

Influence of Viscous, Gravitational, and Capillary Forces on DNAPL Saturation

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Abstract

Four dense nonaqueous phase liquids (DNAPLs)—bromoform, chlorobenzene, tetrachloroethylene, and trichloroethylene—were used to investigate the influence of viscous, gravitational, and capillary forces on DNAPL saturation in a natural aquifer sand. The relative magnitudes of these forces are expressed in terms of two dimensionless groups, the Capillary Number (N_{Ca}), defined as the ratio of the viscous force to capillary force, and the Bond Number (N_{Bo}), defined as the ratio of the gravitational force to capillary force.

Nondimensionalization of the equations governing two-phase flow suggests that DNAPL saturation should be a function of a linear combination of the Capillary and Bond Numbers ($N_{Ca}/k_{rw} - N_{Bo}$), provided the permeability to water (k_{rw}) in the presence of discontinuous DNAPL is considered. Experimental studies in which DNAPL saturations were measured over a range of Capillary and Bond Numbers for upward, horizontal, and downward displacement of DNAPL by water corroborate the results of the nondimensionalization. DNAPL saturations generally decreased with increasing Capillary Number and with decreasing Bond Number until $N_{Ca}/k_{rw} - N_{Bo}$ was greater than approximately 1×10^{-5} , at which point residual saturation was attained. For the DNAPLs used in this study, with adhesion tensions on the order of 26 dynes/cm and Bond Numbers ranging from 1.3×10^{-7} to 2.4×10^{-6} , residual saturation was attained at Capillary Numbers greater than approximately 5×10^{-5} . These results provide a means of estimating the system conditions under which the DNAPLs studied achieve residual saturation in aquifer material.

Introduction

Ground-water contamination by dense nonaqueous phase liquids (DNAPLs), such as carbon tetrachloride and trichloroethylene, has received considerable attention in recent years. Of particular concern is the fact that DNAPLs may become immobile as a result of either capillary trapping or stratigraphic trapping in the subsurface. The immobile DNAPL may occur as globules, lenses, and pools, which are not readily removed by conventional ground-water pumping techniques. This trapped DNAPL can serve as a long-term (on the order of decades to centuries) source of ground-water contamination (Anderson et al., 1987; Mackay and Cherry, 1989) and, consequently, is often the limiting factor in site remediation.

The extent of ground-water contamination and the time required is a function of the quantity and distribution of DNAPL in the subsurface. Unfortunately, the location and quantity of DNAPLs in the subsurface are difficult to predict and detect, owing to the complexity of immiscible liquid transport in porous media. Controlled laboratory studies, while simplistic and generally not directly transferable to field situations, can provide a means of better understanding the factors that influence the entrapment and displacement of DNAPLs in porous media. In this paper, we investigate the influence of viscous, gravitational, and capillary forces on DNAPL saturation (the proportion of the pore space occupied by the DNAPL) obtained in aquifer material after waterflooding (flushing with water) over a range of flow rates.

Background

Numerical modeling of the transport of DNAPL in environmental media has received considerable attention in recent years. Kueper and Frind (1992) provide a comprehensive review of the approach taken by many authors. The majority of the models focus on the transport or infiltration of DNAPL as a continuous phase in the subsurface. In contrast, only a few models consider the entrapment of DNAPL in porous media (Kalarachi et al., 1992; Rostron, 1992). The displacement of DNAPL by waterflooding, or when conventional ground-water pumping techniques are applied, has received comparatively less attention.

Laboratory and field studies have also been conducted to characterize the behavior of DNAPLs in the subsurface and better understand the complexities of DNAPL migration in environmental media (Anderson, 1988; Schwille, 1984, 1988; Wilson et al., 1990; Corapcioglu and Hossain, 1986; Kueper et al., 1989; and Rivett et al., 1991). These studies were largely qualitative, focusing mainly on visualizations of DNAPL movement in porous media. Only a few authors have reported DNAPL saturations in porous media (Schwille, 1984, 1988; Anderson, 1988; Wilson et al., 1990).

Most of our present knowledge of the entrapment and displacement of NAPLs in porous media comes largely from investigations conducted by petroleum engineers with the aim of improving oil recovery from petroleum reservoirs. Studies considering the entrapment and displacement of petroleum hydrocarbons or light NAPLs (LNAPLs) subject to waterflooding (reviewed by Anderson, 1987; Larson et al., 1981; Stegemeier, 1977; and Willhite, 1986) are of particular interest in this research; DNAPL entrapment and displacement in porous media are expected to be governed by the same principles as govern LNAPL behavior. However, most of the waterflooding studies have focused on horizontal waterflooding as a means of displacing the NAPL. Only a few studies have considered the influence of density differences and vertical flow components on

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NAPL displacement. These density effects are likely to be particularly important for DNAPL recovery because the large difference in density between most DNAPLs and water may significantly hinder their recovery.

The general conclusion of the waterflooding investigations is that NAPL saturation in porous media strongly depends on interfacial tension between the immiscible liquids, wettability of the solids with respect to the immiscible liquids (contact angle), and the pore-water velocity attained during waterflooding. The dependence of NAPL saturation on these parameters is commonly expressed in terms of a dimensionless group called the Capillary Number (N_{Ca}):

$$N_{Ca} = \frac{v_w \mu_w}{\gamma_{ow} \cos\theta} \quad (1)$$

where v_w is the pore-water velocity, μ_w is water viscosity, γ_{ow} is the interfacial tension between the NAPL and water, and θ is the contact angle at the solid-water-NAPL interface. The Capillary Number is defined as the ratio of the viscous to capillary forces (Perry and Chilton, 1973).

Figure 1 shows the general shape of the NAPL saturation-Capillary Number relationship for sandstone and bead packs in which the NAPL is subject to horizontal waterflooding. Typically in these experiments, a sand column is first saturated with water, then flooded with the NAPL until the irreducible water saturation is attained, and finally flooded with water until all possible NAPL is removed, i.e., residual saturation is attained. Capillary Numbers greater than approximately 10^{-5} generally cannot be achieved solely with waterflooding (Lake, 1989). Thus, as Figure 1 shows, NAPL saturation is independent of Capillary Number (the plateau region) during most horizontal waterfloods. Capillary Numbers greater than 10^{-5} are typically attained by introducing chemicals which lower the interfacial tension between the NAPL and water (Lake, 1989), allowing more effective displacement of the NAPL. Consequently, as shown in Figure 1, the higher Capillary Numbers induced by chemical flooding result in decreased NAPL saturations. This phenomenon has been used to good effect for remediating soil contaminated with DNAPLs (Ellis et al., 1985; Fountain, 1992; Soerens et al., 1992).

As stated earlier, only a few studies in the petroleum engineering literature have considered vertical displacement of

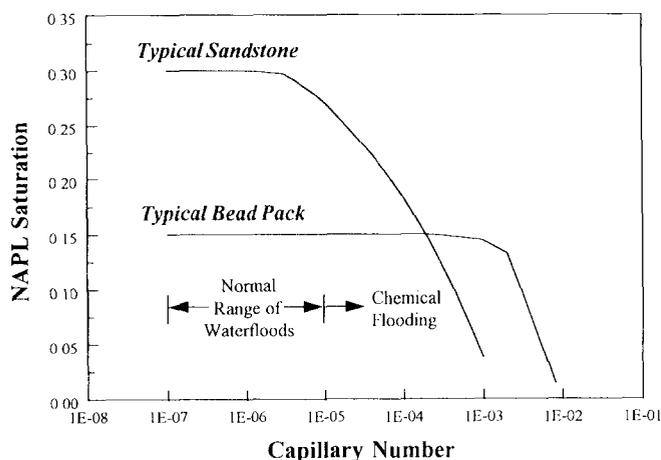


Fig. 1. NAPL saturation as a function of Capillary Number ($v_w \mu_w / \gamma_{ow} \cos\theta$) in petroleum engineering applications (after Morrow et al., 1988; and Lake, 1989).

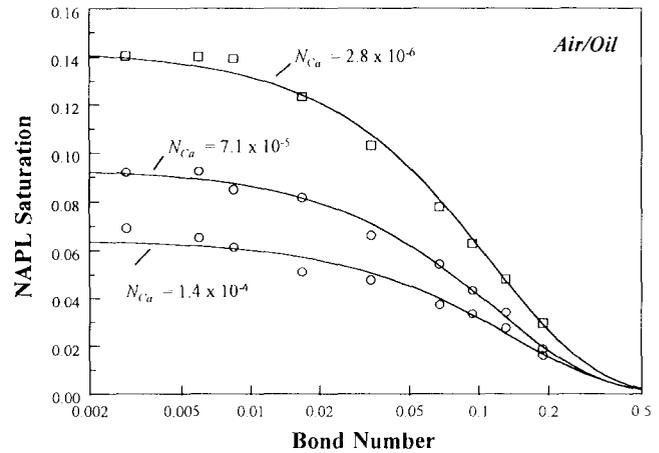


Fig. 2. NAPL saturation as a function of Bond Number [$\Delta\rho g(k/n) / \gamma_{ow} \cos\theta$] for various Capillary Numbers (N_{Ca}) (after Morrow and Songkran, 1981).

NAPLs and the influence of buoyancy, or density difference, on NAPL saturations (Morrow and Songkran, 1981; Morrow et al., 1988). Morrow and coworkers used bead packs to show that, for vertical displacement of a light nonwetting phase by a denser wetting phase, NAPL saturation is inversely correlated with a dimensionless group called the Bond Number (Figure 2). The Bond Number is defined as the ratio of gravitational to capillary forces (Perry and Chilton, 1973) and is expressed as:

$$N_{Bo} = \frac{\Delta\rho g(k/n)}{\gamma_{ow} \cos\theta} \quad (2)$$

where $\Delta\rho$ is the density difference between the immiscible fluids; g is gravitational acceleration; and k and n are the intrinsic permeability and porosity, respectively, of the porous medium. Figure 2 shows that at low values of the Capillary Number, NAPL saturations were significantly reduced by a two-order-of-magnitude increase in the Bond Number. At higher values of the Capillary Number, the influence of buoyancy decreases. Morrow and Songkran (1981) were able to correlate NAPL saturations with a simple, empirically determined, linear combination of the Capillary and Bond Number, showing that the effects of viscous and gravitational forces are superimposed.

The Capillary Number and Bond Number, in combination with static force balance considerations, have been used to estimate the mobility of DNAPLs in the subsurface (Wilson and Conrad, 1984; Hunt et al., 1988; Wilson et al., 1990; Cohen and Mercer, 1993). However, there has been no derivation in the literature of the dependence of DNAPL saturation on both the Capillary Number and Bond Number. In this paper, we use dimensional analysis of the equations governing two-phase flow to evaluate whether DNAPL saturation depends on a linear combination of the Capillary Number and Bond Number, as suggested by the experimental work of Morrow and Songkran (1981). We then describe a series of controlled laboratory experiments designed to assess the influence of gravitational forces (Bond Number) and viscous forces (Capillary Number) on DNAPL saturation in aquifer material.

Derivation of Capillary and Bond Number Relationship

In the following analysis, the equations describing the flow of two immiscible liquids in porous media are nondimensionalized and analyzed with respect to possible conditions in envi-

ronmental settings. The resulting equations demonstrate that NAPL saturations are in general a function of both the Capillary Number [equation (1)] and the Bond Number [equation (2)].

For a system composed of a rigid, nondeformable, homogeneous porous medium and two incompressible, immiscible liquids (e.g., water and an organic liquid), among which there is no interphase mass transfer, the governing equations are:

$$\phi \frac{\partial S_w}{\partial t} = \nabla \cdot q_w \quad (3)$$

$$\phi \frac{\partial S_o}{\partial t} = \nabla \cdot q_o \quad (4)$$

The subscripts w and o denote water and organic liquid, respectively, S is saturation, and q is Darcy velocity. The Darcy velocity for each fluid is defined as follows:

$$q_w = - \frac{kk_{rw}}{\mu_w} (\nabla P_w + \rho_w g \nabla z) \quad (5)$$

$$q_o = - \frac{kk_{ro}}{\mu_o} (\nabla P_o + \rho_o g \nabla z) \quad (6)$$

where k is the intrinsic permeability of the porous medium, k_r is relative permeability (which is a function of water or organic liquid saturation), μ is viscosity, P is fluid pressure, ρ is density, and g is gravitational acceleration. Equations (3) through (6) are constrained by:

$$S_w + S_o = 1 \quad (7)$$

$$P_o - P_w = P_c \quad (8)$$

where P_c is capillary pressure, also a function of water (or organic liquid) saturation.

Differentiating equation (8) yields:

$$\nabla P_o - \nabla P_w = \nabla P_c \quad (9)$$

Equations (5) and (6) can be rewritten in terms of ∇P_w and ∇P_o , respectively,

$$\nabla P_w = - \frac{q_w \mu_w}{kk_{rw}} - \rho_w g \nabla z \quad (10)$$

$$\nabla P_o = - \frac{q_o \mu_o}{kk_{ro}} - \rho_o g \nabla z \quad (11)$$

and substituted into equation (9) to yield:

$$\frac{1}{k} \left(\frac{q_w \mu_w}{k_{rw}} - \frac{q_o \mu_o}{k_{ro}} \right) - (\rho_o - \rho_w) g \sin \alpha = \nabla P_c \quad (12)$$

where α is the angle between the horizontal axis and the direction of flow. Employing the Leverett (1941) function [$P_c^* = P_c (k/n)^{1/2} / \gamma_{ow} \cos \theta$] and setting $\nabla^* = (k/n)^{1/2} \nabla$ in equation (12), the following nondimensional equation is obtained:

$$\frac{1}{k} \left(\frac{q_w \mu_w}{k_{rw}} - \frac{q_o \mu_o}{k_{ro}} \right) - (\rho_o - \rho_w) g \sin \alpha = \frac{\gamma_{ow} \cos \theta}{k/n} \nabla^* P_c^* \quad (13)$$

Multiplying equation (13) by $(k/n \gamma_{ow} \cos \theta)$ and recognizing that $q/n = v$, where v is the average pore fluid velocity, yields:

$$\left(\frac{v_w \mu_w}{\gamma_{ow} \cos \theta} \right) \left(\frac{1}{k_{rw}} \right) - \left(\frac{v_o \mu_o}{\gamma_{ow} \cos \theta} \right) \left(\frac{1}{k_{ro}} \right) - \frac{(\rho_o - \rho_w) g (k/n) \sin \alpha}{\gamma_{ow} \cos \theta} = \nabla^* P_c^* \quad (14)$$

The first term in parentheses on the left-hand side of equation (14) is the Capillary Number as defined in equation (1). A second Capillary Number, defined in terms of the velocity and viscosity of the organic liquid, also appears in equation (14), since the simultaneous flow of both liquids is considered. The third term on the left-hand side of equation (14) is the Bond Number as defined in equation (2), with $\sin \alpha$ included to consider flow directions other than vertical. The water and, consequently, organic liquid saturations are defined by the dimensionless capillary pressure term on the right-hand side of the equation.

If the NAPL becomes immobile and there is no vertical component to water flow (as in horizontal waterflooding), equation (14) reduces to:

$$\left(\frac{v_w \mu_w}{\gamma_{ow} \cos \theta} \right) \left(\frac{1}{k_{rw}} \right) = \nabla^* P_c^* \quad (15)$$

In this case, the term $\nabla^* P_c^*$ represents the capillary pressure, expressed in dimensionless terms, that must be overcome in order to mobilize a mass of NAPL by horizontal waterflooding. Equation (15) is equivalent to the relationships for horizontal displacement of NAPLs developed by Stegemeier (1974) and Lake (1989) in the petroleum engineering literature and described by Cohen and Mercer (1993) for environmental applications. For example, employing the Leverett function and considering a NAPL mass of dimensionless length, $L/(k/n)^{1/2}$, we can write:

$$\nabla^* P_c^* = \frac{\Delta P_c (k/n)}{L \gamma_{ow} \cos \theta} \quad (16)$$

where ΔP_c is the difference in capillary pressure at the front and trailing ends of the NAPL mass. If we assume that the capillary pressure at the trailing end of the NAPL mass is negligible, the capillary pressure that must be overcome in order to mobilize the NAPL is given by the definition of capillary pressure:

$$P_c = \frac{2 \gamma_{ow} \cos \theta}{r} \quad (17)$$

where r is the pore throat radius through which the NAPL must pass (Bear, 1972). Incorporating equations (16) and (17) into equation (15), and using Darcy's law, we obtain:

$$\nabla h_c = \frac{2 \gamma_{ow} \cos \theta}{r \rho g L} \quad (18)$$

where ∇h_c is the critical hydraulic gradient required to mobilize a NAPL mass of length L in the horizontal direction. This relationship is equivalent to the relationship presented by Cohen and Mercer (1993) for horizontal displacement of a DNAPL.

Alternately, for the case in which the NAPL becomes immobile when pore-water velocity is negligible, equation (14) reduces to:

$$z = \frac{2 \gamma_{ow} \cos \theta}{(\rho_o - \rho_w) g} \left(\frac{1}{r} \right) \quad (19)$$

where z is the critical height of NAPL required for downward

penetration of the NAPL through a porous medium with pore throat radius r . The Leverett function and capillary pressure definition were employed as in equation (18). This relationship is equivalent to the relationship presented by Cohen and Mercer (1993) for downward migration of a DNAPL. All the relationships described in Cohen and Mercer (1993) may be similarly derived from equation (14).

If both viscous forces and gravitational forces are considered in the mobilization of a discontinuous NAPL mass, equation (14) becomes:

$$\left(\frac{v_w \mu_w}{\gamma_{ow} \cos \theta} \right) \left(\frac{1}{k_{rw}} \right) - \frac{(\rho_o - \rho_w) g (k/n) \sin \alpha}{\gamma_{ow} \cos \theta} = \nabla * P_c^* \quad (20)$$

Equation (20) suggests that NAPL saturation, defined by the dimensionless capillary pressure term on the right-hand side of the equation, is a function of both the Capillary and Bond Numbers, as proposed by Morrow and Songkran (1981), provided the relative permeability of water in the presence of discontinuous NAPL is considered. The experimental program described in the following sections was designed to verify the dependence of DNAPL saturation on the combination of the Capillary Number and Bond Number described by equation (20).

Experimental Setup and Procedures

The primary goal of the experimental program was to obtain reproducible measurements of DNAPL saturations in a sand-filled column subjected to waterflooding at various flow rates and orientations. Other parameters measured included porosity, absolute permeability of the sand, and permeability of the sand to water in the presence of discontinuous DNAPL. Four DNAPLs were used in this investigation: bromoform, chlorobenzene, tetrachloroethylene, and trichloroethylene. Table 1 lists the properties of these compounds. All data are at 20°C unless otherwise indicated. All the selected compounds are denser than water (0.998 g/cm³), with densities ranging from

1.1063 to 2.8909 g/cm³. The viscosities of the compounds are generally less than that of water, ranging from 0.566 to 0.887 cp, except for bromoform, which has a viscosity of 2.015 cp (interpolated from data at 15°C and 30°C). These compounds are essentially immiscible with water; their solubilities in terms of mole fractions range from 1.62×10^{-5} to 2.23×10^{-4} . Interfacial tensions for organic liquid-water pairs range from 33 to 44 dynes/cm, values that are significantly less than the interfacial tension between water and air (72.75 dynes/cm). Contact angles measured in the aqueous phase on glass surfaces range from 37 to 51 degrees, indicating that the selected compounds are likely to be nonwetting with respect to water in natural aquifer material (Demond, 1988). Table 1 also includes the adhesion tension, which is defined as the product of interfacial tension and cosine of the contact angle and appears in the capillary pressure relationship described by equation (17).

The four compounds—bromoform, chlorobenzene, tetrachloroethylene, and trichloroethylene—were chosen for use in the displacement experiments because they have similar values of adhesion tension (26.5 ± 1.5 dynes/cm), but represent a wide range of densities (1.1063 to 2.8909 g/cm³). This choice was made to ensure that any differences observed in the saturations of these compounds at a given waterflood rate would be the result of density differences (i.e., gravitational forces), rather than differences in capillary pressure.

The waterflood apparatus used includes a sand-filled column that can be oriented at any angle from the vertical, pumps and associated inlet and outlet plumbing for water and the DNAPLs, and a pressure transducer for monitoring the pressure drop in the sand-filled column (Figure 3). The flow system was designed to minimize void volumes in the column and in the inlet and outlet plumbing connected to the pressure transducer, in order to reduce the error in determining saturation and permeability. Water and the DNAPLs were pumped from their respective reservoirs by two peristaltic pumps (Rainin Instruments, Model 48-000) equipped with pump heads capable of delivering flows from 0.025 to 25 ml/min. A burette was used at the outlet end of the column for separating water from the organic liquids. Water was floated off the top of the burette and directed back to the water inlet reservoir. This recirculation

Table 1. Properties of DNAPLs Chosen for Waterflood Experiments

Property	Bromoform	Chlorobenzene	Tetrachloroethylene	Trichloroethylene
Chemical Formula	CHBr ₃	C ₆ H ₅ Cl	C ₂ Cl ₄	C ₂ HCl ₃
Mole. weight	252.73	112.56	165.83	131.39
Density (gm/cm ³)	2.8909	1.1063	1.6228	1.4642
Viscosity (cp)	2.152 (15°C) 1.741 (30°C)	0.799	0.932 (15°C) 0.798 (30°C)	0.566
Solubility (mole frac.)	2.23×10^{-4} [1]	4.92×10^{-5} [1]	1.62×10^{-5} [2]	1.49×10^{-4} [2]
Interfacial tension† (dynes/cm)	37 [3]	33 [3]	44 [3]	35 [3]
Contact angle‡	48° [3]	37° [3]	51° [3]	40° [3]
Adhesion tension* (dynes/cm)	25	26	28	27

All data are from Riddick et al. (1986), unless otherwise indicated by [number]: [1] Sorensen and Arlt (1979); [2] Horvath (1982); [3] Dawson (1992).

† Interfacial tension measured between organic liquid and water.

‡ Contact angle measured in water on glass.

* Adhesion tension = product of interfacial tension and cosine of the contact angle.

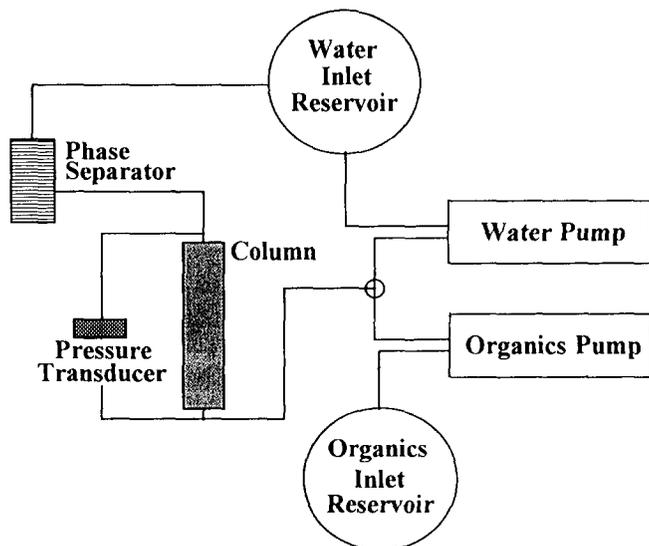


Fig. 3. Schematic diagram of experimental flow apparatus.

system was used to minimize the volume of water required for the experiments, thereby minimizing the dissolution of DNAPL by water as well as the volume of contaminated water requiring disposal. Stainless steel tubing with a small inner diameter of 0.75 mm was used to connect most components of the flow system. Larger diameter Teflon™ tubing, which allowed visual monitoring of the flow process, was used between the inlet reservoirs and pumps to ensure that no air was introduced while the pumps were primed. This flow system proved capable of handling the wide range of flow rates tested.

The waterflood experiments involved a series of interdependent procedures. For each displacement experiment, the column was first packed with sand and carbon dioxide was passed upward through the column for at least 30 minutes to displace the air in the pore space of the sand. Deionized water (saturated with DNAPL) was then slowly introduced into the column at a rate of 2.5 ml/min (0.068 pore volumes/min) to displace the gas. When water appeared at the top of the column, the flow rate was increased tenfold to displace the carbon dioxide-saturated water and any residual gas. At least 10 pore volumes of water were passed through the column at the high rate. The flow rate was then decreased to 2.5 ml/min and the pressure drop in the column was monitored. When the pressure drop in the column stabilized, absolute permeability was calculated using Darcy's Law. The water in the column was reduced to its irreducible saturation by flooding the column with DNAPL (saturated with water). The DNAPLs were introduced at the bottom of the vertically oriented column in order to ensure a stable displacement front. The initial DNAPL flood rate was 2.5 ml/min. After DNAPL appeared at the top of the column, the flow rate was increased tenfold to displace as much water as possible. When no additional water could be displaced from the column, it was weighed in order to calculate the organic liquid saturation. The DNAPL was subsequently displaced by flooding the column with water, starting with low flood rates and increasing to high flood rates. At each flow rate setting, water was pumped through the column until the DNAPL ceased to flow and the pressure drop in the column stabilized. At least four pore volumes of water were pumped through the column after steady pressure conditions were attained. The effective permeability of the sand to water in the presence of discontinuous DNAPL was

then calculated from the measured pressure drop using Darcy's Law, and DNAPL saturation was calculated from the weight of the column.

The same sand was used in each of the displacement experiments in order to ensure reproducibility of the column porosity and permeability. Between runs, the sand was washed with acetone, rinsed thoroughly with water, and dried in an oven set to 105°C. The sand used in the flow experiments was a homogenized sand from an aquifer in Borden, Ontario, where a field-scale transport experiment was conducted (Freyberg, 1986; Mackay et al., 1986; Roberts and Mackay, 1986). The Borden sand was chosen because it is a clean, well-sorted, fine- to medium-grained sand containing little clay or organic matter (Roberts and Mackay, 1986; Ball, 1989). Low clay and organic matter content was desired to ensure that adsorption of organic compounds to the solids was insignificant when compared to the mass of immiscible liquid held in the pores even at residual saturation. The porosity of the repacked sand averaged 0.36 (coefficient of variation = 0.012), a value that agrees reasonably well with the porosity determined by Roberts and Mackay (1986), 0.33, and by Sudicky (1986), 0.34, for sand from the same aquifer. The absolute permeability of the repacked Borden sand averaged 1.15×10^{-8} cm² (coefficient of variation = 0.067), which corresponds to a hydraulic conductivity of 1.13×10^{-3} cm/s. The hydraulic conductivities reported in Sudicky's study range between about 6×10^{-4} and 2×10^{-2} cm/s, which bracket the average value determined in this study.

The column used in the waterflood experiments was a glass column (Altex Scientific, Inc.) with (Teflon™) end caps. Figure 4 shows an exploded view of the column and its fittings. The column is 25 cm in length and has an inner diameter of 2.5 cm. With the end caps installed, the effective internal length of the column is 21 cm. A long column was chosen to minimize the influence of end effects. The end caps have a small fill reservoir with a stainless steel mesh at the face of the end cap. The fill reservoir and mesh cause the liquid to spread radially and evenly before entering the column. A paper filter was placed between the face of the end cap and the sand in the column to keep the fine soil particles from leaving the column and to ensure good capillary contact between the end caps and the sand. The sum of the void volumes in the end caps represents only 0.9% of the internal volume of the column when empty and less than 2.5% of the pore volume when the column is filled with sand.

The pressure drop in the column was measured with a diaphragm type, low-displacement pressure transducer (Validyne, Model DP-45), chosen for its low internal volume. The trans-

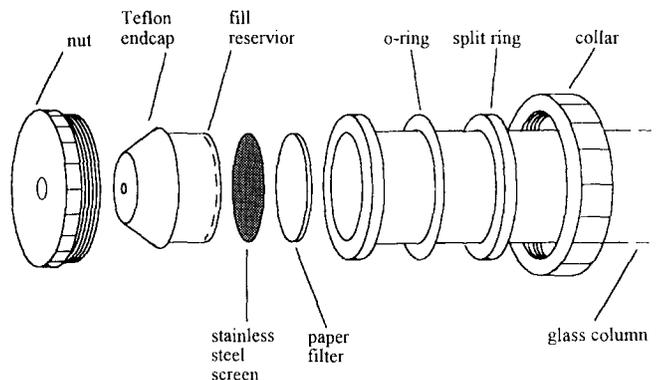


Fig. 4. Exploded diagram of the columns and fittings used in the DNAPL displacement experiments.

Table 2. Trichloroethylene Saturations as a Function of Displacement Direction

Capillary number	N	Upward	CV	N	Horizontal	CV	N	Downward	CV
2.67×10^{-7}	2	0.454	0.10						
8.89×10^{-7}	4	0.413	0.08	1	0.228		2	0.169	0.09
4.45×10^{-6}	3	0.232	0.06	2	0.181	0.14	1	0.165	
8.89×10^{-6}	6	0.182	0.09	2	0.162	0.16	2	0.156	0.10
4.45×10^{-5}	3	0.154	0.10	2	0.142	0.08	1	0.155	
8.00×10^{-5}	6	0.158	0.10	2	0.134	0.07	2	0.149	0.09

The reported saturations are the arithmetic average of the saturations obtained in replicate experiments.

N = number of replicate experiments.

CV = coefficient of variation (standard deviation divided by mean value).

ducer was attached to the inlet and outlet ends of the column via three-way valves. The transducer converts a pressure difference applied through the pressure ports to an AC signal output, which is then amplified and converted to a DC signal by a carrier demodulator (Validyne, Model CD-280). The output DC signal was measured by a digital multimeter (Fluke Instruments, Model 8842A) and recorded by a data recorder (Fluke Instruments, Model 1722A). This system allowed constant monitoring of the pressure drop in the column, which facilitated the determination of steady flow conditions. The steady-state, pressure-drop data were used to calculate absolute permeability of the sand and the permeability to water after DNAPL ceased flowing.

Experimental Results and Discussion

The results of the waterflood experiments are shown in Tables 2 and 3. Reproducibility of the DNAPL saturation measurements from replicate experiments was very good. The coefficients of variation for measurements of DNAPL saturation at a given flow rate and for a given compound are generally on the order of 0.02 to 0.12. The average coefficient of variation is 0.07;

the pooled coefficient of variation is 0.11. The maximum DNAPL saturations obtained after flooding the column with the DNAPL are approximately equal (no statistically significant difference between means at the 0.01 level of significance) for the four compounds tested, averaging 0.79, with a pooled coefficient of variation of 0.02. This maximum organic liquid saturation corresponds to all irreducible water saturation of 0.21. Equivalent results were obtained by Demond and Roberts (1991) for nonhalogenated and halogenated organic liquids in the same sand. Maximum organic liquid saturations of approximately the same magnitude were also reported by Wilson et al. (1990) for various organic liquids (e.g., kerosene, gasoline, p-xylene) in a medium-grained sand.

The initial displacement experiments were conducted with trichloroethylene (TCE) using both horizontal and vertical column orientations with water flow both upward and downward in the vertical column (Table 2). Figure 5 plots the observed TCE saturations versus Capillary Number for upward, downward, and horizontal displacements. The Capillary Number was varied approximately two orders of magnitude (3×10^{-7} to $9 \times$

Table 3. DNAPL Saturations as a Function of Capillary Number in Upward Displacement

Capillary Number	N	Bromoform Saturation	CV	Capillary Number	N	Tetrachloroethylene Saturation	CV
9.58×10^{-7}	2	0.554	0.04	8.56×10^{-7}	2	0.440	0.03
4.79×10^{-6}	2	0.375	0.03	4.28×10^{-6}	2	0.239	0.04
9.58×10^{-6}	2	0.286	0.03	8.46×10^{-6}	2	0.203	0.07
4.79×10^{-5}	2	0.168	0.15	4.28×10^{-5}	2	0.165	0.12
8.62×10^{-5}	2	0.154	0.08	7.71×10^{-5}	2	0.155	0.12
Bromoform Bond Number = 2.41×10^{-6}				Tetrachloroethylene Bond Number = 7.11×10^{-7}			
Capillary Number	N	Trichloroethylene Saturation	CV	Capillary Number	N	Chlorobenzene Saturation	CV
8.89×10^{-7}	4	0.413	0.08	9.05×10^{-7}	2	0.299	0.12
4.45×10^{-6}	3	0.232	0.06	4.53×10^{-6}	2	0.191	0.10
8.89×10^{-6}	6	0.182	0.09	9.05×10^{-6}	2	0.167	0.08
4.45×10^{-5}	3	0.154	0.10	4.53×10^{-5}	2	0.145	0.07
8.00×10^{-5}	6	0.158	0.10	8.15×10^{-5}	2	0.145	0.07
Trichloroethylene Bond Number = 5.51×10^{-7}				Chlorobenzene Bond Number = 1.36×10^{-7}			

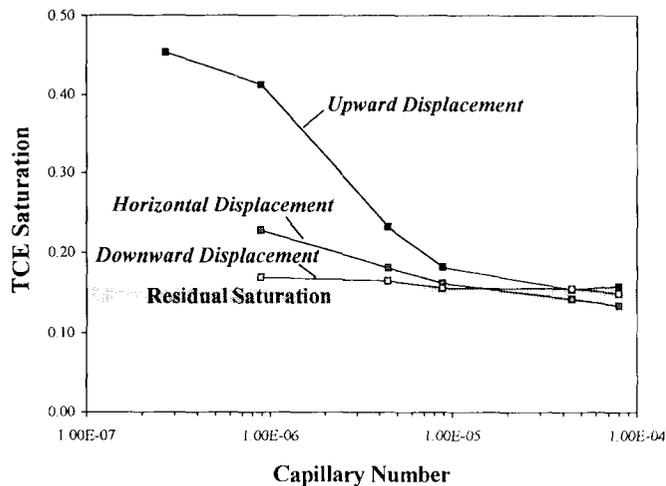


Fig. 5. Trichloroethylene (TCE) saturation as a function of Capillary Number ($v_w \mu_w / \gamma_{ow} \cos \theta$) and displacement direction.

10^{-5}) by increasing the waterflood rates from 0.25 to 22.5 ml/min, corresponding to Darcy velocities ranging from 270 to 24,000 m/yr. TCE saturations obtained at low waterflood rates were highest for upward displacement (0.45), intermediate in value for horizontal displacement (0.23), and lowest for downward displacement (0.17). This is readily explained considering that the density difference between DNAPLs and water hinders upward displacement of the DNAPL by water. At the lowest waterflood rates, the Capillary Number (8.9×10^{-7}) is roughly the same magnitude as the Bond Number for TCE (5.5×10^{-7}). Thus, at these low waterflood rates, the viscous force is counteracted by the gravitational force [as described by equation (20)] and a larger fraction of the DNAPL remains in the pores. In downward displacement, buoyancy enhances the displacement and the combination of the viscous force and gravitational force yields low saturation even at low waterflood rates. Horizontal displacement should be independent of buoyancy effects, as shown by equation (15), and consequently intermediate results are obtained. All three displacement directions, however, yielded similar values of residual saturation, averaging 0.15. There is no statistically significant difference (based on t-tests at the 0.01 level of significance) among the values of residual saturation obtained at high Capillary Numbers for the three displacement directions. This suggests that the viscous forces induced by waterflooding, even at high rates, cannot overcome the capillary forces restraining the residual DNAPL in the sand.

The remainder of the displacement experiments were conducted with a vertical column in which water was introduced from the bottom (upward displacement), allowing buoyancy to play a maximum role in the DNAPL displacement process. Figure 6, which plots DNAPL saturation versus Capillary Number for all four DNAPLs studied—bromoform (BRF), chlorobenzene (CBZ), tetrachloroethylene (PCE), and trichloroethylene (TCE)—shows that the DNAPL saturations decrease with increasing Capillary Number up to a value of approximately 5×10^{-5} , and thereafter are independent of Capillary Number. At the lowest Capillary Numbers shown (equivalent to a Darcy velocity of approximately 270 m/yr), the DNAPL saturations ranged from 0.30 for chlorobenzene, the least dense liquid ($N_{Bo} = 1.30 \times 10^{-6}$), to 0.55 for bromoform, the most dense liquid ($N_{Bo} = 2.41 \times 10^{-6}$). These results may be explained by considering equation (20), which suggests that for a given

Capillary Number in upward displacement, larger Bond Numbers will result in smaller values for the mobilizing force and, consequently, greater DNAPL saturations. The residual saturation observed for all four compounds was approximately 0.15. There is no statistically significant difference (based on t-tests at the 0.01 level of significance) among the values of residual saturation for the four organic liquids investigated. This result can be explained by recalling that the adhesion tension, which is the denominator in the Capillary Number [equation (1)] and is proportional to capillary pressure [equation (17)], does not differ significantly among the four compounds tested (Table 1). Thus, the capillary pressure force exerted at the organic liquid-water interface is essentially equivalent for all four compounds. Consequently, the resulting residual saturations for the four compounds are equivalent.

Figure 7, which plots DNAPL saturation versus Bond Number for Darcy velocities ranging from 270 to 24,000 m/yr, shows that DNAPL saturation increases markedly with increasing Bond Number at the lower waterflooding rates tested. An increase in Bond Number of approximately one order of magnitude results in a significant increase in DNAPL saturation (0.30 for chlorobenzene to 0.55 for bromoform). The depen-

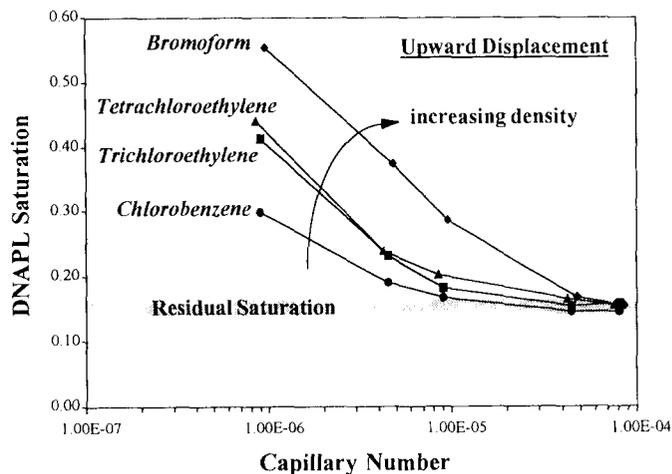


Fig. 6. DNAPL saturation as a function of Capillary Number ($v_w \mu_w / \gamma_{ow} \cos \theta$) for upward displacement experiments.

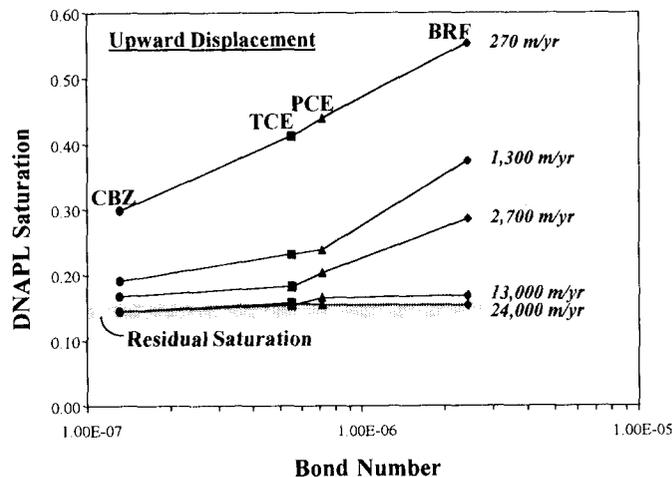


Fig. 7. DNAPL saturation as a function of Bond Number [$\Delta \rho g (k/n) / \gamma_{ow} \cos \theta$] for upward displacement experiments. (BRF = bromoform, CBZ = chlorobenzene, PCE = tetrachloroethylene, TCE = trichloroethylene).

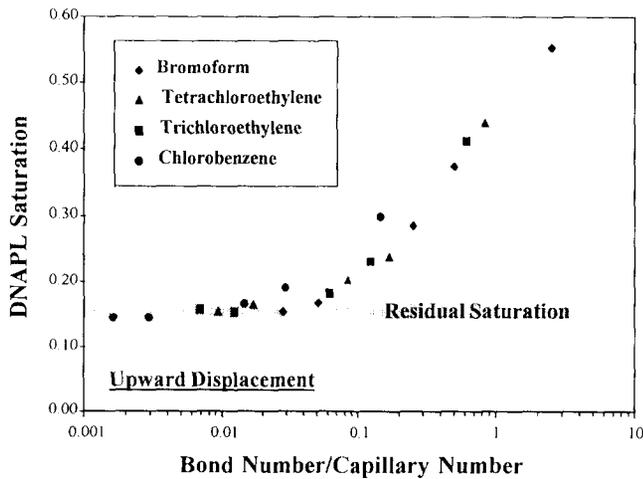


Fig. 8. DNAPL saturation as a function of ratio of Bond Number $[\Delta\rho g(k/n)/\gamma_{ow} \cos\theta]$ to Capillary Number $(v_w \mu_w / \gamma_{ow} \cos\theta)$ for upward displacement experiments.

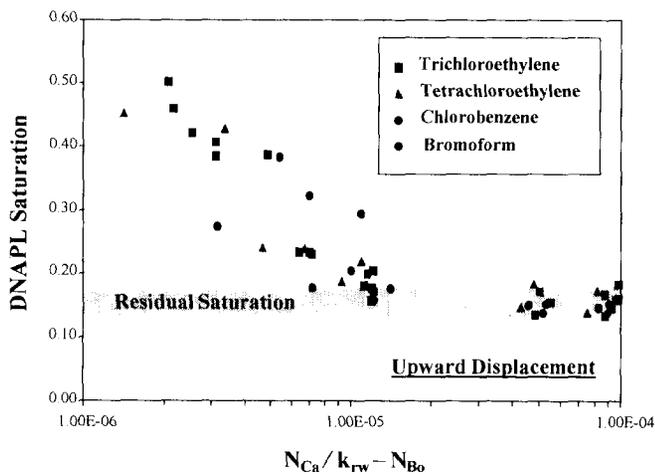


Fig. 9. DNAPL saturation as a function of $N_{Ca}/k_{rw} - N_{Bo}$ for upward displacement experiments.

dence of DNAPL saturation on Bond Number decreases with increasing velocity, as shown by the series of curves in Figure 7. At high flow rates (Darcy velocities greater than 13,000 m/yr), DNAPL saturation becomes independent of Bond Number and residual saturation is attained for all organic liquids tested. The Bond Number is directly proportional to the density difference between the two fluids; thus, in upward displacement of DNAPLs as shown in Figure 7, larger density differences lead to higher DNAPL saturations. Recall that an inverse relationship between NAPL saturation and Bond Number was reported by Morrow and Songkran (1981), as described earlier. In their experiments, a denser fluid (oil) was used to displace a lighter fluid (air); thus, the density difference aided displacement, and NAPL saturation decreased with increasing Bond Number. The experimental results obtained in this investigation, together with the results obtained by Morrow and Songkran, indicate that density differences may play a significant role in the displacement of DNAPLs from porous media, particularly if there is a vertical flow component.

Figure 8 plots DNAPL saturation as a function of the ratio of Bond Number to Capillary Number. Because the magnitude of the capillary force does not differ significantly for the four compounds used in this study, the ratio of Bond Number to

Capillary Number for each DNAPL-water pair is equivalent to the ratio of gravitational to viscous forces acting on the liquids. The result is a convergence of the data for all four compounds. Figure 8 clearly shows the relationship between DNAPL saturation and the magnitude of the Bond Number relative to the Capillary Number. DNAPL saturations attained through upward displacement decrease with decreasing Bond Number or increasing Capillary Number. When the Bond Number is approximately one tenth the Capillary Number, DNAPL saturation reaches a residual saturation that cannot be further reduced by waterflooding.

Figure 9 plots DNAPL saturations versus the combination of Capillary Number (N_{Ca}) and Bond Number (N_{Bo}) defined by equation (20); that is, $N_{Ca}/k_{rw} - N_{Bo}$. The relative permeabilities (k_{rw}) used in equation (20) are based on measured effective permeabilities to water in the presence of discontinuous DNAPL determined during the displacement experiments. In order to incorporate the permeability measurements, all the experimental measurements, rather than average values, are plotted in Figure 9. While there is some scatter in the data, DNAPL saturations are clearly dependent on $N_{Ca}/k_{rw} - N_{Bo}$. DNAPL saturations decrease with increasing values of $N_{Ca}/k_{rw} - N_{Bo}$ until a value of approximately 1×10^{-5} is reached. Thereafter, DNAPL saturation remains constant at a residual saturation of approximately 0.15, suggesting that the combination of viscous and gravitational forces defined by the Capillary and Bond Numbers can no longer exceed the capillary force restraining the residual DNAPL. While these experimental results are not likely to be directly transferable to field situations, the observed relationship between DNAPL saturation and $N_{Ca}/k_{rw} - N_{Bo}$ provides a means of estimating the system conditions under which the DNAPLs studied achieve residual saturation in aquifer material.

Summary and Conclusions

Four DNAPLs: bromoform, chlorobenzene, tetrachloroethylene, and trichloroethylene, with densities ranging from 1.106 to 2.891 g/cm³ were used to investigate the influence of viscous, gravitational, and capillary forces on DNAPL saturation in a natural aquifer sand. The relative magnitudes of these forces are expressed in terms of two dimensionless groups, the Capillary Number (N_{Ca}), defined as the ratio of the viscous force to capillary force, and the Bond Number (N_{Bo}), defined as the ratio of the gravitational force to capillary force. Nondimensionalization of the equations governing two-phase flow indicates that DNAPL saturation is a function of a linear combination of the Capillary and Bond Number, provided the relative permeability to water is considered. The experimental program, in which DNAPL saturations were measured over a range of Capillary and Bond Numbers for upward, horizontal, and downward displacement of DNAPL by water, corroborates the results of the nondimensionalization. Specific findings of this study include:

- Nondimensionalization of the equations governing two-phase flow indicates that DNAPL saturation is a function of a linear combination of the Capillary Number and Bond Number expressed as: $N_{Ca}/k_{rw} - N_{Bo}$.
- The experimental results show that DNAPL saturations depend on the magnitude of $N_{Ca}/k_{rw} - N_{Bo}$; for the DNAPLs studied, saturations decreased with increasing values of $N_{Ca}/k_{rw} - N_{Bo}$ until a value of approximately 1×10^{-5} was reached, at which point residual saturation was attained.

- DNAPL saturations attained through upward displacement decrease with increasing Capillary Number or decreasing Bond Number, until the Bond Number is approximately one tenth the Capillary Number, whereupon DNAPL saturation reaches a residual saturation that cannot be further reduced by waterflooding.

- At low Capillary Numbers (10^{-7} to 10^{-6}), upward displacement yields significantly higher DNAPL saturations than either horizontal or downward displacement, primarily because the density difference between DNAPL and water hinders upward displacement. All three displacement directions, however, yield the value of residual saturation.

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