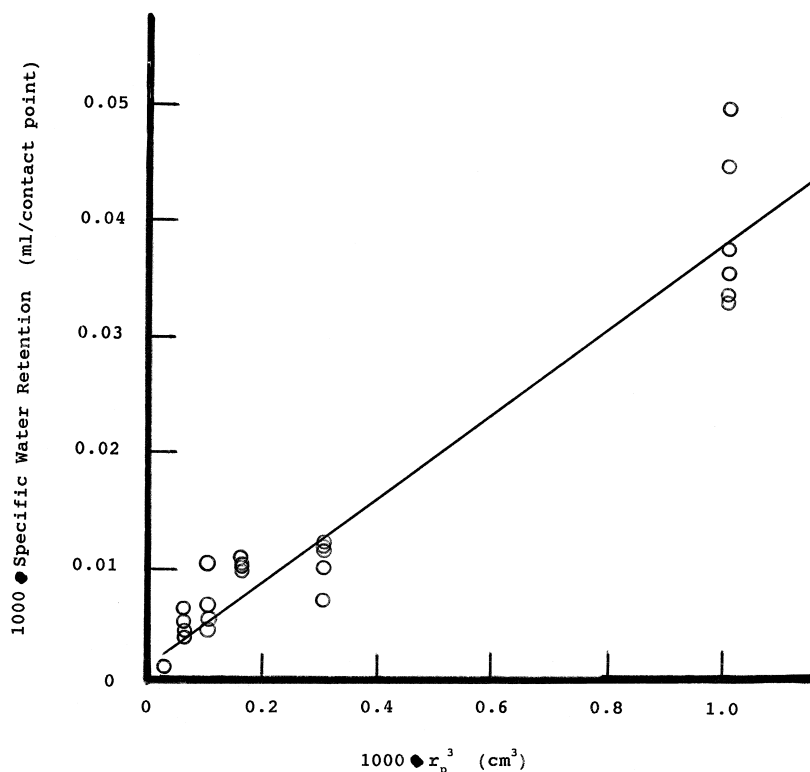

Fig. 4. Correlation of initial specific water retention per interparticle contact point based solely on packing geometry [$R^2 = 0.95$].

Table 3
Comparison of models for initial specific water retention on homogeneous glass bead packing

Method	Regression equation	Calculated contact angle, ϕ_w	R^2
Bead surface area	$2.47E-3+0.0733r_p$ (ml/cm^2)	na	0.56
Packing geometry	$1.56E-6+0.0372r_p^3$ (ml/contact point)	26.2°	0.95
Bond number	$-1.63E-5+0.682\,(r_p/100Bo_w)$ (ml/contact point)	26.9°	0.86

effective packing diameter, i.e. $R^2 > 0.9$. Only weak to moderate correlation for initial specific water retention was observed in this study; see Fig. 3. Volume of water retained correlated solely with packing geometry resulted in a superior coefficient of determination, i.e., $R^2 = 0.95$, as shown in Fig. 4. The linear fit for specific saturation for water and the calculated water wetting angle, for both models, are given in Table 3. As calculated from this correlation, the latter is 26.2°; this value falls within the limits cited by Fisher [6] for cubic and hexagonal packing.

Retention of water is described as a function of bond number in Fig. 5. A lower coefficient of determination, i.e. $R^2 = 0.86$, is achieved with this regression; the independent variable is a function of r_p rather than r_p^3 as in the case of the model based on packing geometry. From a purely mathematical point of view, retention of a pendular
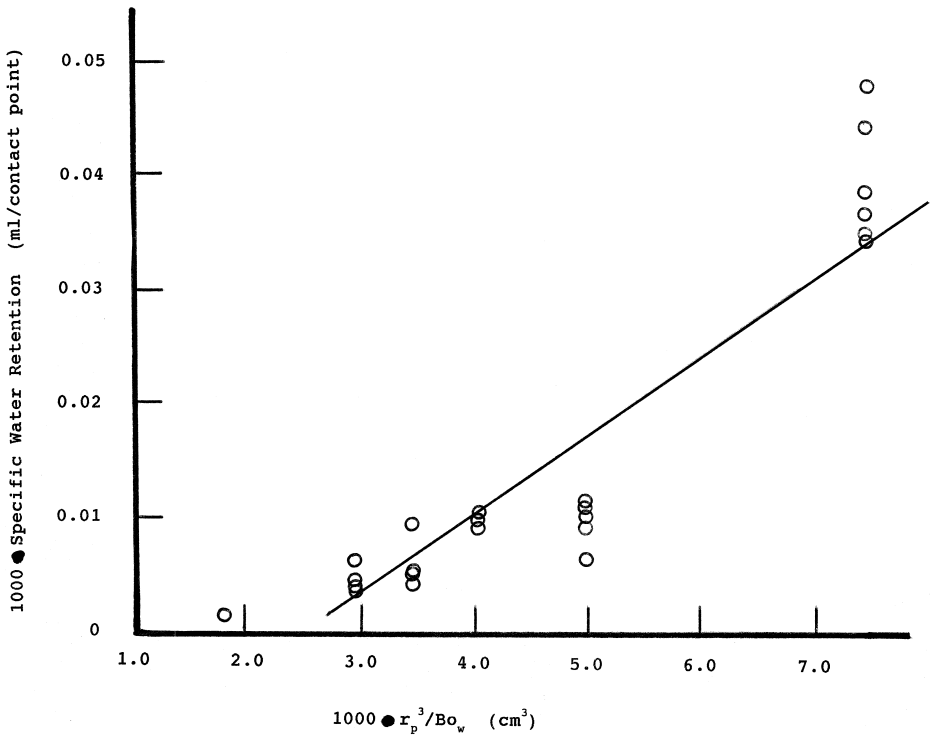

Fig. 5. Correlation of initial specific water retention with bond number [$R^2 = 0.86$].

fluid appears to be related linearly to particle volume; this is consistent with the initial argument. However, to permit estimates of retention in two-phase liquid cups, specific retention must be expressed in terms of local forces as well as particle dimensions.

Equations for the three comparative models of initial specific retention of water, in homogeneous packing, are summarized in Table 3. All forms of the retention model predict that specific retention and relative retention increase in an approximately linear fashion with particle radius (diameter). Further, retention of water is best represented as a function of the number of interparticle contact points rather than as a function of available surface area.

4.1. DNAPL infiltration and drainage

Initial DNAPL retention, as a function of bond number, is illustrated in Fig. 6. Regressions were carried out using the modification of the model proposed by Rugge
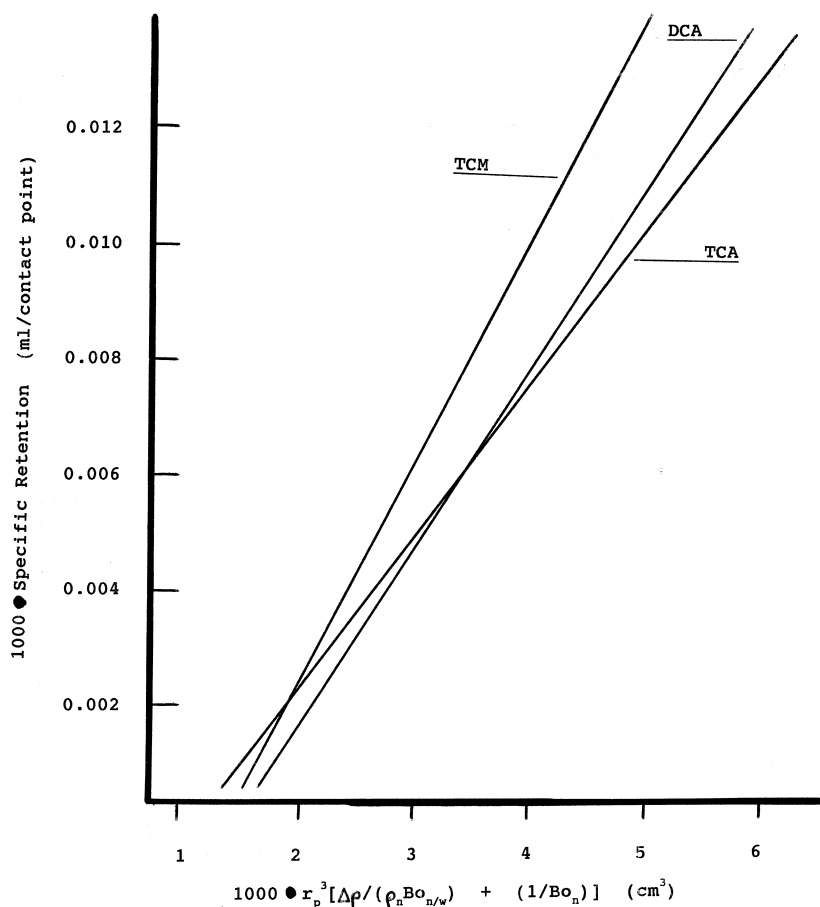

Fig. 6. Specific retention of DNAPLs on water-wetted glass beads [TCA: $R^2 = 0.91$; DCA: $R^2 = 0.95$; and, TCM: $R^2 = 0.91$].

Table 4
Models for specific residual saturation of glass beads by water and DNAPLs

DNAPL	Model equation	R^2
TCA	$S_w = F(e, r_p)[1.2410 \, \Delta \rho r_p^3 / (100 \rho_w Bo_{w/n})]$	0.89
	$S_n = F(e, r_p)[0.26633 \, r_p^3 \{(\Delta \rho / \rho_n Bo_{w/n}) + (1/Bo_n)\}]$	0.91
DCA	$S_w = F(e, r_p)[1.3644 \, \Delta \rho r_p^3 / (100 \rho_w Bo_{w/n})]$	0.94
	$S_n = F(e, r_p)[0.30363 \, r_p^3 \{(\Delta \rho / \rho_n Bo_{w/n}) + (1/Bo_n)\}]$	0.95
TCM	$S_w = F(e, r_p)[1.4342 \, \Delta \rho r_p^3 / (100 \rho_w Bo_{w/n})]$	0.85
	$S_n = F(e, r_p)[0.37649 \, r_p^3 \{(\Delta \rho / \rho_n Bo_{w/n}) + (1/Bo_n)\}]$	0.91

S = Saturation.
ρ_n = DNAPL density.
ρ_w = water density.
$\Delta \rho = \rho_n - \rho_w$.
$F(e, r_p) = [(1 - e)f(e)]/[e(4\pi r_p^3 /3)]$.

[3]. Model equations for residual saturations are summarized in Table 4. Average specific retention of water, in the presence of a NAPL, is given by:

$$V_{w,ave} =]w[[(2\pi \Delta \rho r_p^3)(\rho_w Bo_{n/w})] \cdot [G(\phi_{w/n})]$$

where $G(\phi_{w/n})$ is a function of the tangent and secant of the interphase contact angle. Thus, this contact angle can be calculated from experimental retention data by nonlinear regression. Retention of NAPL and the angle at which the organic phase wets the solid substrate is determined by a similar relation:

$$V_{w,ave} = 2\pi r_p^3 \{([\Delta \rho]/[\rho_n Bo_{w/n}]) + (Bo_n^{-1})\} \cdot G(\phi_n - \phi_{w/n})$$

Predicted contact angles for water, in the presence of DNAPL, and contact (wetting) angles for the DNAPL are given in Table 5. Residual (fractional) saturation is calculated from average retention by division by the packing volume.

Redistribution of the wetting phase to accommodate infiltrating DNAPL results in displacement of water from the packed columns. This behaviour is representative of the response of a soil system to a DNAPL discharge, before redistribution of DNAPL in response to rainfall. Similarly, specific retention of water in packing initially saturated with DNAPL is described in Fig. 7.

Water and DNAPL retention were observed to be functions of DNAPL contact angle, as predicted by Fisher in 1926 [6]. Contact angles for TCA, DCA, TCM and

Table 5
Predicted contact angles for DNAPLs on water-wetted glass beads

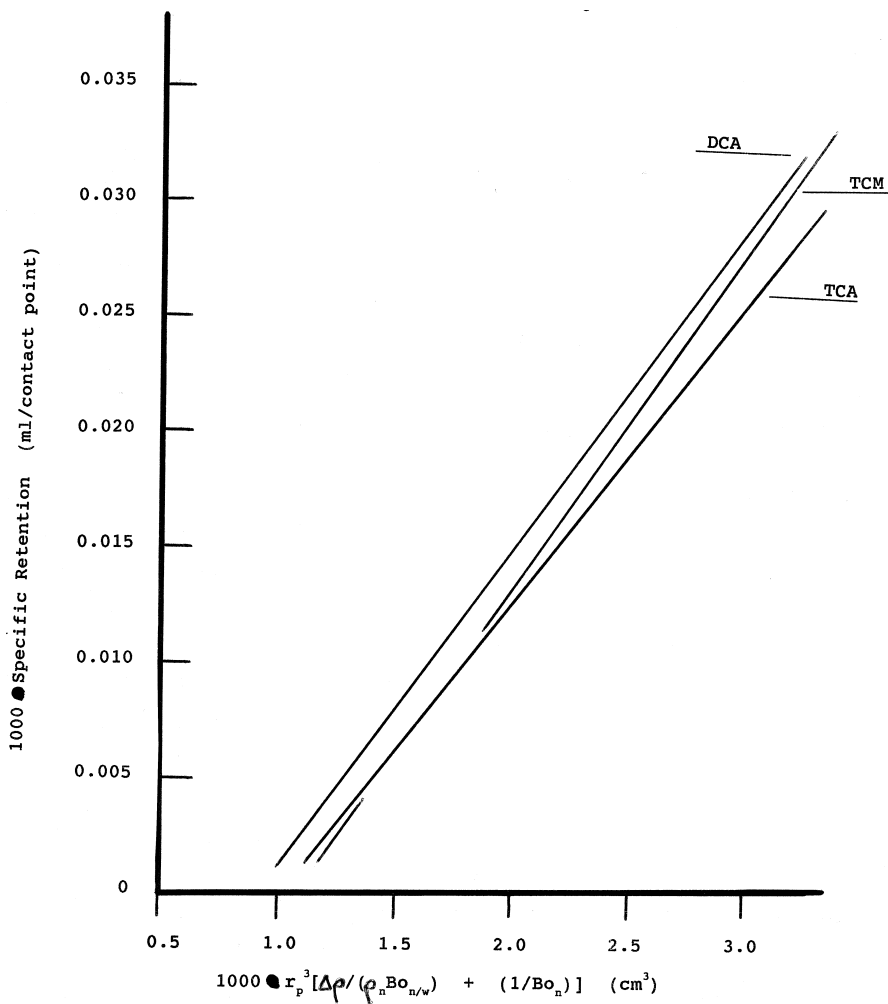| DNAPL	Contact angle
TCA	$\phi_{w/n} = 24.93°$
	$\phi_n = 34.34°$
DCA	$\phi_{w/n} = 26.95°$
	$\phi_n = 37.09°$
TCM	$\phi_{w/n} = 28.15°$
	$\phi_n = 39.63°$

Fig. 7. Specific retention of water on beads saturated with DNAPLs [TCA: $R^2 = 0.89$; DCA: $R^2 = 0.94$; and TCM: $R^2 = 0.85$].

Table 6
Experimental contact angles for DNAPLs on water-wetted glass surfaces at 21°C

DNAPL	Contact angle
TCE	$37.6 \pm 0.7°$
TCA	$34.1 \pm 0.4°$
DCA	$31.2 \pm 0.6°$
TCM	$27.2 \pm 0.8°$

trichloroethylene [TCE] were measured on flat glass surfaces, in the presence of water, by the method described by Demond [8]. Data are summarized in Table 6. Wettability of water-wet bead surfaces by DNAPL and, also, retention angle increased with decreasing DNAPL contact angle; see Table 5.

4.2. DNAPL displacement by a wetting phase (water)

Displacement and redistribution of DNAPLs by percolating water and/or water table fluctuations were simulated by flooding packing with two total macropore (interparticle void) volumes of DNAPL-saturated distilled water. Flooding with a wetting fluid, until no further DNAPL displacement occurred, was intended to approximate an equilibrium state. Pseudo-equilibrium residual saturations of DNAPL and water in homogeneous glass beads can be correlated as linear functions of the bond number. Data and linear regressions for DNAPL residuals are illustrated in Fig. 8; comparable data for water
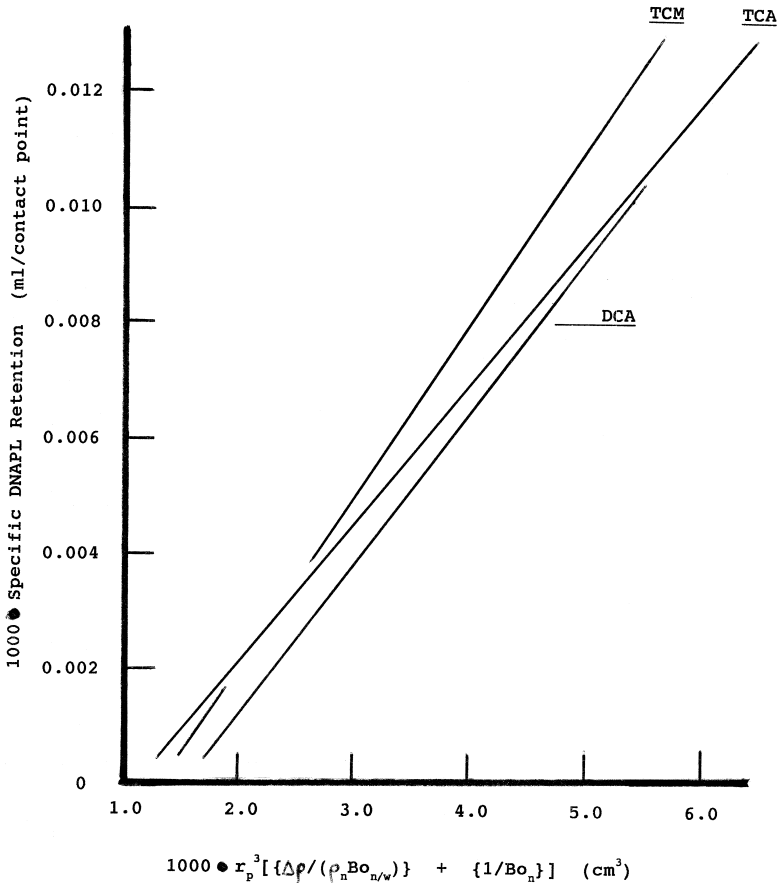

Fig. 8. Equilibrium specific retention of DNAPLs on water-wetted beads after flushing with two pore volumes of water [TCA: $R^2 = 0.89$; DCA: $R^2 = 0.94$; and TCM: $R^2 = 0.92$].
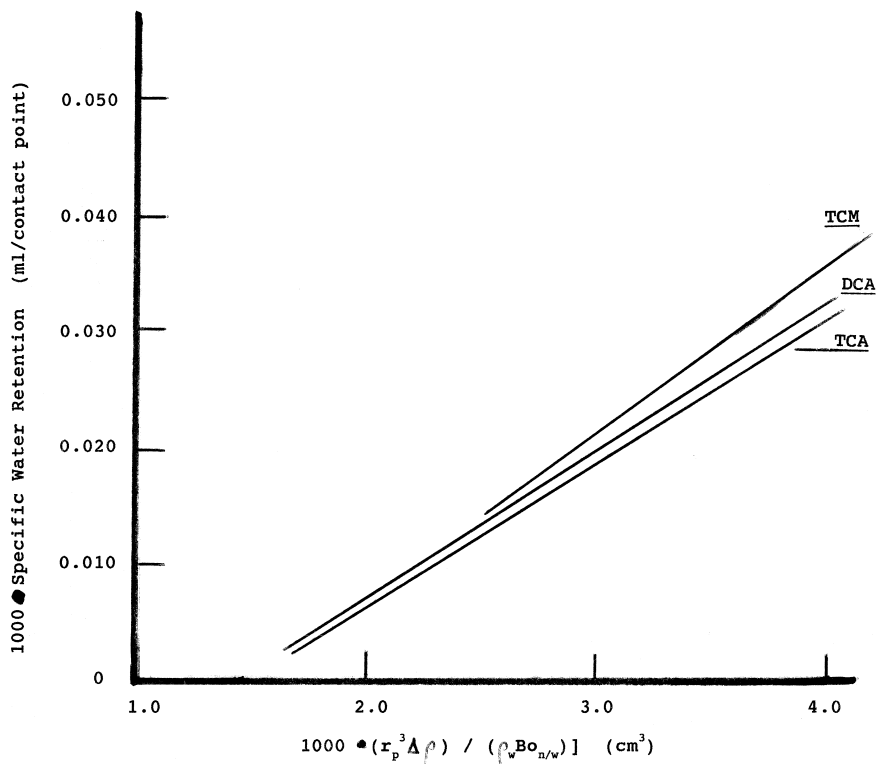
Fig. 9. Equilibrium specific retention of water in contact with DNAPLs in columns packed with glass beads [TCA: $R^2 = 0.91$; DCA: $R^2 = 0.98$; and TCM: $R^2 = 0.92$].

residuals are illustrated graphically in Fig. 9. Coefficients of determination for these regressions on experimental data are 0.9 or greater over the range of packing diameters. The fraction of initial residual DNAPL displaced varied greatly. No trend in DNAPL displacement was observed as a function of wettability (contact angle) in larger beads, i.e. 1.334 and 2.0 mm; however, displaced DNAPL volume generally decreased with increasing DNAPL wetting ability at bead diameters of less than 1.334 mm.

5. Conclusions

Water competes effectively with DNAPLs for available pore space. However, DNAPLs cannot be displaced completely from interparticle contact points, during imbibition of water at low flow rates. Liquid configurations, described in terms of predicted retention angles, change very little, even after flushing with two total pore volumes of water. A significant volume of DNAPL was displaced from 0.5 mm glass beads by water. Thus, DNAPL displacement from sands and soils, with much smaller average particle sizes, may prove to be a significant process in subsurface DNAPL transport.

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