Wettability contrasts between fresh and weathered diesel fuels

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Abstract

The remediation of non-aqueous phase liquid (NAPL) contaminated sites is impeded due to subsurface complexities, including wettability. Wettability quantifies which of two immiscible fluids preferentially coats a solid. At most contaminated sites water-wetting conditions are typically assumed despite mounting evidence that this is not always the case. In this study, wettability was examined for two NAPL samples of contrasting origin: a fresh and a field sample. Wettability was assessed through (i) cyclical, ‘cumulative elapsed contact time’ intrinsic contact angle measurements, (ii) interface jar tests, and (iii) cyclical, pseudo-static capillary pressure–saturation curves.

The work as a whole demonstrated that while the fresh diesel sample was consistently water-wet, the field diesel sample exhibited repeatable cycles of wettability reversal between water drainage and imbibition. And while wettability hysteresis increased with contact time for the field diesel, the occurrence of wettability reversal at each change of saturation direction was independent of contact time. Such behavior is not easily assessed by standard wettability indices. Moreover, it contrasts with the permanent wettability alteration observed for complex organics (e.g., coal tar) observed in most studies. It is hypothesized that the cyclical wettability reversal is related to cyclical changes in intermediate pore wettability due to sorption of surface active compounds (causing NAPL-wetting imbibition) and rupturing of the soil grain water film (causing water-wet drainage). The wettability differences between the two NAPLs may be due to additives (i.e., a surfactant) in the original formulation and/or byproducts from subsurface weathering. These results support better characterization of site-specific wettability, improved model development and more realistic site conceptual models for improved remediation efforts.

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1. Introduction

Remediation efforts at Non-Aqueous Phase Liquid (NAPL) contaminated sites often do not reduce the contamination to health-based standards (National Research Council, 1999). This may be due to an incomplete understanding of subsurface heterogeneities, including wettability (Dwarakanath et al., 2002). Wettability is the affinity of one fluid for a given solid in the presence of another immiscible fluid (Craig, 1971). Many aquifers are composed primarily of quartz sand or other naturally hydrophilic materials (Powers et al., 1996), therefore it is commonly assumed in conceptual models of contaminated sites that the porous medium is strongly water-wetting. This strongly water-wet condition is herein referred to as ‘ideal wettability’. There is mounting evidence, however, that the assumption of ideal wettability may not be appropriate at a significant fraction of contaminated sites (Dwarakanath et al., 2002; Harrold et al., 2001, 2003; Jackson and Dwarakanath, 1999; Powers et al., 1996; Zheng and Powers, 1999).

Wettability can be quantified at the scale of a single interface by measuring the intrinsic contact angle ($\theta_{\text{int}}$), which is dependent on the interfacial tension (IFT) between the immiscible fluids. A surface is typically defined as water-wetting for (approximately) $\theta_{\text{int}}<60°$ to $75°$ (measured through the aqueous phase), NAPL-wetting for $\theta_{\text{int}} > 105°$ to $120°$ and intermediate-wet for $75° < \theta_{\text{int}} < 105°$ (Anderson, 1986). For air/water/quartz, advancing contact angles (i.e., air displacing water) are small...
in the capillary pressure scale of a representative elementary volume, REV), are apparent (Bradford and Leij, 1995a; Demond and Roberts, 1991; Powers and Tamblin, 1995; Powers et al., 1996). Pure NAPL/water/quartz contact angles reported in the literature range from $5^\circ$ to $72^\circ$ (Barranco et al., 1997; Demond and Roberts, 1991; Powers et al., 1996) while NAPLs containing surfactants exhibit larger contact angles (e.g., $15^\circ$ to $180^\circ$) (Demond et al., 1994; Lord et al., 1997a; Molnar et al., 2011; Powers and Tamblin, 1995). Contact angles measured for field or waste NAPL samples on quartz have also shown a wide range of contact angles: from $12^\circ$ to $163^\circ$ (Harrold et al., 2001, 2005; Hsu and Demond, 1997; Trivedi et al., 2001; Ryder and Demond, 2008). For example, the addition of surfactants to an air/water/quartz system can significantly increase measured contact angles (e.g., $47^\circ$) (Desai et al., 1992; Lord et al., 2000). Pure NAPL/water/quartz contact angles reported in the literature range from $5^\circ$ to $72^\circ$ (Barranco et al., 1997; Demond and Roberts, 1991; Powers et al., 1996) while NAPLs containing surfactants exhibit larger contact angles (e.g., $15^\circ$ to $180^\circ$) (Demond et al., 1994; Lord et al., 1997a; Molnar et al., 2011; Powers and Tamblin, 1995). Contact angles measured for field or waste NAPL samples on quartz have also shown a wide range of contact angles: from $12^\circ$ to $163^\circ$ (Harrold et al., 2001; Powers et al., 1996). Wettability is further dependent on the order of fluid contact: a typically water-wet system may be NAPL-wetting if the NAPL phase contacts the solid first (Ryder and Demond, 2008).

The macroscopic effects of non-ideal wettability (i.e., at the scale of a representative elementary volume, REV), are apparent in the capillary pressure–saturation ($P_{c}$–$S$) relationships. As a fluid/fluid/solid system becomes less-water wet, the capillary pressure required to achieve a given saturation decreases, compressing the $P_{c}$–$S$ curve (Bradford and Leij, 1995a; O’Carroll et al., 2005; Powers and Tamblin, 1995; Powers et al., 1996). This compression is typically accounted for by modifying standard Leverett (1941) $P_{c}$–$S$ scaling to include a contact angle term (Bradford and Leij, 1995a,b; Demond and Roberts, 1991; O’Carroll et al., 2005). This contact angle is defined as the operative contact angle ($\theta_{op}$) and is typically less than the intrinsic contact angle $\theta_{r}$. $P_{c}$–$S$ scanning curves are less commonly explored, particularly with respect to wettability, but can reveal valuable characteristics associated with governing surface chemistries and pore-filling behavior on saturation reversals (Gerhard and Kueper, 2003; Kovscek et al., 1993).

NAPLs that are used as solvents and fuels typically contain compounds added to improve their performance. These additives can impact interfacial behavior, specifically those with an amphiphilic structure (i.e., surfactants), which can sorb onto the solid surface, altering surface charge. For example, polybutene amine, the active ingredient in products added to fuels to clean the carburetor and fuel injector, has rendered quartz surfaces neutral wet in the presence of synthetic fuel and water (Powers and Tamblin, 1995). Furthermore, spent solvents and fuels are likely composed of a wide range of constituents that they came into contact with during their useful life. Chlorinated solvents have been used as degreasers and in the dry cleaning industry where surfactant use is common to improve detergency. These additional constituents can have a significant impact on solid phase wettability, rendering the solid surface intermediate to NAPL-wet (Demond et al., 1994; Harrold et al., 2001, 2005; Hsu and Demond, 2007; Jackson and Dwarakanath, 1999; Molnar et al., 2011). Similarly crude oils, coal tars and creosotes, which are comprised of a wide range of constituents, frequently wet quartz surfaces. This has been attributed to the presence of high molecular weight asphaltenes with polar functional groups that reduce adhesive forces (Barranco and Dawson, 1999; Dong et al., 2004; Hugaboom and Powers, 2002; Nelson et al., 1996; Powers and Tamblin, 1995; Powers et al., 1996; Ren et al., 2009; Zheng and Powers, 2003; Zheng et al., 2001).

Weathering processes such as leaching, volatilization and biological decay are all mechanisms by which a NAPL can change composition in the subsurface and potentially induce non-ideal wettability. For example, weathering processes may degrade lighter compounds of petroleum-derived products, leaving behind heavier hydrocarbons that are known to alter wettability (Cuiec, 1990; Powers et al., 1996). As well, oxidation of NAPL systems has been shown to shift water-wetting systems to intermediate- and NAPL-wetting conditions (Cuiec, 1990; Ren et al., 2009).

These studies provide insight into how additives in fuels or weathering of waste/field NAPLs can lead to non-ideal wettability behavior. However a direct correlation between constituents present (or absent) in waste/field NAPLs and wettability alterations is still unclear. This is complicated by the significant number of constituents typically present and the potential for synergistic effects of these constituents impacting wettability. For example, the presence of both organic acid and base surfactants in a NAPL/water/quartz system has been found to alter interfacial activity more than the sum of the individual effects (Hsu and Demond, 2007; Spildo et al., 2001). With multiple additives and impurities in field systems, as well as complex release histories for many field NAPLs, it is therefore a significant challenge to a priori predict the wetting behavior of a given NAPL.

The purpose of this study was to investigate the wettability of a diesel/water/quartz system and, in particular, the contrast between a weathered field diesel and a fresh diesel. Wettability was investigated at (i) the pore scale via cyclical advancing and receding intrinsic contact angle measurements, (ii) at the scale of an interface through time lapse and equilibrium bottle tests, and (iii) at the REV scale through multiple, hysteretic, $P_{c}$–$S$ experiments including detailed scanning curves. The interface-scale analysis was complemented by testing of fluid and interfacial matter composition. The REV scale analysis was augmented through Leverett scaling of different fluid-fluid pairs and $P_{c}$–$S$ curve fitting. This comprehensive analysis of this single fluid pair aims to provide a holistic picture of (i) the wettability that may be expected for a petrochemical recovered from the field, (ii) the types of measurements that are most indicative of the observed behavior, and (iii) the potential underlying causes of that behavior. The potential applications of the information obtained include improving both numerical simulations and remediation of contaminated sites.

2. Materials and methods

2.1. Materials

Two diesel fuel oils were used as the non-aqueous phases in the experiments. A field diesel was obtained from a monitoring well at a contaminated site in London, Ontario. The NAPL was stored in a tightly sealed container in absence of light at 5 °C from time of sampling until time of equilibration for testing to ensure the sample maintained its properties at representative aquifer conditions. The fresh diesel was obtained from a gas station (Drummond Fuels Ltd., Ottawa, ON). Equilibration of the diesels with the aqueous phase occurred at room temperature (25°C), the same temperature employed for experiments. The...
isms were accumulating in the vials. An inoculation loop was used to streak samples from the jar tests onto LB-Agar plates and left to incubate at room temperature for 13 days.

2.4. Interfacial tension and contact angle

Interfacial tension and intrinsic contact angle measurements were obtained using an Axisymmetric Drop-Shape Analysis system (First Ten Angstroms, Portsmouth, VA). The system employs Young–Laplace drop shape analysis applied to high resolution photographs of light non-aqueous phase liquid (LNAPL) drops in water; a j-shaped needle was used to float an LNAPL bubble in water (for IFT) or to introduce an LNAPL bubble against the bottom of a quartz plate (for contact angle). All measurements for both IFT and contact angle were conducted with systems equilibrated in a consistent manner. A beaker with 30 mL of the aqueous phase containing a quartz plate and an inverted vial with 2 mL of LNAPL was allowed to equilibrate for at least 72 h. This setup allowed equilibration between all three phases while still allowing the quartz plate to be removed from the aqueous phase without contacting the NAPL. This setup ensured the contact angle measurements were analogous to the initially water-saturated \( P_{c-S} \) experiments (corresponding to NAPL encountering an uncontaminated aquifer).

LNAPL contact angles were achieved by repeatedly advancing and receding an LNAPL drop on the same area of a quartz plate. Between advancing and receding contact angle measurements, LNAPL drops were left to equilibrate on the quartz plate. Advancing and receding contact angle measurements were taken at multiple equilibration time intervals to investigate temporal contact angle hysteresis. At each time interval, at least five measurements for each of the advancing and receding contact angles were taken and averaged. In cases where the measurements were not consistent (e.g., the receding contact angle varied as the drop receded) or a single value was not easily determined (e.g., due to imperfect resolution of the intersection of the contact line and surface) the maximum and minimum possible contact angles are reported. This cyclical and ‘cumulative elapsed contact time’ contact angle measurement method was developed specifically to imitate the cyclical saturation reversals experienced by the quartz sand in the \( P_{c-S} \) experiments (i.e., NAPL contact times in the porous media varied from experiment to experiment, particularly when conducting scanning curve experiments).

2.5. Capillary pressure–saturation experiments

Capillary pressure–saturation experiments were conducted using a membrane-based stainless steel pressure cell based on an established design (Salehzadeh and Demond, 1999). An air pressure regulator (Model 44-2, Moore Products, Spring House, PA) was used to control NAPL pressure in a reservoir connected to the top of the pressure cell (Fig. 1). Stainless steel porous plates (20 \( \mu \)m pores and 1.6 mm thickness, Mott Corp., Farmington, CT) served as structural support for the upper hydrophobic membrane (PTFE with 0.45 \( \mu \)m pores, Pall Corp., Port Washington, NY) and the lower hydrophilic nylon membrane (0.2 \( \mu \)m pores). The cells were wet-packed in three layers using Milli-Q water that had equilibrated with the NAPL for at least 72 h using a method similar to that used by Chen et al. (2007). 25 pore volumes of the aqueous solution were added to the system using a 25 mL syringe filter. Photographs of light non-aqueous phase liquid (LNAPL) drops in water; a j-shaped needle was used to float an LNAPL bubble in water (for IFT) or to introduce an LNAPL bubble against the bottom of a quartz plate (for contact angle). All measurements for both IFT and contact angle were conducted with systems equilibrated in a consistent manner. A beaker with 30 mL of the aqueous phase containing a quartz plate and an inverted vial with 2 mL of LNAPL was allowed to equilibrate for at least 72 h. This setup allowed equilibration between all three phases while still allowing the quartz plate to be removed from the aqueous phase without contacting the NAPL. This setup ensured the contact angle measurements were analogous to the initially water-saturated \( P_{c-S} \) experiments (corresponding to NAPL encountering an uncontaminated aquifer).

2.2. Weathing

GC–MS analysis was used to establish the degree of weathering by determining the presence of diesel constituents. An Agilent 7890 GC with a DB-5 column (30 m × 0.25 mm i.d., 0.25 \( \mu \)m thickness) was coupled with an Agilent 5675 MSD. The GC–MS method used was based on the weathered diesel analysis method of Lang et al. (2009) for GC–MS analysis. Fresh and field diesel samples were diluted with dichloromethane (DCM) using a 5:1 ratio.

2.3. Interfacial analysis

Bottle tests were performed to observe temporal changes in the diesel–water interface in the absence of a porous medium. Vials were suspended over the camera (Nikon D80) so the interface was directly above the field of view. The 3 mL vials contained 1 mL of de-ionized water and 2 mL of diesel that was filtered through a 0.2 \( \mu \)m syringe filter. Photographs were taken at two-hour intervals over a period of two weeks. Additional tests were performed to determine if microorganisms were accumulating in the vials. An inoculation loop was used to streak samples from the jar tests onto LB-Agar plates and left to incubate at room temperature for 13 days.
were then flushed through the packed cell using a syringe pump (kd Scientific, Holliston, MA).

$P_c$–$S$ data was obtained using an automated pseudo-static system (Chen et al., 2007). The NAPL pressure was gradually increased by increasing the air pressure above the NAPL surface (Fig. 1) at a slow and constant rate (0.2 cm water/min). Pressure readings were collected every 10 s using gauge pressure transducers (FP2000, Honeywell, Morristown, NJ) connected to a datalogger (CR3000, Campbell Scientific, Edmonton, AB). The pressure transducers were used to quantify both phase pressure and saturation (Chen et al., 2007). $P_c$ values were averaged over 0.5% saturation bins, and each resulting $P_c$ data value (composed of, on average, 12–15 measurements) was reported at the midpoint of each saturation bin. A complete $P_c$–$S$ primary drainage/main imbibition curve was completed in approximately 15 h. The system was validated by demonstrating that the $P_c$–$S$ curve for a silicone oil/water/F32-50 sand system determined by a standard static experiment lay within the 95% confidence interval about the mean of four repeat pseudo-static $P_c$–$S$ curves (Drake, 2010).

Six experiments consisting of primary drainage and main imbibition curves were completed for the fresh diesel with F70 sand. In addition, two of the six experiments included scanning loops (6 loops over 3 unique saturation paths and 21 loops over 9 unique saturation paths, respectively). For the field diesel, eight experiments with F70 sand were completed: five with unfiltered and three with filtered field diesel; this resulted in reliable data for three drainage and eight imbibition $P_c$–$S$ curves. One of the eight experiments included scanning curves (13 scanning loops over 11 unique saturation paths).

All data was plotted as apparent saturation (Bradford et al., 1998) to accommodate curve-fitting and comparison between data sets; this is reasonable because the focus in this work is on significant differences in capillary pressure values characterizing the majority of the $P_c$–$S$ main branches and not on the details of the residual water or NAPL at the curve endpoints. A modified form of the van Genuchten (1980) equation, incorporating a translation parameter ($\eta$) that satisfies $(P_c + \eta) \geq 0$ for all $P_c$, enabled fitting of both the positive and negative $P_c$ values observed (Bradford and Leij, 1995a). The best-fit van Genuchten parameters were determined by the method of O’Carroll et al. (2005), which minimized the root mean square difference of saturation values, putting importance on the intermediate saturation range.

Operative contact angles, quantifying the hysteresis between drainage and imbibition for the measured $P_c$–$S$ imbibition curves, were determined through modified Leverett scaling. The fresh diesel/water drainage curve, taken as the reference curve, was scaled to the imbibition curves via the modified Leverett–Cassie equation (O’Carroll et al., 2005):

$$P_c^{\alpha\beta}(S_{\alpha}^{app}) = \frac{\gamma^{\alpha\beta}}{\gamma^{app}} \left( \cos(\theta_{op}^\alpha) P_c^{ref}(S_w^{app}) \right)$$  \hspace{1cm} (1)

where $P_c^{\alpha\beta}(S_{\alpha}^{app})$ is the $P_c$ for a given imbibition curve (fluids $\alpha$ and $\beta$) at apparent saturation of the $\alpha$ phase corresponding to the reference $P_c$ at the same saturation ($P_c^{ref}(S_w^{app})$), $\gamma^{\alpha\beta}$ is the IFT between fluids $\alpha$ and $\beta$, $\gamma^{app}$ is the reference system IFT and $\theta_{op}^\alpha$ is the operative contact angle through the $\alpha$ (wetting) phase. The Leverett–Cassie equation was developed for systems with heterogeneous wettability, however it reduces to Eq. (1) when the porous medium is homogeneous.

3. Results and discussion

3.1. Weathering analysis of diesels

The GC/MS chromatograms for the two diesel samples are consistent with expectations given their origins. The fresh diesel chromatogram (Fig. 2) reveals the strong presence of
straight-chained alkanes (n-alkanes) that peak at regular intervals over the chromatogram range (Christensen and Larsen, 1993); in particular, the major components present are the twelve dominant alkanes ranging from n-C10 to n-C21, which are typical of a diesel fuel (Galperin and Kaplan, 2008). In contrast, the field diesel chromatogram (Fig. 3) exhibits prominent peaks for pristane and phytane while the n-C17 peak is absent and the n-C18 peak is relatively small. While n-alkanes such as n-C17 and n-C18 are subject to biodegradation, their closely related isoprenoid compounds – pristane and phytane – are not; for this reason, the ratio of n-C17 to pristane is typically correlated to the age of a diesel spill (Christensen and Larsen, 1993). Conservative estimates suggest that n-C17 is expected to be completely degraded after two decades in the subsurface, although this can occur in as little as 5–6 years under ideal, aerobic conditions (Hurst and Schmidt, 2005). The absence of n-C17 in the field diesel chromatogram (Fig. 3) suggests that this diesel was significantly weathered. Oxidation products were not observed in either chromatogram. Refined petroleum products commonly have stabilizer additives, included to inhibit oxidation of the fuels during storage (Song et al., 2000). These additives may be present in either or both diesel samples.

3.2. Interfacial analysis

Bottle tests conducted in the absence of porous media revealed that a white matter accumulated at the interface between diesel and water for both diesel types. No interfacial matter was observed for control samples (i.e., diesel not in contact with water) at the same temperature. Samples were filtered prior to each test and no interfacial matter was initially present. Moreover, results revealed that the field diesel sample developed significantly more interfacial matter than the fresh diesel and the matter appeared sooner. The first appearance of the interfacial matter was at 7.5 h for the field diesel, contrasted with 5 days for the fresh diesel. The interfacial matter developed at the lowest point of the interface (visible as a bright white dot) but spread out over the interface with time (appearing as a white film and resulting in the diesel looking cloudy). On the timescale of a P_c–S experiment (20 h to
3 days), and specifically the primary drainage curve (7 h), it is
expected that only the field diesel P_c–S results may be impacted
by the development of this interfacial matter.

The formation of interfacial matter has also been observed
in other studies. Field samples of black diesel and coal tar
formed semi-rigid interfacial films impeding accurate contact
angle measurements (Powers et al., 1996). Similar films have
been observed for waste trichloroethylene (Harrold et al.,
2001), crude oils and field coal tars (Nelson et al., 1996).
Nelson et al. (1996) concluded that the binding of water
molecules to coal tar molecules created this film which acted
as a very thin emulsion layer. They did not see any functional
groups typical of surfactant compounds in GC/MS, NMR and
IR spectra, however they note that very small concentrations
would not be detected. The white interfacial matter in this
study did not form a continuous, semi-rigid film as observed
with the heavier NAPL samples discussed above. Consider-
able effort was expended attempting to identify the precip-
itate. Isolating the matter from the diesel proved to be
very difficult. Neither FTIR nor SEM/EDX analyses provided a
definitive answer regarding composition.

The diesel, interfacial matter, and water from the bottle
tests were additionally streaked on LB-Agar plates to investi-
gate the presence of microorganisms. For both diesels, there
was microbial growth for those samples taken from both the
water phase and the interfacial area but not the diesel. The
numbers of colonies from the water and interfacial matter from
the field diesel sample were substantially higher than those
from the fresh diesel sample, possibly indicating that the
presence and accumulation rate of the interfacial matter may
be related to microorganisms.

There are at least two possible other explanations for the
more significant rate of accumulation of interfacial matter
observed in the field diesel. First, some difference in the
original composition of the two diesels may play a significant
role. Composition variations may have been due to different
intended uses of each diesel and/or the formula of additives
used. Hundreds of additives, which vary between supplier,
may be used to improve performance and these often have
surface active behavior (Song et al., 2000). Analysis for these
compounds is challenging as the target compound(s) must be
known in advance. Second, the final composition of the diesels

Fig. 3. Field diesel GC/MS chromatogram illustrating major alkanes at regular intervals across the chromatogram with C17 notably absent, and pristine and
phytane exhibiting significant peaks.
Physical properties of non-aqueous phases.

<table>
<thead>
<tr>
<th>NAPL</th>
<th>Density (g/mL)</th>
<th>IFT with water (25 °C) (mN/m)</th>
<th>θ_{Advancing} (°)</th>
<th>θ_{Receding} (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh diesel</td>
<td>0.808</td>
<td>28.1 ± 1.5</td>
<td>10.7 ± 0.3</td>
<td>&lt;33\textsuperscript{b}</td>
</tr>
<tr>
<td>Field diesel</td>
<td>0.825</td>
<td>17.2 ± 1.0</td>
<td>29.5 ± 2.2</td>
<td>180°</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Error reported as 95% confidence interval about the mean.
\textsuperscript{b} Visual obstruction made measurement difficult therefore the maximum possible angle is reported here.
\textsuperscript{c} Pinning of contact angle taken as 180°.

(i.e., weathering) may have been significant. As previously discussed, GC–MS chromatograms indicated the field diesel was significantly weathered. In such cases, the biodegradation and oxidation of hydrocarbons may produce more polar compounds (Cuiec, 1990; Lang et al., 2009) reducing hydrophobicity. Therefore, when the diesel was left in contact with water these compounds could preferentially partition to the water phase, changing the diesel phase chemistry and resulting in heavier, non-polar molecules that precipitated out. In addition, the weathering of the field diesel may have resulted in NAPL components binding with water molecules as observed for Nelson et al. (1996).

### 3.3. Interfacial tension and contact angle

The fresh diesel exhibited a greater IFT than the field diesel (Table 1), however both IFT values were relatively low compared to an analogous, single component NAPL; for example, the IFT between pure o-xylene and water is 39 mN/m (Lord et al., 2000). The measured IFT values are consistent with diesel fuels commonly containing additives for improved performance. It is possible that the reduced IFT of the field diesel is associated with the white interfacial matter observed in the jar tests. However, weathered NAPLs do not necessarily exhibit IFT values less than that of un-weathered samples. Harrold et al. (2003) found that surface active constituents present in NAPL sorbed to soil, thereby decreasing their concentration in the NAPL phase and increasing interfacial tension.

Intrinsic contact angles measured with the fresh diesel were consistent with strongly water wet conditions (Table 1, Fig. 4). No significant hysteresis was observed between advancing and receding contact angles and no sensitivity to elapsed contact time (up to 300 min.) was observed (Fig. 4). The maximum θ\textsubscript{int} = 33° (with mean θ\textsubscript{int} = 10.7 ± 0.3) indicated that fresh diesel remained water-wetting even after significant contact time with the solid and repeated reversals of contact line direction. In contrast, the field diesel exhibited considerable contact angle hysteresis that was time-dependent. The field diesel advancing θ\textsubscript{int} was consistent at 29.5° ± 2.2° over 700 min. of total elapsed contact time (Table 1, Fig. 4). The field diesel receding contact angles, however, exhibited intermediate wetting behavior immediately (θ\textsubscript{int} = 146° at 0 min.) and increasing hydrophobicity with elapsed contact time. From 20 min to 110 min of elapsed contact time, observed receding contact angles were not consistent since erratic, “temporary pinning” led to NAPL drop recession that was not smooth and continuous. In Fig. 4, the range between the maximum and minimum observed receding contact angles are indicated by the error bars. After 110 min of elapsed time, the contact line pinned completely – i.e., the baseline of the drop remained static as the drop volume was reduced – and the receding intrinsic contact angles for the field diesel approached 180°.

Harrold et al. (2001) also observed contact angles that increased with the time that the quartz plates were immersed in the NAPL phase prior to measurement. Immersion for 1 min was sufficient to change an initially strongly water-wet plate to weakly NAPL-wet (Harrold et al., 2001). The impact of prior exposure in their study was more significant for waste NAPLs (i.e., from a solvent recovery company) than for pure NAPLs with surfactant additives. Molnar et al. (2011) also observed similar tetrachloroethylene/water contact angle hysteresis due to sorption of a cationic surfactant onto an iron oxide-coated plate at neutral pH. Lam et al. (2002) identifies a number of fluid-fluid–solid systems that exhibited similar “stick/slip” behavior, attributed to chemical bonding between the receding...
drop and the surface. That work further quantified the time dependence of receding contact angles with liquid molecule penetration of the surface and/or sorption and, when the liquid molecules anchored themselves sufficiently firmly on the solid, the drop would not recede whatsoever (Lam et al., 2002). Thus, the time-dependent and pinning behavior observed here is likely due to surface active constituents present in the field diesel sorbing to the solid surface.

3.4. Capillary pressure–saturation main curves

The average of the six fresh diesel/water system primary drainage and imbibition experiments, with 95% confidence intervals, is presented in Fig. 5. The curves are consistent with strongly water-wet conditions, with positive capillary pressures exhibited on both $P_c$–$S$ pathways at almost all saturations. The imbibition curve reaches negative $P_c$ values at water saturations above 96.5%. This is in agreement with the measured advancing and receding intrinsic contact angles (Table 1, Fig. 4). van Genuchten fits reproduced the measured mean behavior except for a slight discrepancy near residual and high water saturation (parameters in Table 2). A similar study on a diesel fuel obtained from a retail outlet also showed strongly water-wetting conditions through advancing contact angle quantification, qualitative bottle tests and USBM/Amott-Harvey indices calculated from $P_c$–$S$ curves (Powers et al., 1996).

Fig. 6 presents the averaged field diesel $P_c$–$S$ data, including three primary drainage and eight main imbibition curves. The field diesel primary drainage data was consistent with intrinsic (advancing) contact angle measurements that indicated strongly water-wet behavior (Table 1, Fig. 4). Capillary pressures on imbibition, however, were negative above an apparent water saturation of 5%, consistent with intermediate- or NAPL-wetting conditions. This indicates a reversal of the fluid phase that preferentially wetted the quartz surfaces once the field diesel contacted the porous medium. This wettability reversal is also consistent with the measured (receding) intrinsic contact angles (Table 1, Fig. 4).

Fig. 7 plots the primary $P_c$–$S$ data for both diesels, with that of the fresh diesel and its 95% confidence intervals scaled by the ratio of their interfacial tensions. The scaled fresh diesel data lies slightly above that of the field diesel, however the 95% confidence intervals overlap suggesting that both systems are strongly water-wet and the operative contact angle is approximately 0°.

Fig. 8 illustrates the Leverett scaling of imbibition curves from the reference fresh diesel drainage curve. An operative contact angle of 71.7° for the fresh diesel imbibition curve was determined using Eq. (1). Strongly water-wet systems typically exhibit capillary pressures on imbibition that are 40–60% of their magnitude on drainage (Gerhard and Kueper, 2003; O’Carroll et al., 2005). In this case, $\cos(71.7°) = 0.31$ indicating slightly greater hysteresis than typical, but suggestive that relatively strong water-wet conditions prevailed. Eq. (1) determined an operative contact angle of 107.7° for the field diesel.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$N$</th>
<th>$\alpha$ [cmwater]$^{-1}$</th>
<th>$\eta$ [cmwater]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh diesel primary drainage</td>
<td>14.04</td>
<td>0.032</td>
<td>0</td>
</tr>
<tr>
<td>Fresh diesel main imbibition</td>
<td>5.18</td>
<td>0.071</td>
<td>5.88</td>
</tr>
<tr>
<td>Field diesel primary drainage</td>
<td>14.90</td>
<td>0.061</td>
<td>0</td>
</tr>
<tr>
<td>Field diesel main imbibition</td>
<td>5.69</td>
<td>0.024</td>
<td>10.84</td>
</tr>
</tbody>
</table>

Table 2
van Genuchten best-fit parameters for LNAPL/water/F70 sand.
diesel imbibition curve, indicating intermediate-wetting to NAPL-wetting conditions. The receding contact angle measured on the quartz slide for the fresh diesel system ($< 33^\circ$) was less than the operative contact angle scaled based on the $P_c$–$S$ experiments (71.7°). This possibly indicates that the intrinsic contact angle, measured on a quartz slide, may not adequately quantify the degree of hysteresis present in porous media. In the field diesel system the intrinsic contact angle (~180°) was considerably larger than that found based on scaling the $P_c$–$S$ curves (107.7°). The reason for this discrepancy could be that the residency time of the NAPL in the $P_c$–$S$ experiments may not have been adequately long to render the porous media extremely hydrophobic.

3.5. Capillary pressure–saturation scanning curves

Two representative experiments, one for each of the fresh and field diesel (Figs. 9 and 10, respectively) that included scanning curves demonstrate the reproducibility of the data. The number of repeat scanning curves that overlap each
other, the variety of saturation pathways explored, and noting that each complete data set was measured in approximately 89 h speaks to the strength of the pseudo-static method.

On primary drainage both system exhibited water wetting behavior since they scale well based solely on interfacial tension. It is important to note that both porous media systems have been flushed with numerous pore volumes of aqueous phase that was pre-equilibrated with either fresh or field diesel. As such, water/diesel interfacial tensions were not equivalent in both systems and soluble diesel constituents would have been exposed to the surface of the quartz grains. Upon saturation reversal, either at residual water saturation or at some intermediate saturation, the shape of the imbibition curves were distinctly different (Figs. 9 and 10). Moreover, the field diesel exhibited cyclical, repeatable wettability reversals (Fig. 10). Wettability reversal phenomena are discussed in significant detail by Kovscek et al. (1993) for a crude oil system. Similar phenomena are likely occurring in the field diesel system however wettability reversal is not permanent as is the case with crude oil. Permanent wettability reversal in crude oil is due to the presence of asphaltenes. On water drainage diesel displaces the aqueous phase as capillary pressure increases and the thickness of the water film surrounding the porous media decreases. When the critical capillary pressure is achieved in a pore the water film surrounding the quartz grains ruptures, leaving monolayer coverage of water molecules surrounding the sand grains (Kovscek et al., 1993). At this point constituents from the field diesel can partition to the solid surface rendering the sand organic-wetting. As suggested by Kovscek et al. (1993), this wettability reversal occurs primarily in the intermediate pore size class as the critical capillary pressure may not be achieved in the largest pores and no NAPL invades the smallest pores. Wettability reversal was not observed in the fresh diesel system, consistent with measured contact angle and the main \( P_{c-S} \) curves.

With decreased capillary pressure little water imbibed into the field diesel system initially as the intermediate pore size range was organic-wet and the largest pores required a significant decrease in capillary pressure prior to water reinvansion. As illustrated in Fig. 10, some water entered the largest pores at positive capillary pressures but negative capillary pressures are required to displace the majority of the NAPL. In the fresh diesel system on water imbibition, water would enter the intermediate sized pores followed by the largest pores as there was no wettability reversal (Fig. 9). For this reason, the water imbibition curves in the fresh diesel system exhibited a reduced slope relative to the field diesel system (i.e., \( dP_c/dS_w \) for field diesel > \( dP_c/dS_w \) for fresh diesel at saturation reversal). In the field diesel system, however, the intermediate sized pores were organic wetting at the end of drainage. As such, it is postulated that, similar to water drainage in an initially water wet system, a critical (minimum, in this case) capillary pressure must be achieved to rupture the NAPL film surrounding the quartz sand grains. At this point the NAPL molecules on the quartz sand grains are displaced by water and pores where this critical capillary pressure has been achieved in the field diesel system become water wetting again.

Upon subsequent saturation reversal (i.e., main drainage scanning curve) the water-wet pores in the field diesel once again followed the main drainage path consistent with a water-wet system (Fig. 10). The shapes of the water drainage scanning curves between the fresh and field diesels are revealing. In general, at the start of a drainage event, a high \( P_{c-S} \) slope and the presence of an entry capillary pressure is evidence that the NAPL was nonwetting and discontinuous in the largest pore bodies (Gerhard and Kueper, 2003). For the fresh diesel (Fig. 9), typical water-wetting behavior was observed in that the primary drainage curve exhibited a distinct entry pressure, but as scanning curve reversal points approach \( S_w = 0.5 \), \( P_{c-S} \) slopes were observed to reduce (i.e., become shallower) (Haines, 1930; Morrow, 1976; Parlane, 1976). This is expected since, at intermediate saturations the NAPL was continuous and no entry pressure needed to be overcome. However, in the field diesel system, all \( P_{c-S} \) drainage curves were equally steep, exhibiting a distinct entry pressure for any NAPL invasion regardless of reversal saturation, further underscoring the cyclic wettability reversal (Fig. 10).

Studies employing laboratory grade NAPLs and controlled concentrations of surfactant additives have observed wettability phase reversal (Demond et al., 1994; Desai et al., 1992; Powers and Tamblin, 1995). In these studies, cationic surfactants sorbed to the quartz surface, reducing hydrophilicity and, at high surfactant concentration, reversed wettability. Lenhard and Oostrom (1998) discuss how a NAPL with a sorbing surfactant can create mixed wettability – where the pores exposed to NAPL become NAPL-wetting and the pores continuously filled with water remain water-wetting. These previous studies provide insight but do not adequately explain the cyclical wettability reversal behavior observed in this study. The interfacial matter observed in the field diesel after a short time, potentially associated with diesel additives (Song et al., 2000), may play a role. In addition, the weathered composition of the diesel fuel may play a role as may any compounds added to the diesel to inhibit degradation during storage. Typical antioxidants include alkylated phenols and secondary amines (Song et al., 2000), both of which may act as surfactants. The a priori knowledge of specific analytes combined with the extremely low detection limits required for these compounds made the identification of any additives not practical in this study.

4. Conclusions

Examination of wettability at the pore scale, interface scale and REV scale suggests that NAPLs recovered from a field site may not be adequately represented by similar fresh NAPLs due to wettability differences. Increased contact time between a field diesel and quartz in the presence of water significantly increased the hydrophobicity of the solid, from intermediate wetting to NAPL wetting. Moreover, a field diesel exhibited cyclical reversals of wettability, with water-wetting behavior on drainage and NAPL-wetting behavior on imbibition; such behavior at the REV-scale is linked to cyclical hysteresis of the intrinsic contact angle. The shape of the \( P_{c-S} \)-S scanning curves in such cases reveals that the invading fluid must overcome the porous medium entry pressure at every saturation reversal, unlike an identical system that is strongly water-wetting irrespective of saturation history.

It is not surprising that a diesel fuel may exhibit NAPL-wetting behavior after contact with the soil, e.g., due to the presence of a surfactant additive in the formulation or polar
compounds produced via weathering. Such compounds, even in small quantities, can precipitate at the interface, sorb to solid surfaces, and alter the soil–liquid interfacial forces. It is hypothesized that the cyclical wettability reversal is related to cyclical changes in intermediate pore wettability due to rupturing of the film surrounding the soil grain at a critical capillary pressure. It is possible that cyclical wettability reversals have not previously been observed because of the challenge of conducting multiple, rapid P–S experiments with the small volumes of NAPL typically available from field sites. Towards this end, the pseudo-static method for P–S curves combined with the “elapsed contact time” method for measuring cyclical intrinsic contact angles, may be a valuable approach to determine the wettability of field soil/NAPL systems. The wettability observed for the field system would need to be incorporated into numerical models to properly predict NAPL migration and remediation at the field site.

Remediation plans must be developed with knowledge of field NAPL wettability to achieve source zone remediation goals. Wettability changes will impact source zone architecture – sub-regions of pools and residual may have significantly different spatial distribution and NAPL/water interfacial area than expected. Thus, at the field scale, this may have implications on local mass flux and, in turn, the potential longevity of a NAPL site. Towards this end, the pseudo-static method for P–S curves must be understood in order to adequately manipulate capillary pressure for NAPL displacement by water.

It is noted that the conclusions in this study are based upon a single detailed comparison of two similar NAPLs. The fresh sample examined in this study exhibited water-wetting behavior however other retail formulations will vary and may possess compounds that will create non-ideal wettability. In addition, only quartz was employed which neglects the potential impacts on wettability of other minerals or organic coatings. The aqueous phase chemistry was simplified by using deionized water at neutral pH. However, this study does isolate and illustrate the impacts of a field NAPL on wettability and the significant differences that may exist between a field and a fresh NAPL.

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References