

CREOSOTE WETTABILITY REVIEW AND EVALUATION AT A PORTION OF THE CABOT CARBON/KOPPERS SUPERFUND SITE

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ABSTRACT

Creosote in the subsurface is acted on by three forces: (1) gravitational (pressure due to gravity), (2) capillary (capillary pressure) and (3) hydraulic (also known as viscous force or hydrodynamic pressure). Due to its high viscosity (~10 cp, and higher with weathering) and similar density (~1.03 to 1.10 g/cc) relative to water (1 cp and 1.0 g/cc), creosote movement and retention in the subsurface are influenced significantly by capillary forces. In general, capillary forces tend to trap creosote while gravitational and hydraulic forces tend to mobilize creosote. Creosote is mobilized when the vector sum of the gravitational and hydraulic forces exceed the capillary force.

There are several parameters (i.e., interfacial tension, pore size, and wettability) that control capillary force and influence creosote mobility. Wettability, the focus of this paper, refers to the tendency of one fluid (the wetting fluid) to spread over and adhesively coat a solid surface in the presence of another fluid (the nonwetting fluid); it depends on interfacial tension and is a major determinant of flow, entrapment, distribution, and recoverability of creosote in the subsurface. Most natural porous media, which have not been invaded by complex organic liquids such as crude oil or creosote, are generally strongly water-wet.

The simplest measure of wettability is the contact angle at the fluid-solid interface; this is referred to as the contact angle method. Other methods used to measure wettability are capillary pressure-saturation measurement methods, the qualitative bottle test method, and the adhesion test method. A comprehensive literature review was performed and data on creosote wettability were compiled. Based on the literature review, during initial creosote invasion below the water table, creosote is the nonwetting fluid and its entry in the subsurface media is resisted by water-filled pores. With time in the subsurface, it is possible for chemical reactions involving creosote, especially at low aqueous phase pH, to cause the media to become more intermediate-wet or creosote-wet along flow paths after contact with creosote. This condition leads to increased creosote trapping, hindering creosote recovery efforts.

Creosote was collected from the Cabot Carbon/Koppers Superfund Site, a wood-treating site in Gainesville, FL that formerly used creosote. Wettability testing was performed utilizing contact angle measurements and qualitative bottle tests. Results are generally consistent with those reported in the literature, indicating water-wet conditions below the water table and creosote-wet conditions in an air-creosote system. Measured contact angles did not change with aging over 42 days, but rapid formation of a semi-rigid interfacial film on the creosote drops may have constrained creosote spreading over time.

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INTRODUCTION

There are several parameters (i.e., interfacial tension, pore size, and wettability) that control capillary force and influence creosote mobility. Wettability refers to the tendency of one fluid to spread over and adhesively coat a solid surface in the presence of another fluid; it depends on interfacial tension and is a major determinant of flow, entrapment, distribution, and recoverability of creosote in the subsurface. The fluid that preferentially spreads over solid surfaces is known as the wetting fluid, and the fluid repelled by capillary forces is the nonwetting fluid. The simplest measure of wettability is the contact angle at the fluid-solid interface (**Figure 1**). Most natural porous media, which have not been invaded by complex organic liquids such as crude oil or creosote, are generally strongly water-wet.

For a water-NAPL system with water being the wetting phase, capillary pressure, P_c , is defined as:

$$P_c = P_n - P_w$$

where P_n is the NAPL pressure and P_w is the water pressure. Capillary pressure is a function of interfacial tension between NAPL and water (σ), contact angle between NAPL and water (θ), and pore size (Bear, 1979):

$$P_c = (2 \sigma \cos \theta) / r$$

where r is the radius of the water-filled pore resisting nonwetting fluid entry.

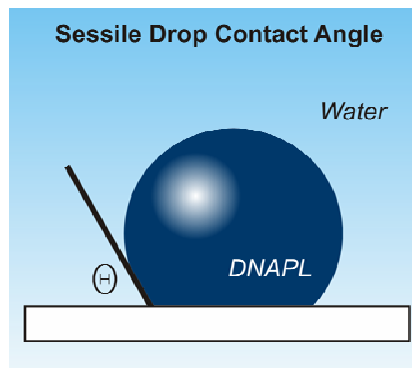


Figure 1. A porous medium is considered water-wet if the contact angle, θ , measured through water is less than 70° , DNAPL-wet if θ is greater than 110° , and neutral (mixed or intermediate) if θ is between 70° and 110° .

Capillary pressure increases as r and θ decrease and as σ increases. The wetting fluid, therefore, will occupy smaller pores and smaller portions of larger pores (thin films), and the nonwetting fluid (that, due to gravitational and/or hydraulic forces, is able to overcome the capillary force and invade a porous medium) will occupy the larger pores, especially within the middle or larger portion of the pore (creating blobs and/or ganglia).

Creosote trapping by capillary forces occurs in two ways: (1) creosote is trapped within the pores at residual saturation; and, (2) creosote is trapped as pools (above residual saturation) on top of less permeable layers (due to insufficient DNAPL entry pressure to displace water in a fine-grained, low-permeability layer beneath the pool). Consequently, once the surface source is eliminated, creosote will migrate until a flow equilibrium is reached whereby the mobile creosote is trapped by capillary forces at residual saturation within pores and/or as pools on top of stratigraphic traps (low-permeability, capillary pressure barriers).

Creosote DNAPLs are typically complex mixtures that contain surface-active, high molecular weight components (e.g., asphaltenes) that can alter or reverse the wettability of porous media that it has invaded given facilitative conditions (i.e., low pH). For example, based on modeling and wettability experiments, Zheng et al. (2001) concluded that, after creosote invasion, quartz would become creosote-wet below pH 5, but remain water-wet at higher pH values. Such a wettability reversal at low pH increases residual saturation and would hinder creosote recovery efforts.

In order to better understand creosote movement and trapping mechanisms at the Cabot Carbon/Koppers Superfund Site (see Mercer et al. 2006 for Site details), a review of creosote wettability literature was performed and determinations were made of wettability using site-specific samples of creosote, groundwater, and soil. A brief discussion of wettability measurement methods is provided. Results of a review of published literature regarding the wettability of creosote in the subsurface are presented. Methods and results of wettability measurements performed on Site-specific samples from the Cabot Carbon/Koppers Superfund Site are discussed, followed by conclusions.

TECHNIQUES TO MEASURE WETTABILITY

Numerous quantitative and qualitative methods have been used to measure wettability (Anderson, 1986b; Adamson, 1982). Four methods that have been used with creosote, as reflected in the literature, are described briefly below. Results of sessile drop contact angle and bottle test measurements of wettability made using several creosote samples from the Cabot Carbon/Koppers Superfund Site are documented later.

Contact Angle Method. The simplest measure of wettability is the contact angle measured into water at the fluid-solid interface. In a DNAPL-water system, if the adhesive force between water and solid phases exceeds the cohesive force within the water as well as the adhesive forces between the creosote and solid phases, then the solid-water contact angle, θ , measured into the water (in degrees) will be acute indicating that water, rather than creosote, preferentially wets the medium. The porous medium is considered water-wet if the θ is less than approximately 70° , DNAPL-wet if θ is greater than 110° , and neutral (mixed) if θ is between 70° and 110° .

Using the sessile drop static contact angle method, a drop of DNAPL is formed at the end of a fine capillary tube and brought in contact with the smooth surface of a porous medium under water within a contact angle cell (**Figure 1**). The drop of DNAPL is allowed to age on the

medium surface and the contact angle can be measured using a goniometer and documented by taking photographs. Generally, a single, flat, polished mineral crystal and oil brine water are used in petroleum engineering studies; but for applications to DNAPL-groundwater-media systems, the smooth surface may be a rock thin section, clay smeared on a glass slide, the top of a cohesive soil sample that has been smeared on a glass slide, the top of a cohesive soil sample that has been sliced with a knife, or a relatively flat surface of silt and sand.

Water receding (associated with DNAPL invasion and water displacement) and water advancing (associated with DNAPL recovery/retraction) contact angles typically, vary as discussed in the literature review, due to hysteresis and can be measured using the capillary tube to expand and contract the volume of the DNAPL drop. Alternatively, a modified sessile drop method can be utilized whereby the drop substrate is tilted to create water advancing and receding contact angles that are documented using high-speed photography or by placing the drop between two flat substrates that are mounted parallel to each other on adjusted posts in the contact angle cell. The substrates can be moved relative to each to expand or contract the drop.

Capillary Pressure-Saturation Measurement Methods. The Amott (1959), U.S. Bureau of Mines (Donaldson et al., 1969), and similar methods estimate wettability by comparing the amount of work, measured by determining capillary pressure-saturation curves, that is required to displace the wetting fluid with the nonwetting fluid and vice versa during repeated cycles of water drainage and imbibition.

Qualitative Bottle Test Method. A qualitative indication of the wettability of unconsolidated sands was developed by Powers et al. (1996) based on a procedure briefly described by Dubey and Doe (1993). Following the exposure of wet sands to NAPL in small glass vials and subsequent addition of water, observation of the pore distribution of NAPL is used to indicate system wettability. The procedure of Powers et al. (1996) involves placing ~20 g of sand in a 40-mL glass vial and equilibrating the sand with groundwater for 24 hours; followed by gravity drainage of excess water from the sand; adding 5 mL of organic phase to the wet sand and allowing it to equilibrate for 48 hours; followed by vigorously shaking the vial contents several times a day over two days; followed by the addition of water and drainage of both fluids from the vial; followed by addition of groundwater; and finally, observation of the NAPL and water in the porous medium. According to Powers et al. (1996): the system is *strongly water wetting* if all NAPL can be separated by gravity; *weakly water wetting* if some NAPL is associated with the sand, 'beads' of NAPL coated with sand grains are visible at sand/water interface, and most of sand retains its natural color; *intermediate wetting* if most of the NAPL is associated with sand and some discrete 'blobs' of NAPL are visible between sand grains; and *oil-wetting* if the sand is completely coated with NAPL and has a homogeneous color throughout.

Adhesion Test Method. Zheng et al. (2001a) describe an adhesion test that has been used by petroleum surface scientists to characterize the wettability of quartz surfaces exposed to crude oils and is similar in nature to contact angle measurements. The quantifiable contact angle is replaced with a qualitative observation of oil droplet's tendency to adhere to the quartz plate when withdrawn. Adhesion of NAPL droplets correspond to oil wetting conditions.

LITURATURE REVIEW AND SUMMARY OF FINDINGS

Prior to 1990, substantial research had been published regarding the wettability of crude oil in petroleum reservoirs (e.g., Anderson, 1986a,b,c; 1987a,b,c). Recently, a number of studies have been performed on (1) the wettability of coal tar and creosote DNAPLs found below ground at wood-preserving and former manufactured gas plant sites, and (2) the impact of coal-derived NAPL interfacial phenomena on contaminant migration and remediation (Villaume et al., 1983; Powers et al., 1996; Barranco and Dawson, 1999; Zheng and Powers, 1999; Zheng et al., 2001a; Zheng et al., 2001b; Hugaboom and Powers 2002; Zheng and Powers, 2003; Dong et al., 2004; Al-Futaisi and Patzek, 2003; and Al-Futaisi and Patzek, 2004). Relatively few measurements of coal tar and creosote wettability in NAPL-water-porous media systems are available in the literature, and no additional data were identified by several knowledgeable scientists contacted during this review. All of the measurements were made using polished quartz slides or quartz sand. A compilation of available published creosote and coal tar wettability data is provided in **Table 1**. As shown, published wettability measurements are limited to coal tar samples from five different sites, creosote samples from three sites, and one commercial creosote product. The most common measurement methods were contact angle and bottle test. The various measurement methods are discussed below.

Based on the literature review, it is generally accepted that most natural porous media, and quartz and other silicate minerals in particular, which have not been invaded by complex organic liquids such as crude oil or creosote, are water-wet due to their surficial negative charge that attracts polar water molecules (see e.g., USEPA, 2005). Thus, during initial NAPL invasion below the water table, coal tar and creosote DNAPLs are nonwetting fluids in the subsurface and their entry will be resisted by water-filled pores. This resistance will tend to be inversely proportional to pore size. Gravity and/or hydraulic forces, however, may overcome capillary resistance and can drive nonwetting DNAPL into formerly water-filled pores. Protonation of basic functional groups on macromolecules in coal tar and creosote, particularly at pH values less than 5, and possible precipitation of asphaltene molecules on the mineral surfaces can increase wetting of these DNAPLs on solids. Thus, while water-filled pores resist DNAPL penetration under creosote-advancing conditions, the subsurface media may become intermediate-wet or DNAPL-wet along its flow path after contact with creosote or coal tar. DNAPL-wet conditions result in higher residual saturation (DNAPL trapping) and DNAPL invading smaller pore spaces. Consequently, recovery of coal-derived DNAPLs may be hindered as a result of increased DNAPL wetting of and adhesion to solids.

Contact Angle Measurements. Contact angles of coal tar measured on quartz slides under static and water-receding conditions over pH values from 3.4 to 12.4 ranged from approximately 25° to 45°, indicative of water-wetting systems (Barranco and Dawson, 1999; Dong et al., 2004). No static or water-receding contact angle measurements were made on any creosote samples. Under water-advancing conditions, Villaume et al. (1983) measured a change in contact angle in a coal tar-water-quartz system from 45° to 125° after 30 days of aging. The change in contact angle from water-wetting to oil-wetting was attributed to the presence of surface-active chemicals in the coal tar. Powers et al. (1996) similarly measured a contact angle, 163°, indicative of oil-wet conditions for a commercial creosote sample under water-advancing conditions. For coal tar on quartz under water-advancing conditions, Barranco and Dawson

(1999) determined contact angles ranging from 4° to 46° between aqueous pH values of 8.0 to 12.4, and oil-wet contact angles ranging from 173° to 176° between pH values of 3.4 to 6.7. The change of wetting conditions from water-wetting to oil-wetting with decreasing pH in coal tar and creosote - water - quartz systems was also documented by bottle test and adhesion test wettability measurements by Powers, Zheng, and co-workers (**Table 1**). Dong et al. (2004), however, measured a water-wetting to intermediate water-advancing contact angles for a coal tar-water-quartz system ranging from 53° to 77°, but did not report the aqueous pH in the system.

Except for the one creosote sample noted above, Powers, Zheng, Hugaboom and co-workers did not report any other contact angle measurements for coal tar or creosote. Powers et al. (1996) reported that rapid development of a semi-rigid film at the NAPL-water interface prevented coal tar from spreading to an equilibrium contact angle on quartz. The formation of films at coal tar-water interface has been studied by Luthy et al. (1993) and Nelson et al. (1996) and appears to result from weak bonds between water molecules and coal-derived NAPL constituents. Similar films were observed at the creosote-water interface during this investigation.

Table 1. Compilation of Creosote and Coal Tar Wettability Data.

Reference	DNAPL Tested	Contact Angle ¹	Bottle Test Results ²	Adhesion Test ³	USBM & Amott-Harvey Tests	Method Description and Notes
Villaume et al. (1983)	Coal tar recovered from a MGP site in Stroudsburg, Pennsylvania	~45° to 125° water advancing after aging ~700 hours	-	-	-	Test media included tap water, a quartz slides, and coal tar. ¹ "The wetting angle [was apparently] . . . measured by placing a drop of the hydrocarbon of interest between two ultra-clean, highly polished mineral surfaces in a water bath. . . The surfaces are then shifted relative to each other so that either the water is made to advance over the hydrocarbon (water displacing hydrocarbon) or the hydrocarbon is made to advance over the water (hydrocarbon displacing water)."
	Creosote purchased in the 1970s (a wood-preserving product)	163° water advancing ^a	oil wetting ^a oil or intermediate wetting @ pH 4.7 and pH 7.2 ^b	changes from water-wet to oil-wet below a pH of 7.2 ^c	intermediate wetting ^a	¹ For the contact angle measurements : "A wet slide was immersed into the oil phase to equilibrate for 7d. Prior to the measurement of the contact angles, the slide

						was briefly rinsed in toluene to remove the bulk organic phase coating the slide." ^a
(a) Powers et al. (1996) (b) Zheng and Powers (1999) (c) Zheng et al. (2001)	Creosote recovered from a wood-preserving facility in Massachusetts	-	water or weakly water wetting @ pH 7.2; oil or intermediate wetting @ pH 4.7 ^b oil wetting @ pH 4.3; water wetting @ pH 9.2 ^d	Changes from water-wet to oil-wet below a pH of 5.1 ^c	-	² For the bottle tests : "As with contact angle measurements, the method of exposing the solid surfaces to an organic phase had an effect on the resulting wettability." The procedure of Powers et al. (1996) involves placing ~20 g of sand in a 40-mL glass vial and equilibrating the sand with groundwater for 24 hours; followed by gravity drainage of excess water from the sand; followed by vigorously shaking the vial contents several times a day over two days; followed by the addition of water and drainage of both fluids from the vial; followed by addition of groundwater; and finally, observation of the NAPL and water in the porous medium. " ^a
(d) Hugaboom and Powers (2002)	Creosote recovered from a wood-preserving site in Illinois	-	water or weakly water wetting @ pH 7.2; oil or intermediate wetting @ pH 4.7 ^b	Changes from water-wetting to oil-wetting below a pH of 5.2 ^c	-	² For bottle tests : If strongly water-wetting, all NAPL can be separated by gravity; if weakly water-wetting, some NAPL is associated with sand, 'beads' of NAPL coated with sand grains are at sand/water interface, and most of sand retains its natural color; for intermediate wetting, most of NAPL is associated with sand and some discrete 'blobs' of NAPL may be visible between sand grains; and for NAPL wetting, sand is completely coated with NAPL with a homogenous color throughout.

(a) Powers et al. (1996)(b) Zheng and Powers (1999)(c) Zheng et al. (2001)(d) Hugaboom and Powers (2002)	Creosote recovered from a wood-preserving site in Illinois	-	water or weakly water wetting @ pH 7.2; oil or intermediate wetting @ pH 4.7 ^b	Changes from water-wetting to oil-wetting below a pH of 5.5 ^c	-	³ Adhesion experiments were conducted [to characterize the wettability of quartz surfaces exposed to creosote and coal tar]. . . . This test is similar in nature to contact angle experiments, although the quantifiable contact angle is replaced with a qualitative observation of the oil droplet's tendency to adhere to the quartz plate when withdrawn. Adhesion of NAPL droplets corresponds to an oil-wetting condition. The procedure for the adhesion test involves preequilibrating the quartz slides with an appropriate buffer at an ionic strength of 0.01 M before placing approximately 5 10-uL droplets on each slide. Droplets were retracted into the syringe over a one-minute period after 15 min of contact. Droplets that retracted cleanly and completely were labeled as nonadhesive. Drops that broke during retraction and left fluid on the slide were considered adhesive. . . . Adhesion tests were conducted for each DNAPL as a function of pH." ^c
	Coal tar recovered from a former MGP site in Pennsylvania	-	water or weakly water wet @ pH 7.2; oil or intermediate wet @ pH 4.7 ^b oil wet @ pH 4.7; water wet @ pH 7.2; water wet @ pH 9.9 ^d	Changes from water-wetting to oil-wetting below a pH of 5.0 ^c	-	³ Adhesion tests: NAPLs [used in this study] were selected based on our previous observations that they alter the wettability of quartz sand and their measurable presence of organic bases. ^c
	Coal tar recovered from buried holding tank at MGP site in Connecticut	-	oil wetting ^a oil or intermediate wetting @ pH 4.7 and pH 7.2 ^b	-	-	Test media included deionized water that was adjusted to a desired pH and ionic strength, quartz slides for contact angle and adhesion experiments, and NAPL, as well as quartz sand and 40-mL vials for bottle tests.

Barranco and Dawson (1999)	Coal tar recovered from a well at a former MGP site in Baltimore, MD	~5 to 35° static and water receding @ pH 3.4 to 12.4 46 to 4° water advancing @ pH 8.0 to 12.4; 173 to 176° water advancing @ pH 3.4 to 6.7	-	-	-	Test media included quartz slides, coal tar, and water with controlled pH and ionic strength. Barranco and Dawson (1999) reported that, for static and water advancing conditions, initial (5 minute) contact angles ranged from ~ 5 to 15° and that these values increased to stabilized values of ~25 to 35° after 24 hours of aging.
Dong et al. (2004)	Coal tar recovered from a MGP site in the United Kingdom	53 to 77° water advancing; 40 to 45° water receding	-	-	-	Test media included water, quartz slides, and coal tar. The contact angles were aged to equilibrium.

Note: As reflected by our review of the literature, little published data regarding the wettability of creosote and coal tar on geologic media are readily available. Knowledgeable scientists (Richard Luthy of Stanford University, Susan Powers of Clarkson University, Richard Jackson of Intera, Inc., and Neale Misquitta of Key Environmental) knew of no additional published or unpublished measurements.

NAPL-Water Capillary Pressure-Saturation Measurement Methods. The only wettability determination on a coal tar or creosote sample using the capillary pressure-saturation measurement methods was performed by Powers et al. (1996) using a sample of coal tar and clean quartz sand. The experiment began with determination of the primary drainage curve and proceeded through at least two full cycles of drainage and imbibition to ensure that the curves were reproducible. The data were interpreted using the USBM and Amott-Harvey wettability indices; both methods determined the system to be intermediate wet.

Qualitative Bottle Tests. Bottle tests were used by Powers et al. (1996), Zheng and Powers (1999), Zheng et al. (2001), and Hugaboom and Powers (2002) to characterize the wettability of coal tar and creosote samples on quartz as a function of aqueous phase pH. As documented in **Table 1**, these investigators determined oil or intermediate wetting conditions to be present at an aqueous phase pH of 4.7 and water-wetting conditions to prevail at water pH values of 7.2, 9.2, and 9.9, with two exceptions. The commercial creosote sample and one coal tar sample were also found to be oil or intermediate wetting at pH values of 4.7 and 7.2. None of the other studies reviewed used bottle tests to characterize wettability.

Adhesion Tests. Zheng et al. (2001) used adhesion tests to determine the pH of wetting change between water-wet and oil-wet conditions on one coal tar and four creosote samples studied by Powers, Zheng, and coworkers. Consistent with chemical modeling analysis performed to evaluate reversal pH values, the researchers found that based on adhesion tests “the observed wetting reversal pH was approximately 5 for four of the samples [and that] a much higher value (pH 7.2) was observed for the commercial creosote sample.”

MEASUREMENT OF WETTABILITY AT CABOT CARBON/KOPPERS SUPERFUND SITE

Wettability of Site creosote on Hawthorn Group (HG) Clay, Surficial Aquifer (SA) Sand, other quartz sands, and glass was examined by making contact angle measurements and performing bottle tests. Creosote was collected from various Site wells (**Table 2**) at the Cabot Carbon/Koppers Superfund Site (see Mercer et al., 2006).

Contact Angle Measurement. Glassware (test cells and glass slides) was cleaned using an HCl solution, rinsed with tap water, cleaned with methanol, rinsed with tap water, and then rinsed distilled water prior to initiation of contact angle measurements. Substrate materials included a glass slide, HG Clay (from 20 to 23 feet bgs at boring FW-8) that was smeared on glass slides, and Surficial Aquifer Sand (from 11 to 14 feet bgs at FW-8) placed directly in test cells. Site groundwater from well M-28R (initial pH 5.1) was added to the test cells. Approximately 90 minutes after preparing the test cells, a few drops of creosote recovered from wells PW-1 (Surficial Aquifer), HG-10S, HG-11S, or HG-12S were then carefully placed on the substrate surface in each test cell using a 3-mL capacity microsyringe. Drop volume varied, but was typically about 0.06 mL. Using a 5-megapixel digital camera, photographs were taken of drops in each test cell approximately 1 hour, 24 hours (see **Figure 2**), and 42 days after drop placement. An attempt was made to photograph the drops in the horizontal plane of the creosote-substrate interface to facilitate contact angle measurement. Contact angles were determined using a graphical goniometer positioned over each contact angle.



Figure 2. Various photographs of creosote in test cells after 24 hours.

Results of the contact angle measurements are compiled in **Table 2**. As shown, creosote contact angles on the HG Clay and glass slide below water typically ranged from 35° to 40°, indicative of water-wet conditions. Contact angles of creosote on Surficial Aquifer Sand, also indicative of water-wet conditions, were difficult to measure due to the irregular surface of the sand. Creosote wet the glass slide (contact angle ~170°) in the air-creosote system. Measured contact angles did not change with aging over 42 days, but rapid formation of a semi-rigid interfacial film on the drops may have constrained creosote spreading over time.

Table 2. Results of contact angle measurements using Gainesville Site creosote.

Test Cell ID	DNAPL Source Well	Substrate	<u>Contact Angle*</u>			Comment*
			1-Hour Exposure	1-Day Exposure	42-Day Exposure	
1	HG-10S	Glass slide	~170°	~170°	~170°	DNAPL wet relative to air
2	HG-10S	Glass slide	30°	35°	35°	water-wet; adhesion to glass slide noted
3	HG-10S	Hawthorn Clay	35°	35°	40°	water-wet
4	HG-10S	SA Silty Sand	<80°	<80°	<80°	water-wet; difficult to measure angle on sand; adhesion to glass jar noted
5	HG-11S	Hawthorn Clay	45°	30-45°	NM	water-wet
6	HG-11S	SA Silty Sand	<70°	<70°	<70°	water-wet; difficult to measure angle on sand
7	HG-12S	Hawthorn Clay	35°	30°	35°	water-wet
8	HG-12S	SA Silty Sand	<70°	<70°	<70°	water-wet; difficult to measure angle on sand
9	PW-1	Hawthorn Clay	40°	35°	40°	water-wet
10	PW-1	SA Silty Sand	NM	<70°	NM	water-wet; difficult to measure angle on sand
12	HG-10S	Hawthorn Clay	40°	35-43°	40°	water-wet

3&5	HG-10S & HG-11S	PVC	NM	NM	>140°	DNAPL wets PVC relative to water
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*Notes:

- (1) A semi-rigid film developed at the interface between creosote drops and water within hours. This film appears to constrain changes in contact angle with time (see references and movies).
- (2) The pH of water in the test cells prior to introducing creosote was measured to be in the range of 5.1 to 5.9. After 42 days of aging with creosote in the test cell, the pH of water was determined to be ~6.5 in each cell.
- (3) NM = Not Measured; SA = Surficial Aquifer

As noted, the formation of films at coal tar-water interface has been studied by Luthy et al. (1993) and Nelson et al. (1996) and appears to result from weak bonds between water molecules and coal-derived NAPL constituents. Barranco and Dawson (1999): (1) postulated that these semi-rigid films occur due to the presence of asphaltenes in creosote; (2) reported that other studies have shown that similar films that develop on crude oil can strongly adhere to the oil-solid interface and change water wet systems to neutral or oil-wet systems; and (3) found experimentally that coal tar films, which adhered quartz, formed in aqueous solutions of pH ranging from 2.4 to 8.0, but not in aqueous solutions of pH greater than 8.0. Semi-rigid interfacial films were observed to develop in experiments conducted during this investigation when creosote was exposed to water, but not air. The overall effect of these films on creosote movement in the subsurface is unknown.

As discussed below, it was observed during the bottle tests, in particular, that creosote adheres to glass preferentially to quartz grains. The pH of groundwater from well M-28R increased from a value of 5.1 at the time of its placement in the test cells (approximately 1 hour before creosote drop placement) to 6.5 at the end of the 42-day aging period. No pH measurements were made during the 42-day testing period. For comparison, recent field measurements indicate pH ranges of 4.8 to 4.9 in the Surficial Aquifer and 6.5 to 8.5 in deeper units at the Gainesville Site.

Qualitative Bottle Tests. A series of bottle tests were performed to examine creosote wettability on Surficial Aquifer Sand and two commercial quartz sands, including a medium quartz sand (“Pavestone High Desert Sand” from Home Depot) and a very coarse quartz sand (Morie #2) that is used as a well sandpack. Bottle tests methods were similar to those described by Powers et al. (1996) except that most of the tests were performed under saturated conditions (the bottles were filled with sand, water, and creosote with little air space) because the main objective of this investigation was to examine fluid wettability below the water table. Bottle test procedures and results are documented in **Table 3**. The Surficial Aquifer Sand and commercial quartz sands were water-wet in all cases, including an experiment where the aqueous pH was maintained below 4.5 by the addition of HCl. Creosote adherence to the glass vials, but not quartz sand, was observed in most of the tests.

Table 3. Results of bottle tests to examine creosote wettability in creosote-water-quartz systems.

Vial ID	Creosote Added to 40-mL Glass Vial	Sand Source	Water Source	Aqueous Phase pH	TEST RESULT Wetting Relative to Water in Saturated Condition	Comment
1	5 mL HG-10S	medium quartz sand	M-28R	~6.5	creosote is nonwetting fluid	Water was added to the 40-mL vial after placement of the sand. This entrapped air in the sand. Initially injected the creosote at the water-sand interface; then vial was shook gently for 24 hours; then shook vigorously a few times a day for two days.
2	3 mL HG-10S	medium quartz sand	M-28R	~6.5	creosote is nonwetting fluid	Water was added to the 40-mL vial after placement of the sand. This entrapped air in the sand. Creosote was injected into the center of sand; most of the creosote flowed up the injection hole to the sand-water interface. The sample was then shook gently for 24 hours; then shook vigorously a few times a day for two days.
3	3 mL HG-10S	medium quartz sand	M-28R	~6.5	creosote is nonwetting fluid	A small amount of water was added to the 40-mL vial after placement of the sand. The sand was unsaturated. Creosote was initially injected to the top of the (unsaturated) wet sand and infiltrated downward. The vial was shook gently for 24 hours and then vigorously a few times a day for two days. The vial was subsequently filled with water and examined again.
4	3 mL HG-10S	Surficial Aquifer Sand from FW-8 (11-14')	M-28R	~6.5	creosote is nonwetting fluid	Water was added to the 40-mL vial after placement of the sand. This entrapped air in the sand. Creosote was initially injected into the sand layer and along the edges of the glass-sand interface. The vial was then shook gently for 24 hours and then vigorously a few times a day for two days.
5	3 mL HG-10S	medium quartz sand	M-28R	~6.5	creosote is nonwetting fluid	Water was added to the 40-mL vial after placement of the sand. This entrapped air in the sand. Creosote was initially injected into the sand layer and along the edges of the glass-sand interface. The sample was then shook gently for 24 hours and vigorously a few

						times a day for two days.
6	3 mL HG-12S	medium quartz sand	M-28R	~6.5	creosote is nonwetting fluid	Sand was added through water to eliminate trapped air. Creosote was injected into the sand and the vial was shaken vigorously a few times a day for several days.
7	3 mL HG-12S	Surficial Aquifer Sand from FW-8 (11-14')	M-28R	~6.5	creosote is nonwetting fluid	Sand was added through water to eliminate trapped air. Creosote was injected into the sand and the vial was shaken vigorously a few times a day for several days.
8	5 mL PW-1	Morie #2 very coarse quartz sand	tap water	~6.5	creosote is nonwetting fluid	Creosote was added to vial nearly filled with water. The vial was then filled with water and shaken vigorously several times a day for 3 days. Creosote and water were then drained by gravity and then the vial was refilled with water.
9	5 mL PW-1	Morie #2 very coarse quartz sand	tap water	<4.5	creosote is nonwetting fluid	Creosote was added to vial nearly filled with water. The vial was then filled with water and shaken vigorously several times a day for 3 days. Creosote and water were then drained by gravity and then the vial was refilled with water. HCl was used to reduce the pH to <4.5
10	5 mL PW-1	Morie #2 very coarse quartz sand	tap water	~6.5	creosote is nonwetting fluid	Creosote was added to vial where the sand had been drained of water by gravity; thus retaining a high moisture content prior to injection of creosote at the top of the wet sand. The vial was shaken vigorously several times a day for 3 days. Creosote and water were then drained by gravity and then the vial was filled with water.

CONCLUSIONS

A comprehensive literature review was performed on wettability with emphasis on creosote. Depending on the fluids and the media, NAPL can be the wetting fluid, the nonwetting fluid, or there can be mixed wetting. However, according to USEPA (2005, p. 22),

"In the saturated zone, water is typically the wetting-fluid (i.e., it forms a continuous layer on, or preferentially wets, the particles) and LNAPL is the non-wetting fluid (i.e., it resides inside the pore spaces and is surrounded by a film of water). In the unsaturated zone, where there is an air phase in addition to the

water and LNAPL, the air is the non-wetting fluid, the water is still typically the wetting fluid, and the LNAPL resides between the two other fluids."

USEPA (2005) further state, "If LNAPL is not continuous from one pore to the next, then LNAPL will not flow from one pore to the next: it will be immobile, which is referred to as the LNAPL residual saturation." Although this recent USEPA document focuses on LNAPL, the same general conditions apply to DNAPL. For example, another recent publication, NRC (2005, p. 50) indicates,

"For many natural minerals, including quartz and carbonates, water is more strongly attracted to the mineral surface than are common DNAPL constituents. Thus, in such media, water generally is the wetting phase, distributing itself along the solid surfaces and in small-aperture pore regions and fractures."

Thus, based on the literature review, during initial DNAPL invasion below the water table, creosote is the nonwetting fluid and its entry into the subsurface media will be resisted by water-filled pores. With time in the subsurface, it is possible for chemical reactions involving creosote, especially at low aqueous phase pH, to cause the media to become more intermediate-wet or DNAPL-wet along flow paths after contact with creosote. This condition leads to increased DNAPL trapping, hindering creosote recovery efforts.

The wettability testing performed during this study utilized contact angle measurements and qualitative bottle tests, the two most common measurement techniques used for creosote in the literature review. Results are generally consistent with those reported in the literature. Contact angles of creosote on Surficial Aquifer Sand below water were indicative of water-wet conditions. Creosote contact angles on HG Clay and glass slides below water typically ranged from 35° to 40°, indicative of water-wet conditions. Creosote wet the glass slide (contact angle ~170°) in the air-creosote system. Measured contact angles did not change with aging over 42 days, but rapid formation of a semi-rigid interfacial film on the creosote drops may have constrained creosote spreading over time.

To further test the water-wet results, qualitative bottle tests were performed. Based on these results, the Surficial Aquifer Sand and commercial quartz sands were water-wet in all cases, including a test where the aqueous pH was maintained below 4.5 by the addition of HCl. Creosote adherence to glass vials, but not quartz sand, was observed in most of the tests. These bottle test and the contact angle test results demonstrating water-wet conditions are consistent with the field observation that DNAPL creosote found in wells at the Gainesville Site is associated with a coarse-grained sand deposit located above the middle clay in the Hawthorn Group.

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