Residual Saturation of Coal Tar in Porous Media

Technical Report

Residual Saturation of Coal Tar in Porous Media

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REPORT SUMMARY

The presence of coal tar as a non-aqueous phase liquid (NAPL) in the subsurface at former manufactured gas plant (MGP) sites is a subject of interest to both regulators and regulated companies. Coal tar NAPL can exist as a free (mobile) product or residual (immobile) product, both of which are defined using residual saturation as the critical separating point on this continuum. Because values of coal tar residual saturation are not readily available in the literature, EPRI and its member utilities initiated this research project to develop residual saturation values for a number of soil and coal tar samples from MGP sites.

Background

Physical and chemical properties of NAPL and porous media govern the movement and entrapment of NAPL in the subsurface and therefore determine the amount of NAPL that constitutes residual saturation. Site remediation performance criteria are based in part, on the presence or absence of NAPL in amounts above the residual saturation point. Definitions of free and residual products as well as residual saturation present challenges for field personnel who must quickly, consistently, and accurately identify and record the presence of free or residual product or the absence of NAPL in their site investigation reports.

Objectives

- To quantify relevant physical-chemical properties (i.e., density, viscosity, surface tension and interfacial tension) of coal tars collected from MGP sites.
- To characterize the properties of soils collected from coal-tar-contaminated MGP sites (that is, cation exchange capacity, particle size analysis, carbon content, specific surface area, and water retention characteristics).
- To measure the residual saturation of coal tar in two-phase (water and coal tar) soil systems for paired and unpaired soil-tar samples.
- To develop and evaluate empirical correlations between measured residual coal tar saturation and properties of the soils (for example, carbon content) and coal tars (such as viscosity).

Approach

Paired samples of uncontaminated soil and coal tar (free product) were submitted for this study. Investigators conducted laboratory tests at Georgia Institute of Technology using a column test method to obtain residual saturation values for coal tar NAPL. They measured relevant coal tar properties and soil properties and performed two-phase (water and coal tar NAPL) residual saturation measurements using either glass or stainless steel columns. Finally, they analyzed the resulting data by statistical methods to obtain correlations between NAPL and soil properties when compared with residual saturation values.

Results

Two-phase laboratory studies were completed to develop coal tar residual saturation values for nine soils and six coal tars obtained from former MGP sites. The resulting residual coal tar saturation values ranged from a low of 7.7% to a high of 22.6% on a volumetric basis. The corresponding coal tar concentrations at residual saturation ranged from a low of 25,000 mg/kg to a high of 72,000 mg/kg on weight basis (mass of coal tar per mass of solid). These values indicate that a substantial amount of coal tar can be retained by soils as immobile NAPL (residual product). Both soil and coal tar properties play an important role in determining the residual saturation point of coal tar NAPL. Statistically significant correlations were observed between coal tar residual saturation and two soil properties (total carbon content and median grain size) and two coal tar properties (interfacial tension and viscosity).

EPRI Perspective

The laboratory studies described in this report have generated a comprehensive data set that includes determinations of both paired and unpaired coal tar residual saturation values. These studies also resulted in development of a batch method for measuring residual coal tar saturation in the laboratory, based on existing laboratory techniques for similar type light and dense non-aqueous phase liquids. Furthermore, while the batch method described here was developed for readily determining coal tar molecular weight, the approach also provides for an independent measurement of the aqueous phase pore volume of coal tar. The residual saturation value determined in the laboratory for each sample gives an indication of what may occur in the field. Caution should be taken, however, in applying these laboratory values directly to field conditions. The dissolution and movement of coal tar constituents through groundwater or the vadose zone remains a separate issue. Additional work is recommended to shed light on displacement and recovery mechanisms of coal tar above the residual saturation point.

Keywords

Coal tar
Residual saturation
MGP sites
Free product
Non-aqueous phase liquid

ABSTRACT

The presence of coal tar as a non-aqueous phase liquid (NAPL) in the subsurface at former manufactured gas plant (MGP) sites is a subject of interest to both regulators and regulated companies. Coal tar NAPL can exist as a free (mobile) product or residual (immobile) product, both of which are defined using residual saturation as the critical separating point on this continuum. Unfortunately, values of coal tar residual saturation are not readily available in the literature, and site remediation performance criteria are based in part on the presence or absence of NAPL in amounts above the residual saturation point. Definitions of free and residual products as well as residual saturation, therefore, present challenges for field personnel who must quickly, consistently, and accurately identify and record the presence of free product or residual product or the absence of NAPL in their site investigation reports. EPRI and its member utilities initiated this research project to develop residual saturation values for a number of soil and coal tar samples from MGP sites.

Two-phase (water and coal tar) laboratory studies were completed for nine soils and six coal tars obtained from MGP sites. The resulting residual coal tar saturation values ranged from a low of 7.7% to a high of 22.6% on a volumetric basis (volume of coal tar per volume of pore space). The corresponding residual coal tar concentrations ranged from a low of 25,000 mg/kg to a high of 72,000 mg/kg (mass of coal tar per mass of solid). From a regulatory perspective, these results establish that a considerable amount of coal tar, on the order of 2.5 to 7.2% (on a weight basis), can be retained in natural soils as residual (immobile) NAPL. Both soil and coal tar properties were shown to play an important role in determining residual coal tar saturation. Statistically significant correlations were observed between residual coal tar saturation and two soil properties (total carbon content and median grain size) and two coal tar properties (interfacial tension and viscosity). These statistical correlations provide a method for site managers to estimate the amount of coal tar retained in soils as an immobile NAPL (residual product).

The laboratory studies successfully generated a comprehensive data set that included both paired experiments (six coal tars and soil samples from the same sites) and unpaired experiments (one coal tar and four soil samples). In addition, a reliable and reproducible batch method for measuring residual coal tar saturation in the laboratory was developed, based on nonreactive tracer tests conducted before and after the entrapment process. This approach provides for an independent measurement of the aqueous phase pore volume and corresponding volume of coal tar. Such an approach eliminates errors associated with methods that rely on measurement of small changes in column weight or measurements of the introduced and effluent coal tar volumes.

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1

INTRODUCTION

The presence of coal tar, as a non-aqueous phase liquid (NAPL), in the subsurface at manufactured gas plant (MGP) sites is a subject of interest to both regulators and the regulated companies. Coal tar NAPL can exist as a “free product” or as a “residual product”. Free product is a “separate phase” material present in amounts (e.g., concentration or saturation) greater than its “residual saturation” point in a porous medium. Similarly, residual product is defined as a separate phase material present in amounts (e.g., concentration or saturation) less than its residual saturation point in a porous medium. Site remediation performance criteria are based in part, on the presence or absence of NAPL in amounts above the residual saturation point, therefore these definitions present challenges for the field personnel who must quickly, consistently, and accurately identify and record the presence of “free product” or “residual product”, or absence of NAPL in their site investigation reports.

Values of coal tar residual saturation are not readily available in the literature. This research project was initiated to develop “residual saturation” values for coal tar using soils and coal tar samples from a number of MGP sites.

Cohen and Mercer (1993) used the terminology “mobile NAPL”, which corresponds to the regulatory term “free product”. Cohen and Mercer defined mobile NAPL as the amount of NAPL that is above “residual saturation”, and is able to flow in a porous medium. They further defined residual saturation in a porous medium below the water table (i.e., in a two phase system consisting of water and NAPL) as the amount of NAPL that is immobile and is trapped by capillary forces as discontinuous ganglia under ambient groundwater flow conditions. Cohen and Mercer defined residual saturation in the vadose zone (i.e., in a three phase system consisting of air, water and NAPL) as the amount of NAPL below which NAPL drainage will not occur.

The term saturation (S) refers to the fractioned volume of pore space occupied by a particular phase, for example, water (S_w), NAPL (S_N) or gas (S_g). The sum of the saturation values for all phases present in a porous medium must equal unity. Thus, for a porous medium containing water and NAPL in the pore space, $S_w + S_N = 1$. To convert from NAPL saturation S_N to mass concentration(s), the following relationship can be used provided that the soil porosity (n), soil bulk density (ρ_b) and NAPL density (ρ_N) are known:

$$\text{Conc.}\left(\frac{mg_{NAPL}}{kg_{solid}}\right) = \mathrm{S}_N\left(\frac{mL_{NAPL}}{mL_{voids}}\right) \times n\left(\frac{mL_{voids}}{mL_{total}}\right) \times \rho_N\left(\frac{g_{NAPL}}{mL_{NAPL}}\right) \times \frac{1}{\rho_b}\left(\frac{mL_{total}}{g_{solid}}\right) \times \left(\frac{1000\,mg_{NAPL}}{g_{NAPL}}\right) \times \left(\frac{1000\,g_{solid}}{kg_{solid}}\right)$$

For a soil or porous medium that is initially saturated with water ($S_w = 1$), water will be displaced (water drainage) from the pore space when the pressure necessary for NAPL entry is exceeded (see Figure 1-1). When the residual water saturation (S_{wr}) is reached, no additional water will be released from the soil. For water-wetting soils, the residual water forms a thin film around the soil particles and typically occupies between 20 and 30% of the pore space (S_{wr} = 0.2-0.3). In a two-phase system where water and NAPL completely fill the pore space, the remaining pore space will contain NAPL (S_N = 0.7-0.8). As water is allowed to reenter the soil (water imbibition), mobile NAPL (free product) will be displaced from the pore space until the residual NAPL saturation is reached (S_{Nr}) as shown in Figure 1-1.

This research project was initiated to develop "residual saturation" values for a number of soil and coal tar samples from MGP sites. The coal tar residual saturation results for nine soils and six coal tars are reported in this report. Characterization of relevant soil and coal tar properties was also completed as part of this project.

1.1 Controlling Factors

Physical and chemical properties of NAPL and porous media govern the movement and entrapment of NAPLs in the subsurface and, therefore, determine the amount of NAPL that constitutes "residual saturation". The volume of NAPL released, area covered by the release, and the time duration of the release all influence the NAPL migration and the residual saturation amount. Collectively, gravity, capillary pressure and hydrodynamic forces, as well as NAPL density and viscosity of NAPL influence NAPL migration and retention characteristics in porous media. Haag and Morley (1986) and Zytner et al. (1993) indicate that the NAPL retention capacity of soils is a function of soil porosity, soil bulk density, and NAPL density and viscosity. Empirical correlations have been developed to relate the residual saturation of NAPL with capillary and gravitational forces, and grain size parameters (Chevalier and Fonte, 2000). Constitutive relationships have also been presented to describe the entrapment and residual saturation of NAPLs in two- and three-phase systems (van Geel and Sykes, 1997; Wipfler et al., 2001).

1.2 Residual Saturation Values for a Number of NAPLs

Only limited data are available for the residual saturation of coal tar in porous media. Residual saturation data for coal tars and other relevant NAPLs obtained from scientific literature are summarized in Table 1-1. From the data presented in Table 1-1, it is clear that oil, petroleum products and chlorinated solvents have been examined by several researchers, resulting in the reporting of a number of residual saturation values for different soils and soil types. These data suggest that NAPL residual saturation values increase as the permeability or median grain size of the soils decreases. Only two residual saturation studies for coal tar in unconsolidated porous media are reported in Table 1-1, with values ranging from 0.20 to 0.47 (Barranco and Dawson, 1999; Hugaboom and Powers, 2002). In these studies the residual coal tar saturation was found to be a function of the aqueous phase pH, which was attributed to the presence of asphaltenes and changes in surface wettability. In both studies, the solid phase consisted of clean quartz sand, and data are not available for residual coal tar saturation in field soils.

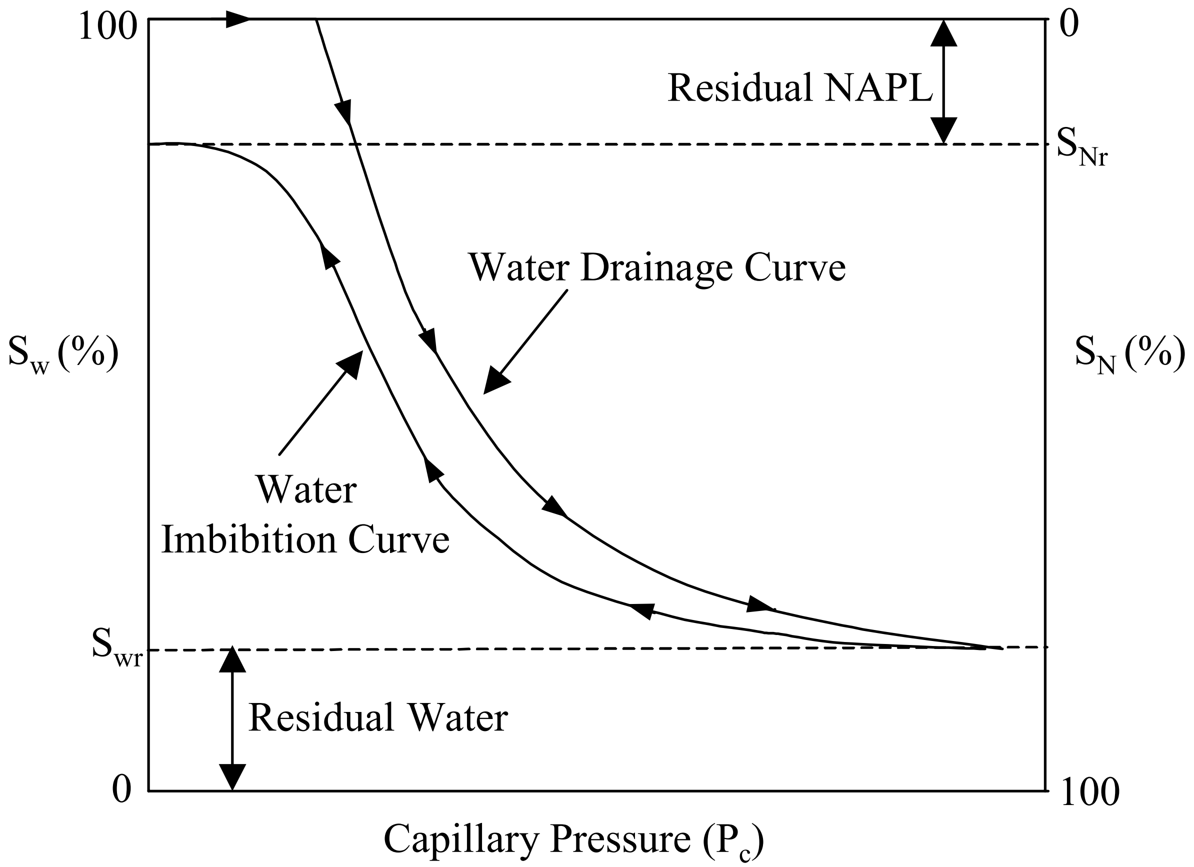

Figure 1-1
Capillary Pressure-Saturation Relationships for a Two-Phase (Liquid) System containing Water (Wetting Phase) and NAPL (Nonwetting Phase). Hypothetical Water Drainage and Imbibition Curves are shown for a System that is initially Saturated with Water (S_w = 100%)

Table 1-1
Residual Saturation Data for Various Soils and NAPLs

NAPL Type	Soil Types	S_{Nr} (Residual Saturation) (in cm^3/cm^3)	C_{Nr}, Soil (Concentration) (in mg/Kg)	ρ_N (Density) (in g/Cm^3)	Reference
Gasoline	Coarse Gravel	0.01	1,000	0.7	Fussell et al (1981)
Gasoline	Coarse Sand and Gravel	0.01	1,697	0.7	Fussell et al (1981)
Gasoline	Medium to Coarse Sand	0.02	3,387	0.7	Fussell et al (1981)
Gasoline	Fine to Medium Sand	0.03	5,833	0.7	Fussell et al (1981)
Gasoline	Silt to Fine Sand	0.05	10,000	0.7	Fussell et al (1981)
Gasoline	Coarse Sand	0.15-0.19	24,954-31,609	0.7	Hoag & Marley (1986)
Gasoline	Medium Sand	0.12-0.27	19,767-44,476	0.7	Hoag & Marley (1986)
Gasoline	Fine Sand	0.19-0.60	31,065-98,100	0.7	Hoag & Marley (1986)
Gasoline	Well Graded-Fine Coarse Sand	0.46-0.57	80,500-103,250	0.7	Hoag & Marley (1986)
Gasoline	Sandy Loam	0.42-0.59	94,500-132,750	0.75	Zytner et al. (1993)
Gasoline	Medium Aeolian Sand	0.27-0.31		0.70	Wilson et al. (1990)
Middle Distillates	Coarse Gravel	0.02	2,286	0.80	Fussell et al. (1981)
Middle Distillates	Coarse Sand & Gravel	0.02	3,879	0.80	Fussell et al. (1981)
Middle Distillates	Medium to Coarse Sand	0.04	7.742	0.80	Fussell et al. (1981)
Middle Distillates	Fine to Medium Sand	0.06	13,333	0.80	Fussell et al. (1981)
Middle Distillates	Silt to Fine Sand	0.10	22,857	0.80	Fussell et al. (1981)
Fuel Oil	Coarse Gravel	0.04	5,143	0.90	Fussell et al. (1981)
Fuel Oil	Coarse Sand & Gravel	0.05	8,727	0.90	Fussell et al. (1981)
Fuel Oil	Medium to Coarse Sand	0.08	17,419	0.90	Fussell et al. (1981)
Fuel Oil	Fine to Medium Sand	0.10	30,000	0.90	Fussell et al. (1981)
Fuel Oil	Silt to Fine Sand	0.20	51,429	0.90	Fussell et al. (1981)
Mineral Oil	Ottawa Sand (0.5 mm)	0.11	20,116	0.90	Pfannkuch (1983)
Mineral Oil	Ottawa Sand (0.35 mm)	0.14	25,602	0.90	Pfannkuch (1983)
Mineral Oil	Ottawa Sand (0.25 mm)	0.172	31,454	0.90	Pfannkuch (1983)
Mineral Oil	Ottawa Sand (0.18 mm)	0.235	42,975	0.90	Pfannkuch (1983)
Mineral Oil	Glacial Till	0.15-0.28	13,500-25,200	0.90	Pfannkuch (1983)

Table 1-1
Residual Saturation Data for Various Soils and NAPLs (Continued)

NAPL Type	Soil Types	S_{Nr} (Residual Saturation) (in cm^3/cm^3)	C_{Nr}, Soil (Concentration) (in mg/Kg)	ρ_N (Density) (in g/Cm^3)	Reference
Mineral Oil	Glacial Till	0.12-0.21	10,800-18,900	0.90	Pfannkuch (1983)
Mineral Oil	Alluvium	0.19	61,071	0.90	Pfannkuch (1983)
Mineral Oil	Loess	0.49-0.52	154,000-163,800	0.90	Pfannkuch (1983)
Mineral Oil	Sandstone	0.35-0.43		0.9	Rathmell et al (1973)
Mineral Oil	Sandy Soil	0.095	16,700	0.875	EPRI (1998)
Paraffin Oil	Coarse Sand	0.12	27,000	0.9	Converly (1979)
Paraffin Oil	Fine Sediments	0.52	147,086	0.9	Converly (1979)
Paraffin Oil	Ottawa Sand	0.11-0.23	20,382-42,618	0.9	Converly (1979)
Light Oil & Gasoline	Soil	0.18	40,800	0.75	API (1980)
Diesel & Light Fuel Oil	Soil	0.15	34,000	0.9	API (1980)
Lube & Heavy Fuel Oil	Soil	0.20	53,067	0.9	API (1980)
O-Xylene	Sand	0.19	-	0.88	Lenhard & Parker (1987)
O-Xylene	Coarse Sand	0.01	1,936	0.88	Boley & Overcamp (1998)
P-Xylene	Medium Aeolian Sand	0.2-0.27	-	-	Wilson et al. (1990)
Trichloroethene	Medium Sand	0.20	70,448	1.46	Lin et al. (1982)
Trichloroethene	Fine Sand	0.15-0.20	62,344-83,125	1.46	Lin et al. (1982)
Trichloroethene	Loamy Sand	0.08	30,713	1.46	Cary et al. (1989)
Trichloroethene	Sandy Loam	0.75-0.92	328,000-401,208	1.46	Zytner et al., (1993)
Tetrachloroethene	Fine to Medium Sand	0.002-0.20	830-83,025	1.62	Poulson & Kueper (1992)
Tetrachloroethene	Sandy Loam	0.85	413,000	1.62	Zytner et al. (1993)
Tetrachloroethene	Coarse Ottawa Sand	0.15-0.25	-	1.62	Anderson (1988)
Tetrachlorethene	Medium Aeolian Sand	0.26-0.29	-	1.62	Wilson et al. (1990)
Crude Oil	Sandstone	0.16-0.47	-	-	Wang (1988)
Crude Oil	Petroleum Reservoirs	0.25-0.50	-	-	Chatzis et al. (1988)
Coal Tar	Siltstone	0.01-0.03	-	-	Cohen & Mercer (1993)
Coal Tar	Sandstone	0.17-0.24	-	-	Cohen & Mercer (1993)
Coal Tar	Coarse Ottawa Sand	0.29-0.47	90,800-147,200	1.051	Hugaboom and Powers (2002)
Coal Tar	Medium Sand	0.50-0.75	119,600-179,400	1.047	Barranco & Dawson (1999)

1.3 Research Objectives

The four objectives of the coal tar residual saturation research project are to:

Quantify relevant physical and chemical properties (i.e., density, viscosity, surface tension, and interfacial tension) of coal tars collected from MGP sites;

Characterize the properties of soils collected from coal tar contaminated MGP sites (i.e., cation exchange capacity, particle size analysis, carbon content, specific surface area, and water retention characteristics);

Measure the residual saturation of coal tar in two-phase (water and coal tar) soil systems for paired and unpaired soil-tar samples; and

Develop and evaluate empirical correlations between measured residual coal tar saturation, and properties of the soils (e.g., carbon content) and coal tars (e.g., viscosity).

2

MATERIALS AND METHODS

Paired samples of uncontaminated soil and coal tar NAPL (free product) were collected and sent by the nine participating EPRI member companies for the laboratory experiments. However, five coal tar samples did not meet the requirements for use in the residual saturation experiments. As a result utilities for sites 1 and 2 collected new low viscosity tar samples from their sites and sent them as the replacement samples. Tar samples from sites 3, 6, and 8 contained high amounts of solids and could not be used. No new liquid tar samples could be obtained from these three sites. Therefore, tar sample from site 7 was used to conduct the residual saturation tests for soils from sites 3, 6, and 8. The following sections provide descriptions of the experimental methods used to determine soil and coal tar properties, soil water retention curves, and coal tar residual saturation for the nine sites.

Table 2-1
Amounts of Soil and Coal Tar Samples Received from Participating Utilities

Soil Identification Number	Amount of Usable Tar Received	Amount of Uncontaminated Soil Received
1	1L	2L
2	1L	1.92L
3	0	1.88L
4	3.78L	4L
5*	NA	NA
6	0	2L
7	1.92L	0.94L
8	0	3.78L
9	2L	5L
10	3.84L	2

- *Note that Site 5 Soil was not tested at Georgia Institute of Technology (not in this table)
- Coal tar from Site 7 was used to conduct residual saturation experiments for the soils from sites 3, 6 and 8.
- NA - Not Applicable

2.1 Coal Tar Properties

A total of twelve coal tar samples were received from ten MGP sites (1A, 1B, 2A, 2B, 3, 4, 6, 7, 8, 9, 10, and 11). Three of the samples (3, 6 and 8) contained large amounts of solids and were not used in the laboratory tests. The first set of tar samples obtained for 1A and 2A were highly viscous and were replaced by a second set of tars from the same site, but with lower viscosities. The first coal tar sample received from Site 9 contained approximately 95% solids (i.e., contaminated soil), and was replaced with a second tar sample. Finally, contingency tar sample 11 was supplied by one of the utilities in case the viscosity of the Site 1B tar sample was still too high. When applicable, water was removed from the top of the tar sample using a glass pipette. For the samples from Sites 4 and 9, free water was also separated from the tar phase by centrifugation at 3000 RPM for 15 minutes. The tar samples were mixed with a stainless steel spatula prior to use.

2.1.1 Liquid Density

The liquid density of each coal tar was determined in triplicate using 25-mL glass pycnometers. The weight of the pycnometer empty, completely filled with water, and completely filled with coal tar was determined using a Mettler AG 245 analytical balance (± 0.0001g). The water measurement was used to determine the volume of the pycnometer.

2.1.2 Dynamic Viscosity

The viscosity of each coal tar was measured using a Haake RS75 Rheometer equipped with double gap cylinder sensor (Model DG41). A constant temperature of 22°C was maintained using a recirculating water bath. Viscosity measurements were performed at a shear rate of 200 s^{-1}. The viscosity of coal tar from Site No. 2B was also determined at 40°C. To test for non-Newtonian behavior, viscosities of a representative tar were measured at shear rates ranging from 200 to 1000 s^{-1}.

2.1.3 Surface Tension

The surface tension of coal tar (and air) was determined by the du Nouy ring method using a Thermo-Haake DCA 322 dynamic contact angle system. Approximately 40 mL of tar was transferred to the 100 mL test reservoir. Prior to use, the platinum-iridium ring was placed in a flame to oxidize residual contaminants. The ring was immersed in the liquid tar and then retracted through the tar-air interface. The surface tension was computed from the force required to pull the ring through the gas-tar interface, using a correction factor that accounted for the dimensions of the ring and the density of the tar. The surface tension of water (72.41 dyne/cm at 22°C) was also measured as a reference standard.

2.1.4 Interfacial Tension

The interfacial tension between tar and water was determined by the drop weight method developed by Harkins and Brown (1919). The experimental system consisted of a Harvard

Apparatus syringe pump (Model 22), a gas-tight glass syringe and a stainless steel needle with a tip diameter of either 0.0595 or 0.0254 cm. The syringe was connected to the stainless steel needle with Teflon tubing. Coal tar was introduced at flow rates ranging from 0.1 to 0.3 mL/min and drops were allowed to form on the tip of the needle, which was oriented vertically downward into a water reservoir. Drops of tar (5-10) were allowed to form over a specified period of time to obtain an average drop weight. Using a correction factor developed by Harkins and Brown, the interfacial tension was then calculated from the average drop weight and the dimensions of the stainless steel tip. The interfacial tension of dodecane and water (48.38 at 22°C) was measured as a reference standard.

2.2 Soil Properties

Soil samples from nine MGP sites were received in either 8 oz. glass jars or ~1 L glass or plastic containers. Prior to analysis, the soil from each site was mixed/homogenized and air-dried at room temperature (~22°C) for at least one week. Large stones, branches, roots, and foreign material (e.g. broken glass) were removed from the soil samples. The air-dried soil was then placed in a ceramic mortar and gently ground with a pestle to break up soil aggregates.

2.2.1 Cation Exchange Capacity

The cation exchange capacity (CEC) of each soil was determined in duplicate following the extraction procedure described by Pennell et al. (1991). Approximately 1 g of air-dried soil was added to a 50 mL polyethylene centrifuge tube, followed by 20 mL of 1M NH_4Cl. The contents of the tube were mixed thoroughly using a bench-top vortex (2-5 minutes), and then separated by centrifugation at 3000 RPM for 15 minutes. The supernatant was transferred by pipette to a clean borosilicate glass flask. The NH_4Cl wash procedure was repeated five times to achieve complete removal of exchangeable cations. The collected supernatant was then passed through a 2 µm filter to remove fine particles. Concentrations of Al, Ca, Mg, Fe, Na, and K in the supernatant solution were determined using an Inductively Coupled Plasma Spectrophotometer (ICP) Trace Analyzer (Thermal Jarrell Ash Co.). Calibration curves for each cation were prepared by dilution of 1000 mg/L high purity standards (Fisher Scientific).

2.2.2 Particle Density

Soil particle (solid) density was determined in triplicate using 25-mL glass pycnometers. Approximately 10 g of air-dried soil was added to the pycnometer, followed by Nanopure water until the pycnometer was completely filled. The weight of the pycnometer empty, containing soil, completely filled with water and soil, and completely filled with water was determined using a Mettler AG 245 analytical balance (± 0.0001g). Prior to use, each pycnometer was calibrated with water.

2.2.3 Particle Size Analysis

Particle size distribution curves were generated following standard sieve analysis procedures (Das, 1999). A stack of ten ASTM sieves was employed, with opening sizes ranging from

4.00 mm to 0.053 mm (5, 10, 20, 30, 40, 60, 100, 140, 200 and 270 mesh sieves). The mass of soil retained on each sieve and in the bottom pan was determined using a Mettler PM4000 top-loading balance (±0.01 g). Particle size distribution curves were then plotted as the percent passing (finer) versus the sieve opening size (semi-logarithmic scale). Soil retained on the 5-mesh sieve was discarded, while the remainder was homogenized for use in subsequent soil analyses and residual coal tar saturation measurements.

2.2.4 Soil Water Retention Curves

Soil water retention curves were determined for each soil using Tempe cells obtained from Soil Moisture Equipment Corp. (Figure 2-1). Each Tempe cell consisted of a brass column (6 cm ht. x 5.7 cm i.d.), two plexiglass endplates, and viton o-rings to provide a gas-tight seal between the outside edge of the column and the endplate. A porous ceramic disk with a bubbling pressure of 1 bar was placed in the lower (bottom) end plate. The Tempe cells were then packed with air-dried soil under gentle vibration in 1-cm increments. Prior to water saturation, the packed Tempe cells were flushed with CO_2 gas to promote more rapid dissolution of entrapped gas.
The packed cells were saturated with de-aired Nanopure water containing 500 mg/L (0.0045 M) $CaCl_2$ as a background electrolyte using a low-speed peristaltic pump (Model QG-20, Fluid Metering Inc.) operated at a flow rate of 1 mL/min. After complete water saturation was achieved, pressure was applied incrementally to the top of the cells over a range of 0 to 1 bar (1033.6 cm H_2O). A low-pressure regulator, configured in series with a nullmatic-type regulator (Soil Moisture Equipment Corp.), was used to apply pressure to the cells. To ensure that the system was leak free, the pressure source was closed at each pressure increment and the change in the pressure over time was observed. At each pressure increment, the cell was removed from the apparatus and the soil water content was determined gravimetrically using a Mettler PM4000 top-loading balance (± 0.01 g). Equilibrium conditions were assumed when the weight difference of the cells over two consecutive days was less than 0.1 g. Moisture release curves were developed in duplicate for each soil, with F-70 Ottawa sand included as a reference soil.

2.2.5 Specific Surface Area

Specific surface area measurements were performed using an ASAP 2010 surface area analyzer (Micromeretics, Inc.). Oven-dried soil (1 to 2 g) was placed in a borosilicate glass pellet cell and out-gassed with He for 12 hours at 105°C. The cell was then transferred to a liquid N_2 bath (77°K) and exposed to a range of N_2 pressures using an automated control system. Using a nonlinear statistical procedure (SYSTAT, Inc.), the N_2 adsorption data were fit to the Brunauer, Emmett and Teller (BET) equation over a relative vapor pressure (P/P_0) range of 0.05 to 0.35 (Sing et al., 1985). If the number of adsorbed layers is assumed to be infinite, the BET equation may be expressed as:

Figure 2-1
Tempe Cells Used to Measure Water Retention Characteristics (Moisture Release Curves) of the Soil Samples

$$C_s = \frac{(C_{s,m})(c)(P/P_0)}{(1 - P/P_0)[1 - P/P_0 + c(P/P_0)]}$$

where C_s is the amount of N_2 adsorbed or solid-phase concentration at equilibrium, $C_{s,m}$ is the amount of N_2 adsorbed at monolayer coverage, c is a parameter related to the heat of adsorption, P is the vapor pressure (partial pressure), and P_0 is the saturated vapor pressure. Specific surface area (*SSA*) values were calculated in the following manner, assuming the cross-sectional area of adsorbed N_2 to be 0.162 nm^2:

$$SSA = \frac{(C_{s,m})(N_A)(Molecular\ Area)}{Molecular\ Weight}$$

where N_A is Avogadro's Number (6.0222×10^{23} $mole^{-1}$). The specific surface area measurements were performed in duplicate, with F-70 Ottawa sand (SSA = 0.16 m^2/g) serving as a reference soil.

2.2.6 Total Carbon Content

The carbon content of the uncontaminated soil samples was determined in duplicate using a Shimadzu Total Organic Carbon device (TOC-5050A) equipped with a Solid Sample Module (SSM-5000A) and an infrared detector for CO_2 determination. A small amount of air-dried soil (0.01 g to 0.3 g) was placed in a ceramic cell and combusted at 900°C. Calibration curves were prepared using at least five different amounts of anhydrous dextrose powder, which contained 40% carbon by weight. To ensure accuracy of the carbon analysis, the total carbon contents of three reference soils, F-70 Ottawa sand (0% OC), Marlette B (0.6% OC) and Marlette A (2.2% OC), were also measured.

2.3 Residual Saturation of Coal Tar

Two-phase (water and coal tar) residual saturation measurements were made using either glass or stainless steel columns. Initially, borosilicate glass columns were used to allow for visual observation of coal tar imbibition and displacement. In subsequent experiments, however, stainless steel columns of similar size and configuration were employed to avoid endplate movement and column failure at greater applied pressures.

The glass column apparatus consisted of a Kontes borosilicate glass preparative chromatography column (4.8 cm i.d.), equipped with an adjustable endplate that allowed the bed length to be varied from 1 to 13 cm (Figure 2-2a). The bottom endplate was fitted with a 40-mesh polypropylene screen and a 0.22 µm Teflon filter (Osmonics, Inc.) to provide organic-wetting conditions. The top endplate was lined with a 40-mesh polypropylene screen and Whatman No. 42 filter paper to provide water-wetting conditions.

Figure 2-2
a) Glass (Teflon Endplates) and b) Aluminum (Stainless Steel Endplates) Columns used to Measure Coal Tar Residual Saturation

The stainless steel column apparatus consisted of a custom designed aluminum column (5.0 cm in length and 5.20 cm i.d.) and two stainless steel endplates (Figure 2-2b). The stainless steel endplates were fitted with viton o-rings to provide a water-tight seal between the soil column and the endplate. The bottom endplate was lined with a 100-mesh stainless steel screen, a 70-mesh polypropylene screen, and a 0.22 μm Teflon filter (Osmonics, Inc.) to provide organic-wetting conditions. The top endplate was lined with a 100-mesh stainless steel screen and Whatman No. 42 filter paper to provide water-wetting conditions. All connections to the column systems consisted of stainless steel tubing and fittings.

The columns were packed with air-dried soil under gentle vibration in 1-cm increments. Layering between sand increments was minimized by mixing the bed surface with a spatula between and after each addition of soil. For all columns, the bed length was approximately 5 cm, with bulk densities ranging from 1.2 to 1.7 g/cm^3 and pore volumes ranging from 32 to 56 mL. After packing was complete, the columns were flushed with CO_2 gas for approximately 20 minutes to facilitate dissolution of any entrapped gas during the water saturation process. The packed columns were saturated with de-aired Nanopure water containing 500 mg/L (0.0045 M) $CaCl_2$ as a background electrolyte. Water was introduced in an upflow mode using either a low-speed peristaltic pump (Model QG-20, Fluid Metering Inc.) or a Rainin HPLC pump (Dynamix SD-200) at flow rates ranging from 1 to 8 mL/min. Approximately 12 pore volumes of water were flushed through each column to achieve complete water saturation, which was confirmed by sequential weight measurements. Soil column properties, including porosity and bulk density, were determined gravimetrically by weight difference during the packing and water saturation procedure.

Following complete water saturation of the column, liquid coal tar was introduced at a flow rate of 20 mL/hr using a Harvard Apparatus (Model 22) syringe pump. The coal tar was first injected in an upflow mode through the lower endplate, which was lined with organic-wetting filter paper. After approximately 1 pore volume of coal tar had been introduced into the column, the pump was disconnected and the column was rotated 180 degrees. Additional coal tar was then introduced through the water-wetting filter to promote complete exploration of the pore space near the end plate. To achieve residual saturation conditions, the column was disconnected from the coal tar pump and returned to its original orientation. Nanopure water (containing 500 mg/L $CaCl_2$) was introduced in a downflow mode through the endplate lined with water-wetting filter paper using either the HPLC or peristaltic pump. The column was flushed with water periodically in the opposite direction to displace any coal tar trapped in the endplates. During the entire tar displacement process, a total of approximately 20 pore volumes of water were introduced into the column at a flow rate of 8 mL/min. For Site 2B coal tar, the column was wrapped with heat tape, maintained at 40°C for 24 hours, following the introduction of coal tar. The heating process was necessary to achieve water displacement of Site 2B coal tar from the column without the use of a high pressure water flood.

The most common approach used to determine NAPL saturation (S_N) in a soil column is based upon the difference in the weight of the water-saturated soil column and the weight obtained following NAPL entrapment, assuming that the density of the NAPL is known. For a DNAPL, this relationship may be expressed as:

$$S_{NAPL} = \frac{Column\,Wt._{Water} - Column\,Wt._{DNAPL+Water}}{\left(\rho_{DNAPL} - \rho_{water}\right) pv_T}$$

where pv_T is the total pore volume. For the coal tars reported herein, the density contrast between coal tar and water was very small (i.e., 0.065 to 0.107 g/mL). Hence, very small differences in column weight before and after coal tar entrapment would need to be detected in order to accurately determine residual coal tar saturation values. For example, assuming an aqueous pore volume of 40 mL and a density contrast of 0.085 g/mL, a difference in the column weight of only 0.68 g would yield a residual saturation of 20%. Given that the stainless steel column apparatus weighed approximately 950 g, this represents a weight change of less than 0.1%. A mass balance approach was also considered, which involved measuring the total volume or mass of tar introduced into the column and the amount displaced during water flushing. Although this approach was used as an estimate of residual saturation, the coal tars were rather viscous and adhered to glass and metal surfaces and tubing, making it difficult to obtain accurate measurements of the displaced tar volume or mass.

To overcome the limitations noted above, non-reactive tracer tests were performed before and after the coal tar entrapment process to quantify the change in aqueous phase pore volume and the corresponding residual coal tar saturation. An aqueous solution (~1.5 pore volumes) consisting of 0.01 M KI and background electrolyte were flushed through the column using a Rainin SD-200 HPLC pump. The tracer tests were performed in an upflow mode to prevent preferential channeling of tracer through columns. Measured tracer breakthrough curves (BTCs) were fit to an analytical solution of the one-dimensional (1-D) advective-dispersive reaction (ADR) transport equation using the CXTFIT2 program. Assuming conditions of homogeneity, local equilibrium, linear and ideal sorption, and the 1-D ADR equation may be written in dimensionless form as:

$$R_F \frac{\partial C_w^*}{\partial pv} = \frac{1}{P_e} \frac{\partial^2 C_w^*}{\partial X^2} - \frac{\partial C_w^*}{\partial X}$$

$$R_F = 1 + \frac{\rho_b K_D}{n s_w};\ C^* = \frac{C}{C_O};\ pv = \frac{vt}{L};\ P_e = \frac{vL}{D_H};\ X = \frac{x}{L}$$

Here, R_F is the retardation factor, ρ_b is the soil bulk density, K_D is the linear distribution coefficient between the solid and aqueous phases, n is soil porosity, S_w is the water saturation, C^* is the normalized concentration of dissolved solute in water, C is the actual solute concentration in water, C_o is the solute concentration in the influent water, pv is the aqueous phase pore volume, v is the pore-water velocity, t is time, and L is the length of the column, P_e is the Peclet number, D_H is the hydrodynamic dispersion coefficient, X is dimensionless distance, and x is the actual distance from the column inlet.

The residual coal tar saturation of each column was calculated from the change in the water saturation (S_w), or aqueous phase pore volume, before and after coal tar entrapment. Here, it was assumed that the non-reactive tracer did not chemically react with either the soil or the coal tar. The former was confirmed through results of the initial tracer test (i.e., R_F = 1.0), performed prior to the introduction of coal tar.

3
RESULTS

3.1 Soil Characterization Results

Particle size distribution curves, based on sieve analysis, for the nine MGP soils are shown in Figure 3-1. From these curves, characteristic particle diameters (d_{60}, d_{50}, d_{10}) were obtained, which correspond to the point at which the distribution curve equals 60, 50 and 10 percent of particles passing through the sieves (percent finer). The median grain size (d_{50}) of the MGP soils ranged from 0.10 to 0.30 mm. The characteristic particle diameters were then used to calculate the coefficient of uniformity (C_u) and coefficient of gradation (C_g). These data, as well as textural classifications (% gravel, % sand, % silt + clay) based on the United States Department of Agriculture (USDA) and Unified Soil Classification System (USCS), are summarized in Table 3-1. Graphical comparisons of characteristic particle diameters (d_{50}, d_{10}) and textural classifications are presented in Figures 3-2 and 3-3, respectively. With the exception of Site No. 9, which contained less than 1% gravel, all of the MGP soils would be classified as "gravelly sands", based on the modified textural classification approach of Das (1999), which accounts for the presence of gravel.

The particle density and total carbon (TC) content of the MGP soils ranged from 2.32 to 2.80 g/cm^3, and from 0.07 to 14.85 % (wt), respectively (Table 3-2). The cation exchange capacity (CEC) and specific surface area (SSA) of the MGP soils ranged from 18.08 to 105.1 meq/100g, and from 1.31 to 11.65 m^2/g, respectively (Table 3-2). As expected, the soil from Site No. 7, which had the highest organic carbon content (14.85 %), also possessed the lowest particle density (2.32 g/cm^3) and highest CEC (105.1 meq/100g). A graphical comparison of total carbon content and specific surface area of the nine MGP soils is presented in Figure 3-4. The measured properties reported here are within the range of values typically observed for natural surface soils (e.g., see Miller and Gardiner, 2001).

Soil water retention curves for the nine MGP soils are shown in Figure 3-5, plotted as the volumetric soil water content (θ) versus the negative pressure head or suction (h). The data points shown in Figure 3-5 represent average values obtained from duplicate measurements (Tempe cells). The moisture release curve data were fit to the van Genuchten (VG) and Brooks-Corey (BC) equations using a nonlinear, least squares regression procedure (SYSTAT, ver. 5.03). The van Genuchten (1980) and Brooks-Corey (1964) equations may be expressed in terms of the effective water saturation (S_e):

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{1}{\left(1 + |\alpha h|^n\right)^{(1-1/n)}} \quad (VG)$$

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \left(\frac{h}{h_b}\right)^{-\lambda} \quad (BC)$$

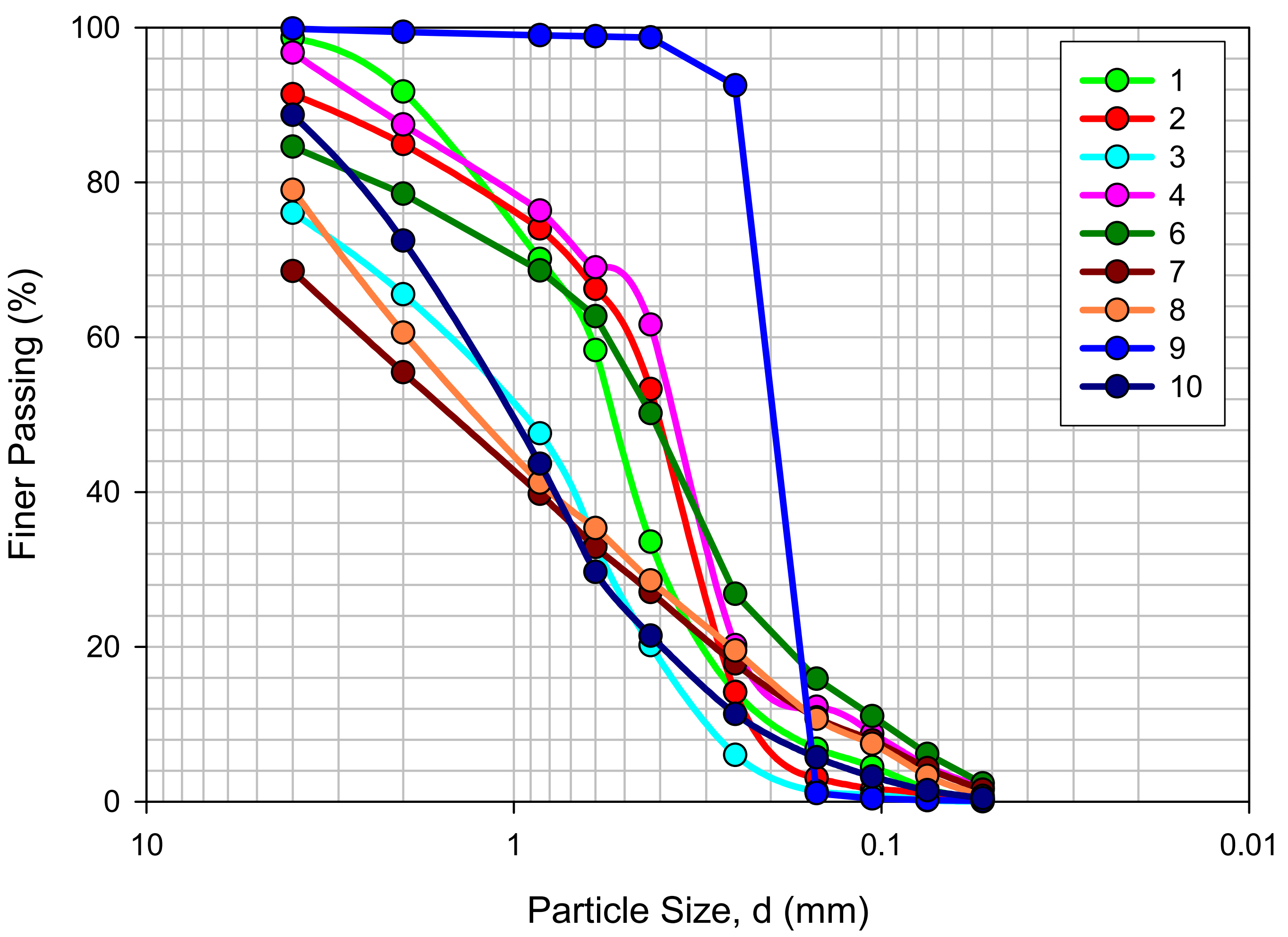

Figure 3-1
Particle Size Distribution Curves of Soil Samples Collected from Nine MGP Sites. Sample 5 not analyzed

Table 3-1
Physical Properties of Soils Based on Particle Size (Sieve) Analysis

Site Identifier	d_{60} (mm)	d_{50} (mm)	d_{10} (mm)	C_u †	C_g ‡	USDA Particle Size Classification			USCS Particle Size Classification		
						% Gravel > 2 mm	% Sand 2-0.05 mm	% Silt+Clay < 0.05 mm	% Gravel 76.2-4.75 mm	% Sand 4.75-0.075 mm	% Silt+Clay < 0.075 mm
1	0.57	0.51	0.18	3.17	1.33	8.3	91.5	0.2	1.0	97.4	1.6
2	0.48	0.41	0.23	2.09	0.93	15.1	84.7	0.2	7.0	92.1	0.9
3	1.63	0.97	0.30	5.43	0.62	34.5	65.5	0.0	22.0	77.8	0.2
4	0.42	0.37	0.12	3.50	1.67	12.6	85.6	1.8	2.0	93.4	4.6
6	0.55	0.43	0.10	5.50	1.33	21.5	76.2	2.3	15.0	78.8	6.2
7	2.60	1.60	0.13	20.00	0.74	44.6	53.9	1.5	28.0	67.7	4.3
8	2.00	1.36	0.14	14.29	0.76	39.4	59.9	0.7	16.0	80.7	3.3
9	0.02	0.02	0.016	1.25	1.01	0.6	99.3	0.1	0.0	99.8	0.2
10	1.49	1.08	0.23	6.48	1.09	27.6	72.0	0.4	8.0	90.6	1.4

† $C_u = d_{60} / d_{10}$

‡ $C_g = d_{30}^2 / (d_{60} \times d_{10})$

Sample 5 not analyzed

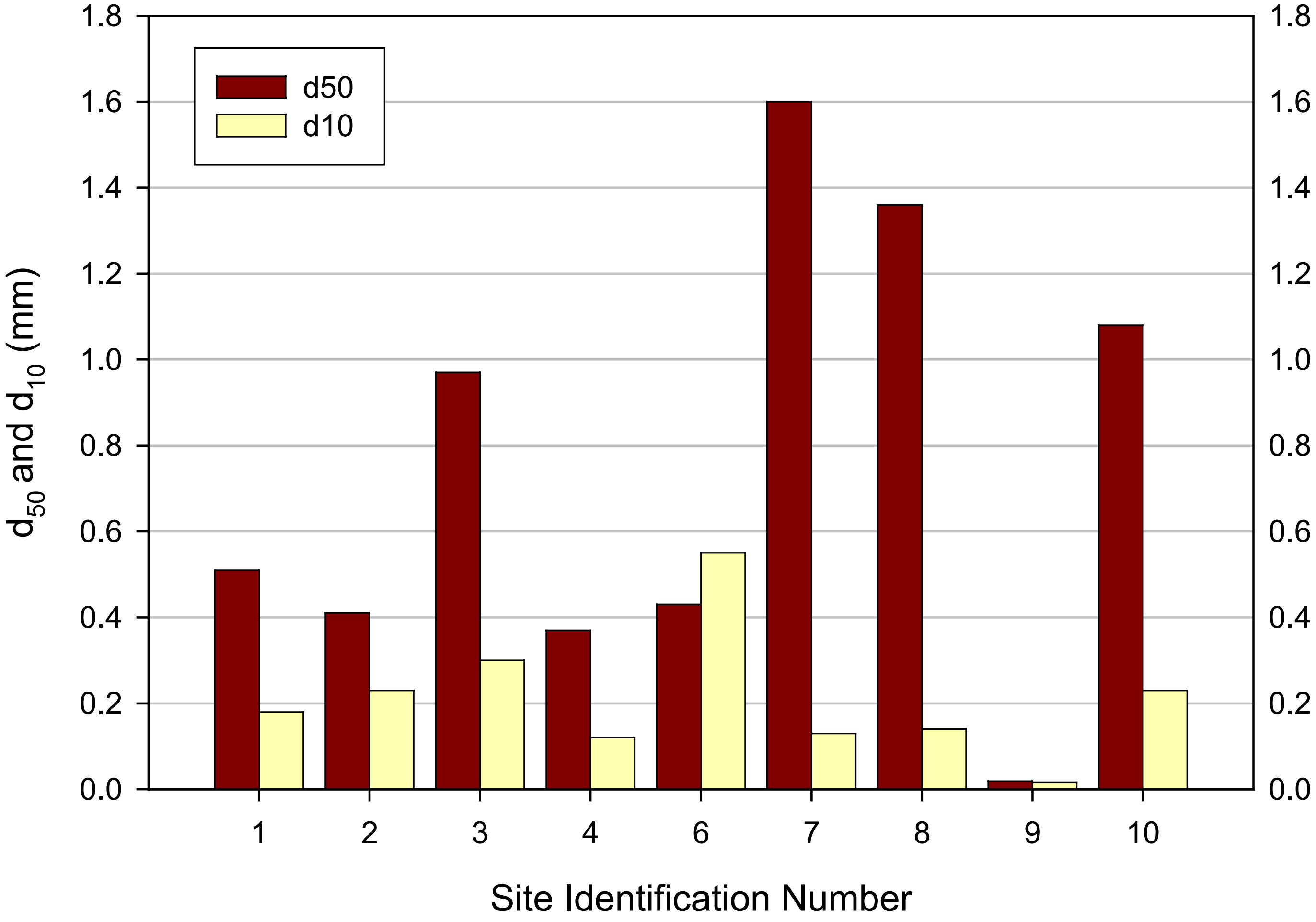

Figure 3-2
Characteristic Particle Diameters (d_{60} and d_{10}) of Soils Collected from Nine MGP Sites. Site 5 not analyzed

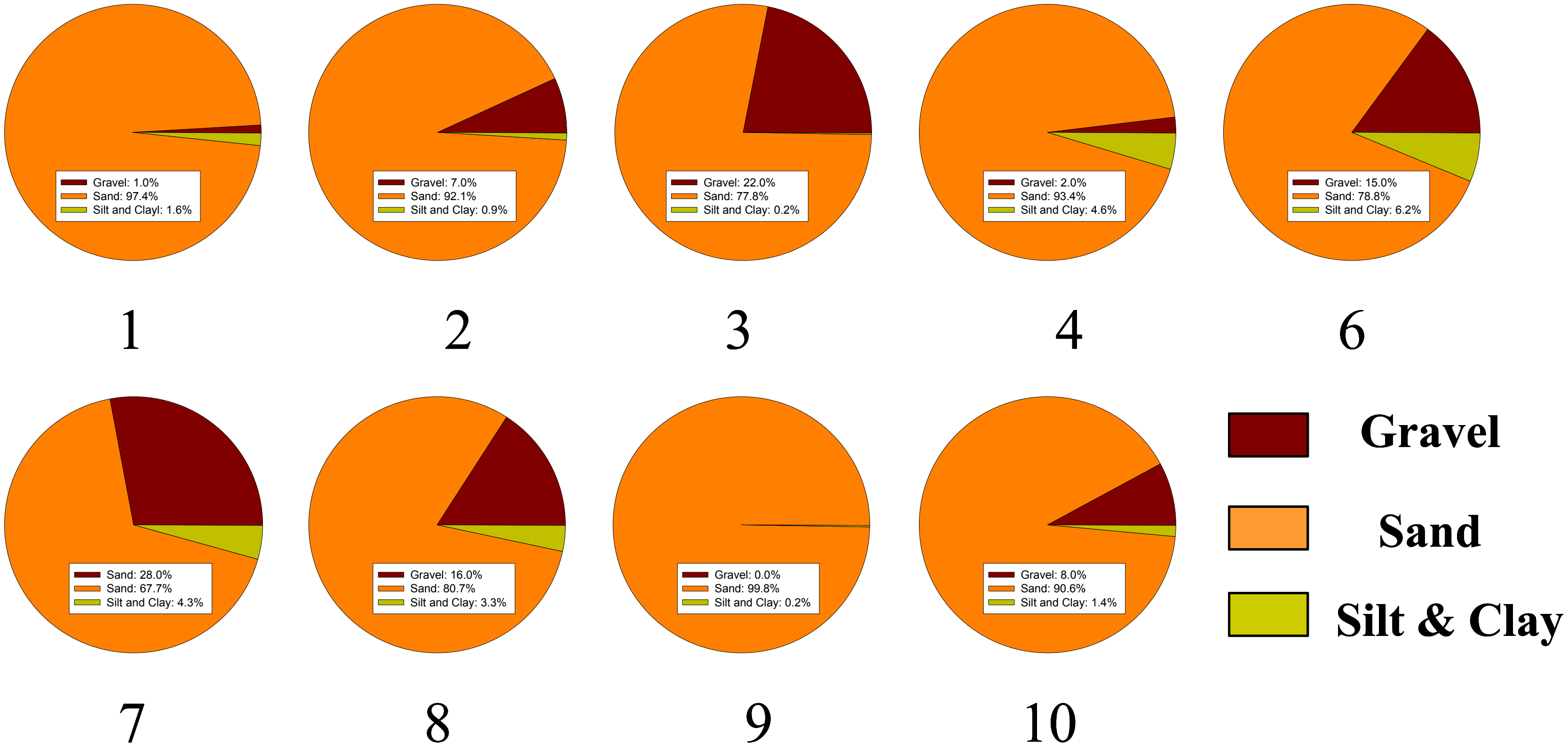

Figure 3-3
Textural Classification of Soils Collected from Nine MGP Sites Based on the Unified Soil Classification System (Gravel: 76.2-4.75 mm; Sand: 4.75-0.075 mm; Silt and Clay: < 0.075 mm) Site 5 not analyzed

Table 3-2
Physical and Chemical Properties of Soils

Soil Identifier	Particle Density (g/cm^3)	Total Carbon (TC) (%)	Cation Exchange Capacity (CEC) (meq/100g)	N_2/BET Surface Area (m^2/g)
1	2.58 (±0.06) *	0.50	7.09	7.47
2	2.62 (±0.04)	0.56	18.08	7.36
3	2.80 (±0.03)	1.17	21.86	2.10
4	2.73 (±0.02)	0.99	84.29	6.51
6	2.56 (±0.10)	3.72	35.36	1.31
7	2.32 (±0.10)	14.85	105.1	5.89
8	2.57 (±0.06)	0.88	45.42	11.65
9	2.64 (±0.05)	0.07	not measured	not measured
10	2.61 (±0.09)	2.68	56.48	10.33

* Standard deviation (s.d. = $s/\sqrt{n-1}$)

Site 5 not analyzed

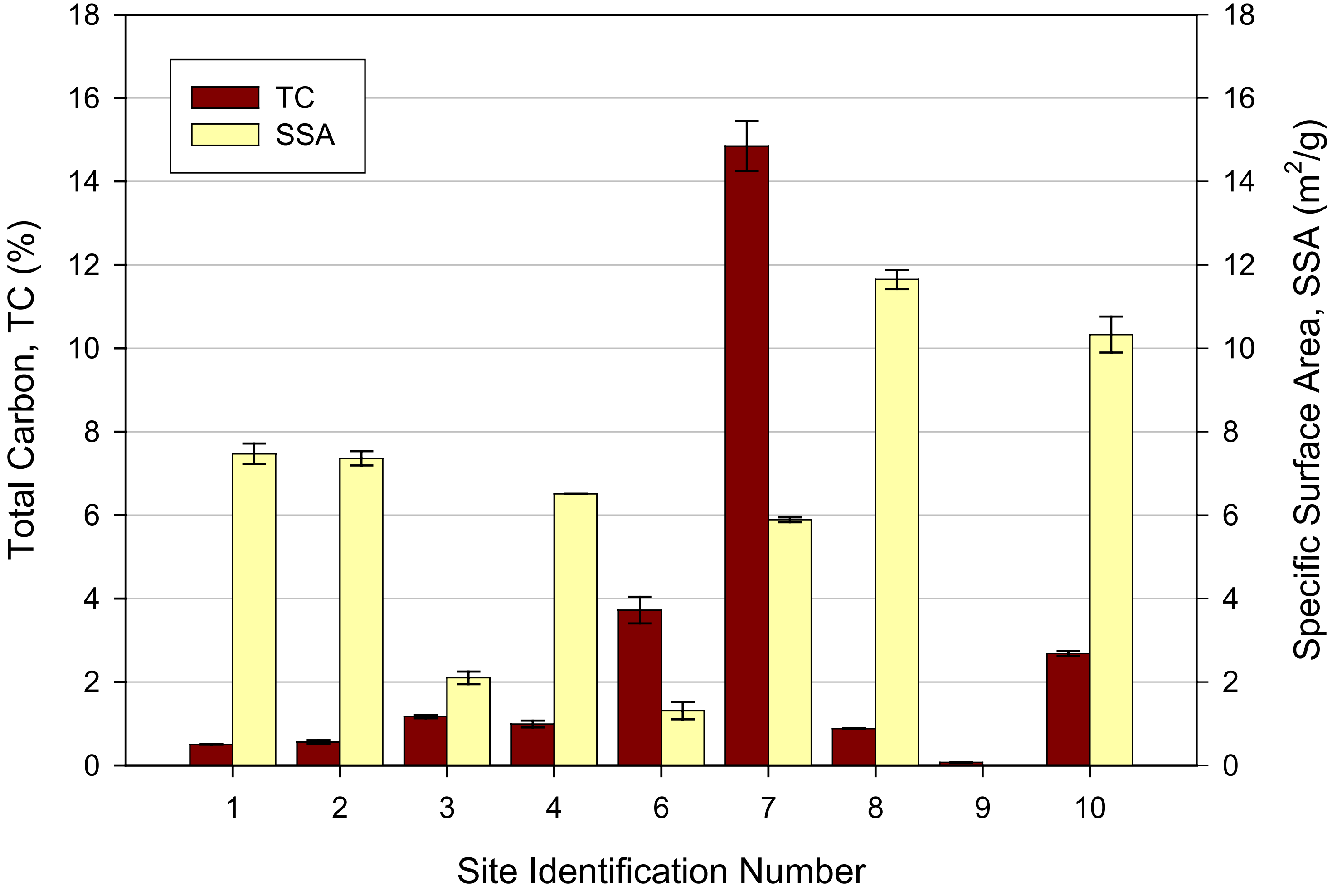

Figure 3-4
Total Carbon and Specific Surface Area of Soils Collected from Nine MGP Sites. Site 5 not analyzed

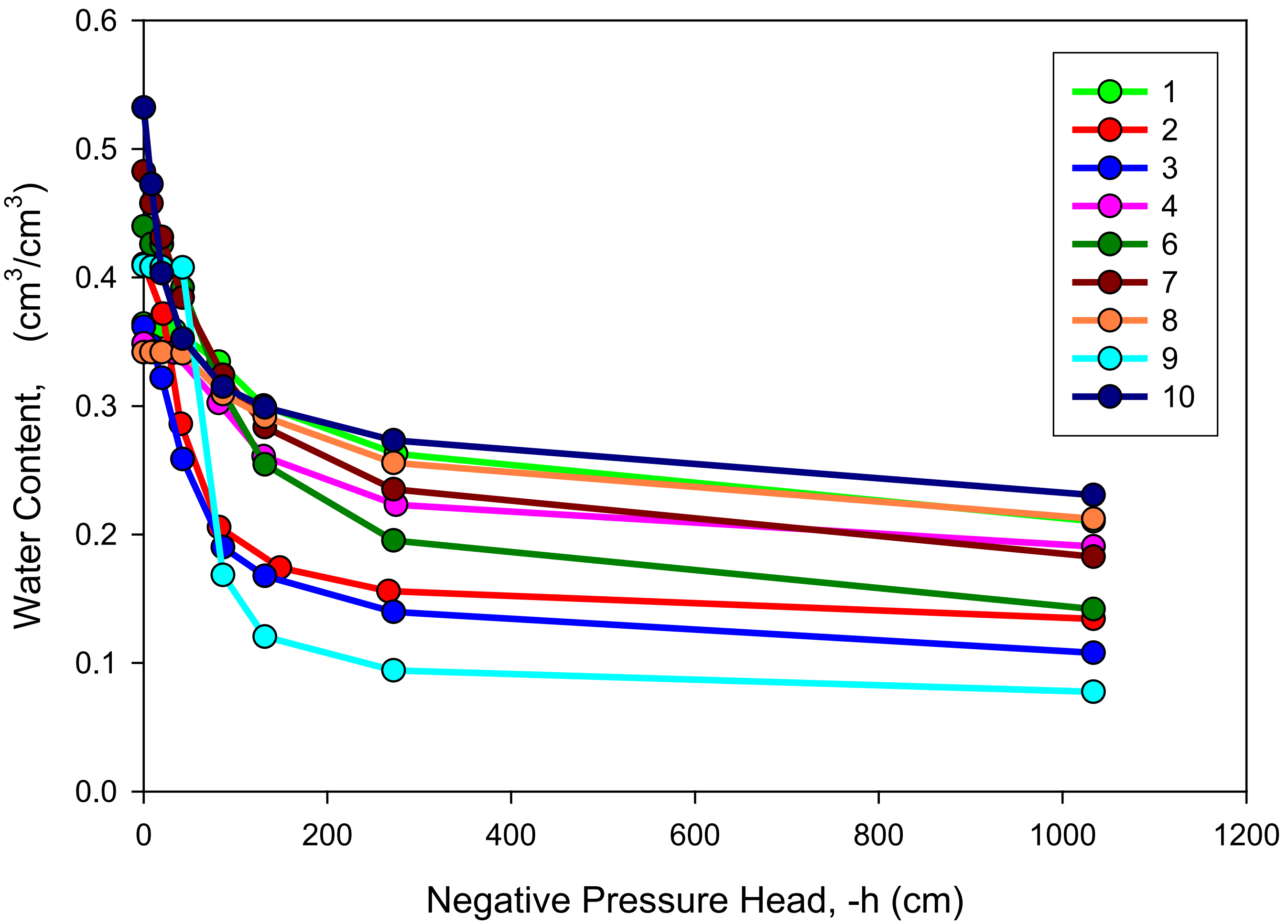

Figure 3-5
Soil Water Retention (Release) Curves of Soils Collected from Nine MGP Sites. Site 5 not analyzed

The saturated and residual volumetric water contents (θ_s and θ_r, respectively) were obtained from the observed endpoints of each moisture release curve, so that only the parameters α and n or h_b and λ were obtained from the fitting procedure. The van Genuchten and Brooks-Corey parameters for the nine MGP soils are summarized in Table 3-3. Representative fits of the van Genuchten (VG) and Brooks-Corey (BC) curves to the moisture release curve data for Sites No. 4 and 9 are presented in Figure 3-6. Here, the x-axis is plotted on a Log scale to illustrate differences in the fitted curves near the bubbling pressure (h_b). The bubbling pressure corresponds to the negative pressure or suction at which air first enters the soil. The residual water content represents the amount of water held within the soil by capillary forces, which cannot be removed by applying additional negative pressure. Comparisons of bubbling pressure, saturated and residual water content values for the nine MGP soils are shown graphically in Figure 3-7. These parameters characterize the water holding capacity of a soil, and can be scaled by using the Leverett (1941) function approach to describe pressure-saturation relationships (retention curves) for other non-wetting phases, such as NAPLs.

3.2 Coal Tar Characterization Results

Measured values of coal tar density, viscosity, surface tension (air-coal tar), and interfacial tension (water-coal tar) are presented in Table 3-4. The liquid density and viscosity of the coal tars ranged from 1.054 to 1.144 g/cm3, and from 32.0 to 425.3 centipoise (cP), respectively, at 22°C. Most of the measured densities were only slightly greater than those of coal tars used in other studies for which residual saturation data have been reported (1.051 and 1.047 g/cm^3 at 25°C) (Barranco and Dawson, 1999; Hugaboom and Powers, 2002). In contrast, the measured viscosities were all greater than those of coal tars studied previously (19.4 cP at 25°C and approximately 16.6 cP at 25°C), and are more representative of coal tars encountered in the field. Surface and interfacial tension values obtained at 22°C ranged from 23.3 to 37.96 dyne/cm, and from 24.43 to 27.83 dyne/cm respectively (Table 3-4). These values are consistent with published values at neutral pH. It should be noted that both Barranco and Dawson (1999) and Hugaboom and Powers (2002) reported sharp declines in coal tar-water interfacial tension above pH ~9.0. Measured physical properties of the six coal tar samples (Site No. 1, 2, 4, 7, 9, and 10) used in the residual saturation experiments are compared graphically in Figures 3-8 and 3-9.

3.3 Residual Saturation Determinations and Results

As described in the Materials and Methods section of this report, the experimental approach used to determine the residual coal saturation involved a sequence of four steps: (1) pack columns with air-dried soil, (2) introduce de-aired water until complete water saturation is reached ($S_w = 1.0$, $S_N \approx 0.0$), (3) introduce coal tar to displace mobile water until residual water saturation is reached ($S_w \approx 0.2$; $S_N \approx 0.8$), and (4) introduce water to displace mobile (free product) coal tar until residual coal tar saturation is reached ($S_w \approx 0.8$; $S_N \approx 0.2$). Representative photographs of this process are shown in Figures 3-10, 3-11, and 3-12 for Sites 9, 2 and 6, respectively. Here, it is important to note that after complete water saturation (lower left-hand corner) the soils are much darker in color. This effect became more pronounced as the total carbon content of the soils increases, from 0.07 % for Site No. 9 to 3.72% for Site No. 6. Therefore, great care must be taken when attempting to visually assess the presence or absence of coal tar liquid (NAPL) in field soil cores at or near residual saturation.

Table 3-3
Soil Water Retention Characteristics Obtained from van Genuchten and Brooks-Corey Equations

Site Identifier	Bulk Density (g/cm^3)	van Genuchten Parameters[†]				Brooks-Corey Parameters			
		θ_{sat}	θ_{res}	α	n	θ_{sat}	θ_{res}	h_b (cm)	λ
1	1.640 (±0.000)*	0.365	0.188	0.009	1.91	0.362	0.123	56.9	2.89
2	1.423 (±0.000)	0.413	0.138	0.0314	2.39	0.391	0.129	23.7	1.03
3	1.788 (±0.009)	0.360	0.100	0.0326	1.91	0.343	0.091	23.3	1.44
4	1.722 (±0.000)	0.346	0.187	0.0111	2.38	0.344	0.174	57.5	1.24
6	1.411 (±0.007)	0.435	0.130	0.0146	2.15	0.421	0.112	48.2	1.31
7	1.168 (±0.008)	0.478	0.122	0.0313	1.52	0.457	0.089	23.7	2.72
8	1.691 (±0.000)	0.344	0.196	0.0313	1.96	0.342	0.094	49.9	4.07
9	1.557 (±0.000)	0.411	0.093	0.0145	6.36	0.408	0.079	42.3	0.55
10	1.221 (±0.000)	0.534	0.190	0.1264	1.42	0.532	0.149	3.6	4.59

* Standard deviation (s.d. = $s/\sqrt{n-1}$)

[†] van Genuchten equation: $\dfrac{\theta-\theta_r}{\theta_s-\theta_r}=\dfrac{1}{\left(1+|\alpha h|^n\right)^{(1-1/n)}}$, [‡] Brooks-Corey equation: $\dfrac{\theta-\theta_r}{\theta_s-\theta_r}=\left(\dfrac{h}{h_b}\right)^{-\lambda}$

Site 5 not analyzed.

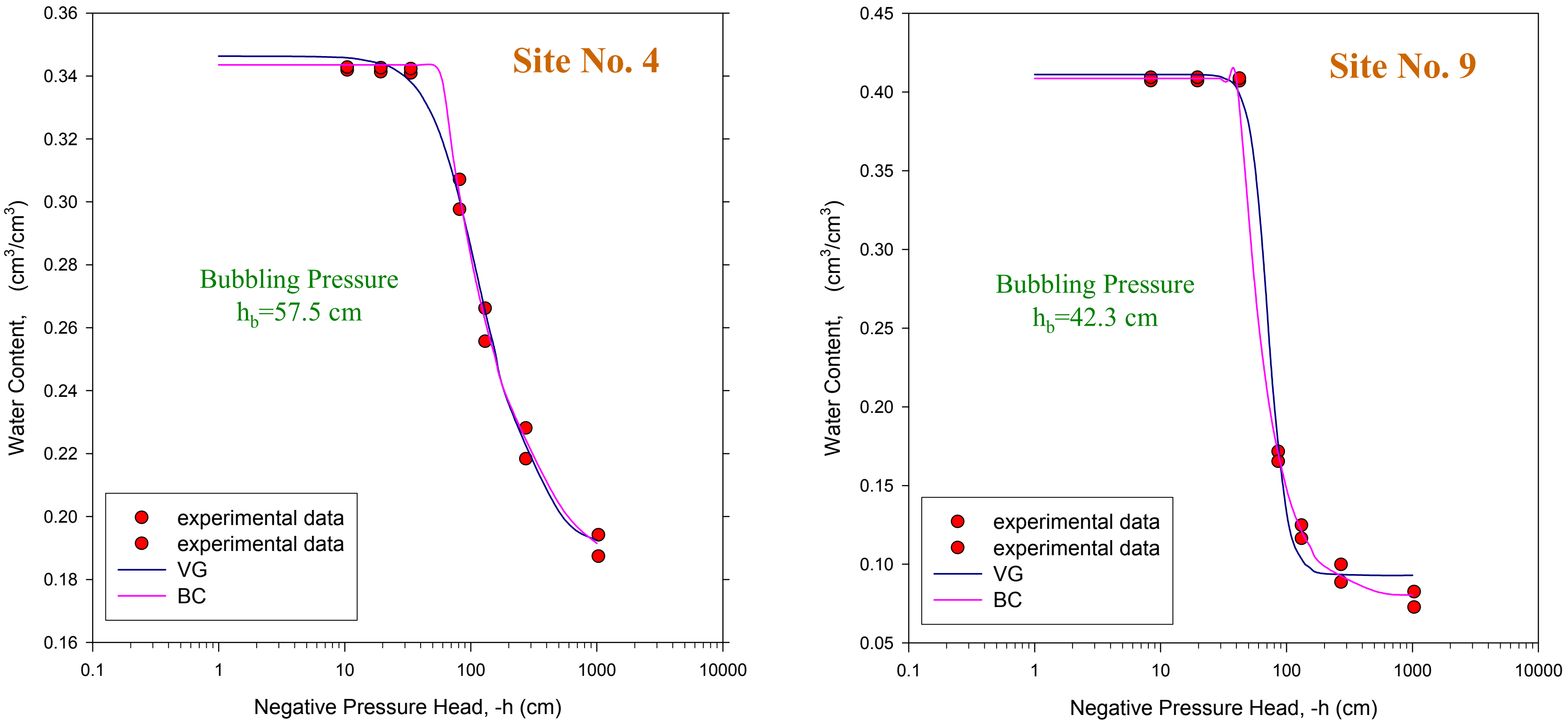

Figure 3-6
Fits of van Genuchten (VG) and Brooks-Corey (BC) Equations to Moisture Release Curve Data Obtained for Soils from Site No. 4 and Site No. 9, Respectively

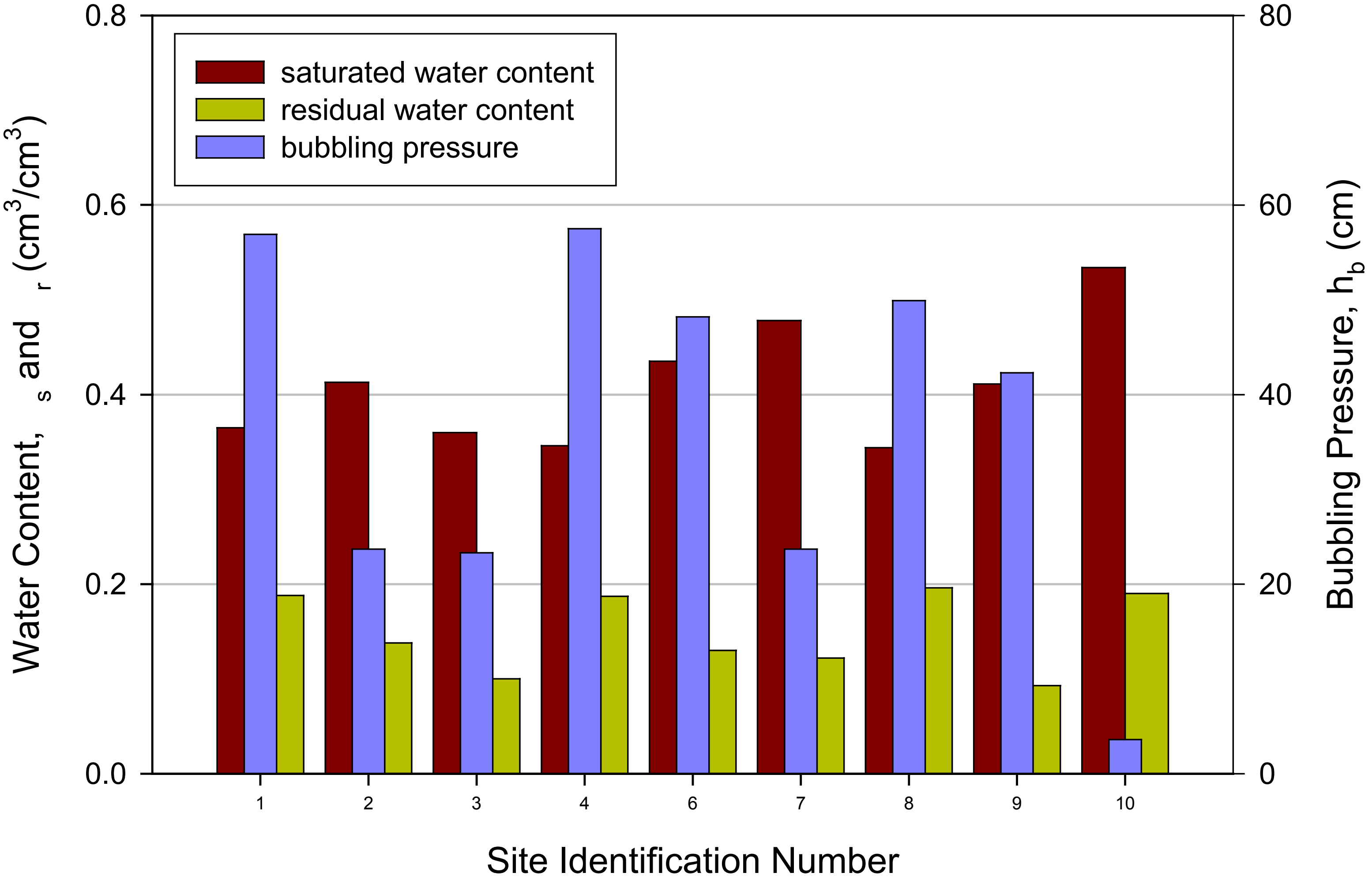

Figure 3-7
Bubbling (Air Entry) Pressure, Saturated Water Content and Residual Water Content of Soils Collected from Nine MGP Sites. Site 5 not analyzed

Table 3-4
Physical Properties of Coal Tar Samples

Coal Tar Site Identifier	Density (g/cm^3), 22°C	Viscosity[†] (cP), 22°C	Surface Tension[‡] (dynes/cm), 22°C	Interfacial Tension (dynes/cm), 22°C
1A	1.074 (±0.000)*	Not measured (high)	Not measured	Not measured
1B	1.066 (±0.002)	63.6 (±0.1)	33.75 (±0.09)	26.70 (±0.05)
2A	1.144 (±0.000)	Not measured (high)	37.96 (±0.04)	Not measured
2B	1.104 (±0.002)	425.3 (±0.7)	26.67 (±0.98)	27.83 (±0.25)
3	Not measured	Not measured	Not measured	Not measured
4	1.062 (±0.002)	144.6 (±0.8)	34.35 (±0.26)	22.55 (±0.65)
6	Not measured	Not measured	Not measured	Not measured
7	1.076 (±0.000)	32.0 (±0.1)	34.17 (±0.35)	25.79 (±1.27)
8	Not measured	Not measured	Not measured	Not measured
9	1.054 (±0.001)	51.0 (±0.1)	23.44 (±0.07)	22.37 (±0.08)
10	1.062 (±0.000)	62.9 (±1.4)	33.63 (±0.52)	24.43 (±0.52)
11	1.054 (±0.000)	34.7 (±0.1)	Not measured	Not measured

* Standard deviation (s.d. = $s/\sqrt{n-1}$)

[†] Haake Rheostress 75, shear rate = 200 1/s, [‡] Cahn DCA-322

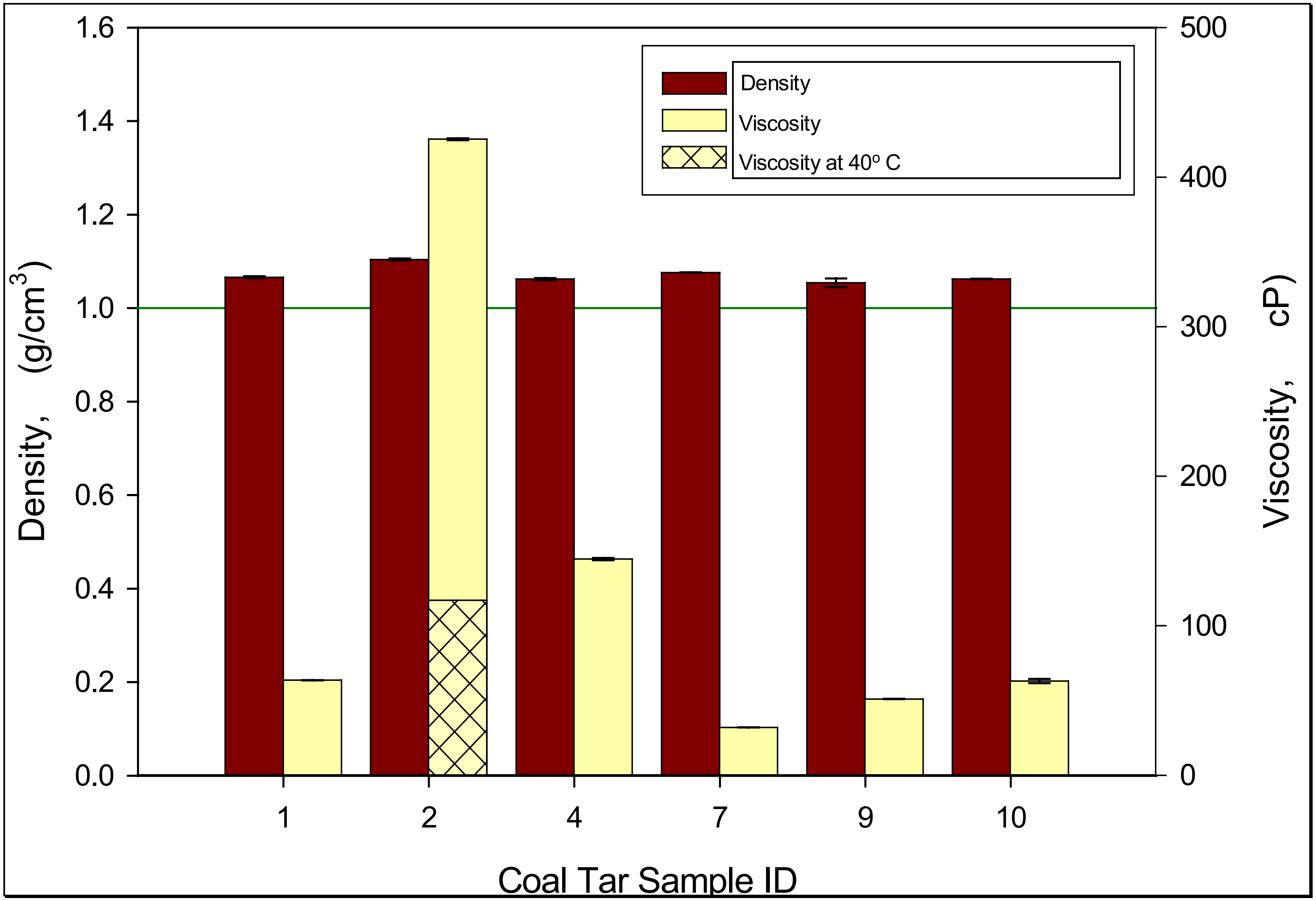

Figure 3-8
Liquid Density and Dynamic Viscosity of Coal Tars Collected from Six MGP Sites

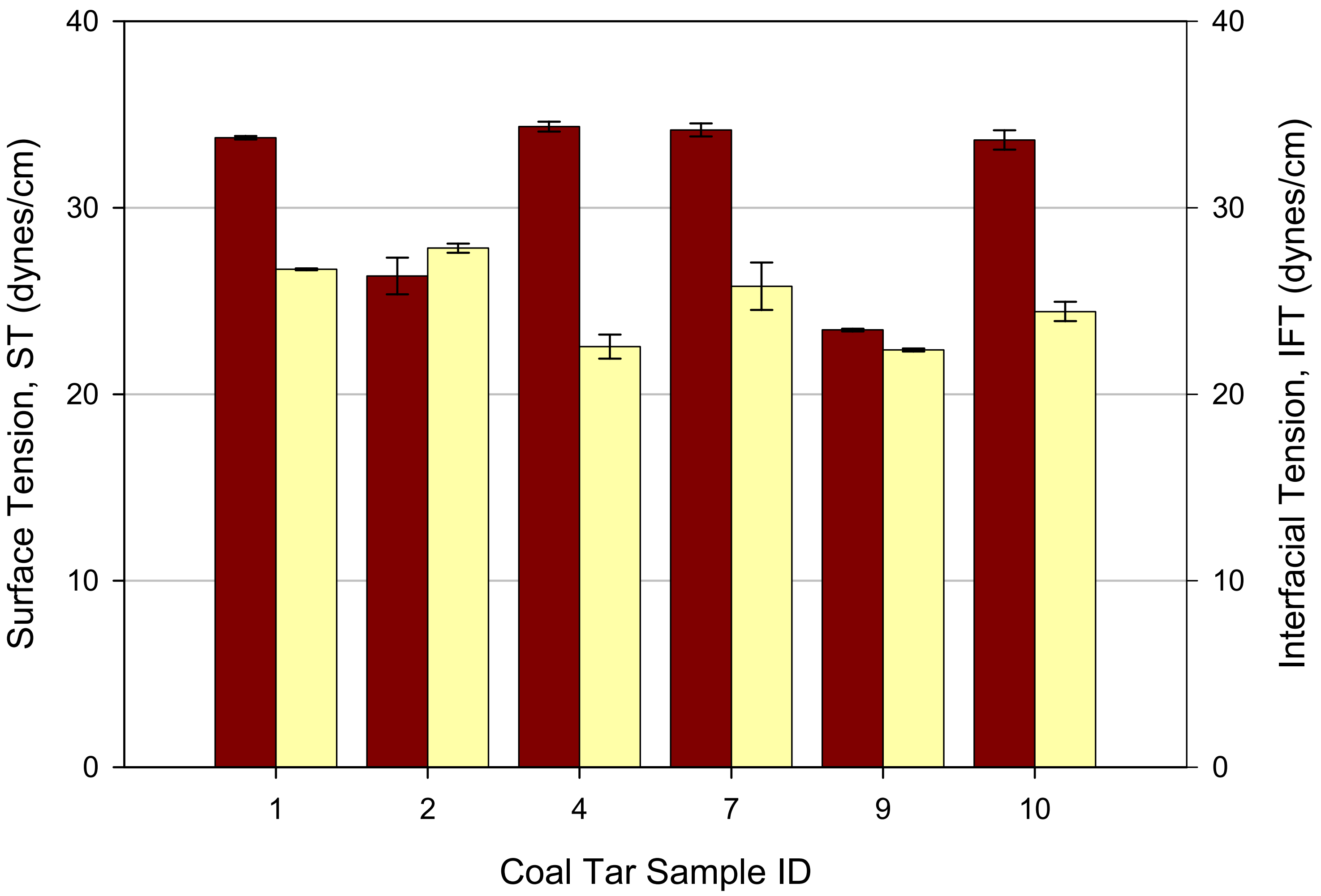

Figure 3-9
Surface Tension (Tar-Air) and Interfacial Tension (Tar-Water) of Coal Tars Collected from Six MGP Sites (Left Bar is Surface Tension, Right Bar is Interfacial Tension)

The actual determination of coal tar residual saturation was based on the results of non-reactive tracer tests conducted before and after coal tar entrapment. This methodology was necessary because the coal tar densities were similar to that of water, and thus, the usual approach based on the change in column weight did not provide accurate results. Representative breakthrough curves (BTCs) for non-reactive tracer tests conducted before and after coal tar entrapment are shown in Figure 3-13. Here, the retardation factor (R_F) decreased from 1.0 prior to coal tar injection to 0.8 following the establishment of residual saturation. The early breakthrough of tracer is a direct consequence of the presence of entrapped coal tar in the pore space and consequently a reduced aqueous phase pore volume. Based on the observed change in R_F values, the reduction in aqueous phase pore volume was computed, with the volume of residual coal tar accounting for the difference.

Results of the coal tar residual saturation experiments are summarized in Table 3-5. All reported values represent averages of at least two column experiments, although most experiments were conducted in triplicate. It should be noted that the coal tar from Site No. 2B had a viscosity of 423 cP at 22°C, and as a result the column had to be heated to 40°C (μ = 116.3 cP) to complete the column test. Residual coal tar data are reported in terms of both volumetric saturation (S_{Nr} volume of coal tar per volume of pore space) and mass concentration (C_{Nr}, mass of coal tar per mass of solid). The residual coal tar saturations ranged from 0.08 to 0.23 cm^3/cm^3, while the corresponding residual concentrations ranged from approximately 25,000 to 72,000 mg/kg (2.5 to 7.2 % weight). Graphical comparisons of the residual coal tar saturations and concentrations, including standard deviations, are shown in Figure 3-14. The soils from Site No. 1 and 9 were comprised almost entirely of sand-size particles, and possessed relatively low total carbon contents (Tables 3-5 and 3-6), while coal tar viscosities were in the mid-range (63.6 and 51.0 cP, respectively). Column tests for these two sites resulted in similar residual coal tar concentrations (48,000 and 50,000 mg/kg, respectively), indicating that sandy soils can exhibit a relatively high capacity to retain coal tar as residual immobile product.

The measured residual saturation values were lower than those reported by Barranco and Dawson (1999) and Hugaboom and Powers (2002), which were approximately 0.30 and 0.65 cm^3/cm^3 respectively at neutral pH. This slight difference is most likely due to experimental procedures, the most significant factor being that in this work the columns were flushed with water in both upflow and downflow modes to displace mobile (free product) coal tar, ensuring that no coal tar was trapped in the endplates or remained in the dead volume. In addition, Barranco and Dawson (1999) utilized the change in total column weight to determine coal tar saturation, while Hugaboom and Powers (2002) calculated coal tar saturation from the difference in the volume of coal tar introduced and volume of coal tar collected in the effluent during displacement. Both of these measurement techniques are subject to substantial error because even minor variations in the column weight or effluent volume of coal tar impact the resulting residual saturation value considerably.

Relevant properties of six soil cores at residual coal tar saturation are summarized in Table 3-6.

By using the coal tar chemical concentrations data for the six coal tars and by assuming, based on earlier EPRI research, that on average about 30% of the tar matrix is quantitatively characterized by means of chemical analysis for mono-nuclear aromatic hydrocarbons (MAH) and poly-nuclear aromatic hydrocarbons (PAH), we have calculated the soil concentration values for the coal tar constituents present in soils containing coal tar NAPL at residual saturation. These results are given in Table 3-7. The total MAH concentrations in the 8 soils range from 400 mg/Kg to 3400 mg/Kg and the PAH concentrations range from 6100 mg/Kg to 19,500 mg/Kg. Of course these concentrations are subject to change depending on a more accurate characterization of tar for MAH, PAH and pitch amounts.

Results obtained from the soil characterization, coal tar characterization, and residual saturation studies were used to develop empirical correlations to describe residual coal tar saturation as a function of both soil and coal tar properties. The intent was to generate relatively simple correlations that could be used to estimate and predict residual coal tar saturation based on a reasonable number of measurable properties. A unique characteristic of this data set is that both paired (coal tar and soil from the same site) and unpaired (one coal tar and four soils) experiments were conducted. For the unpaired data set, both coal tar and soil properties were varied (paired coal tar and soil samples from Site No. 2, 4, 8, 9, 10), while in paired experiments only the soil properties varied (coal tar from Site No. 7, soils from Site No. 3, 6, 7 and 8). The relationship between measured residual coal tar saturations and corresponding values calculated from the best-fit correlation ($r^2 = 0.84$) for the paired data set is shown in Figure 3-15. The unpaired correlation incorporates four parameters; total carbon content (TC) and median grain size (d_{50}) of the soils, and dynamic viscosity (μ) and interfacial tension (IFT) of the coal tars. The relationship between the measured residual coal tar saturations and estimated values from the best-fit correlation ($r^2 = 0.72$) for the unpaired data set is shown in Figure 3-16. The paired correlation incorporates the only two parameters; total carbon content (TC) and median grain size (d_{50}) of the soil.

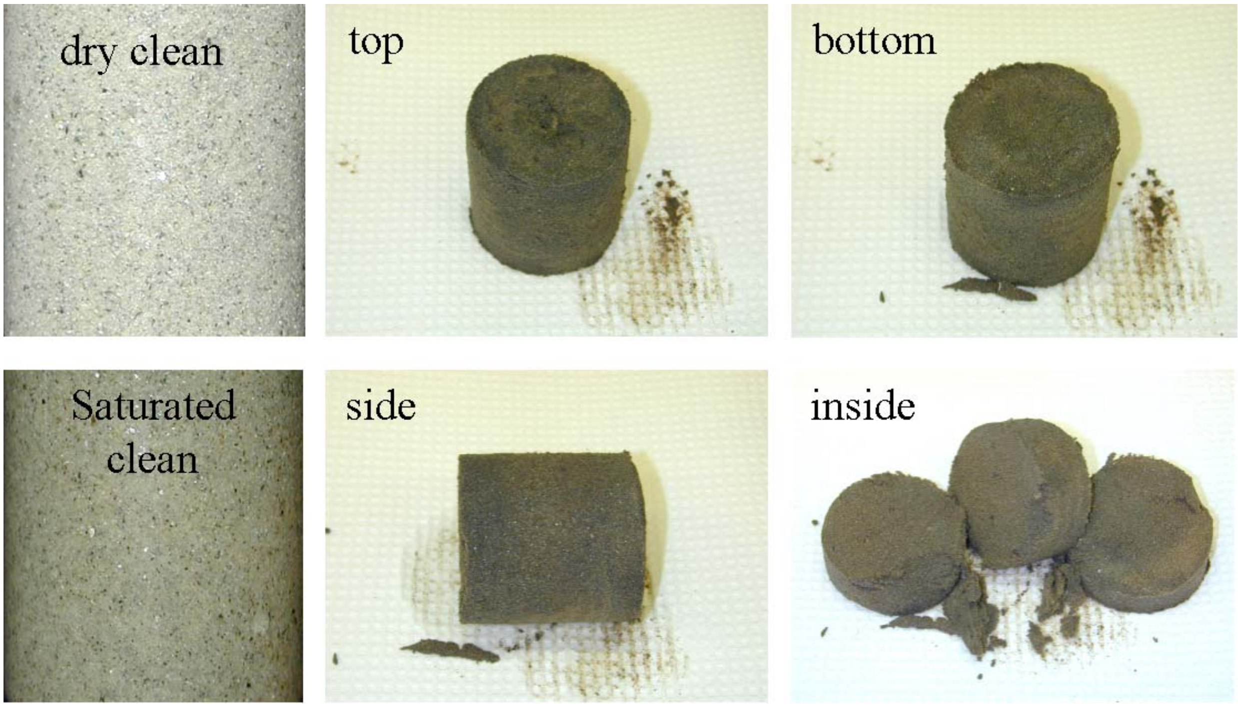

Figure 3-10
Images of Air-Dry and Water-Saturated Soil Sample from Site No. 9 (Clean), and the Extruded Soil Core at Residual Coal Tar Saturation

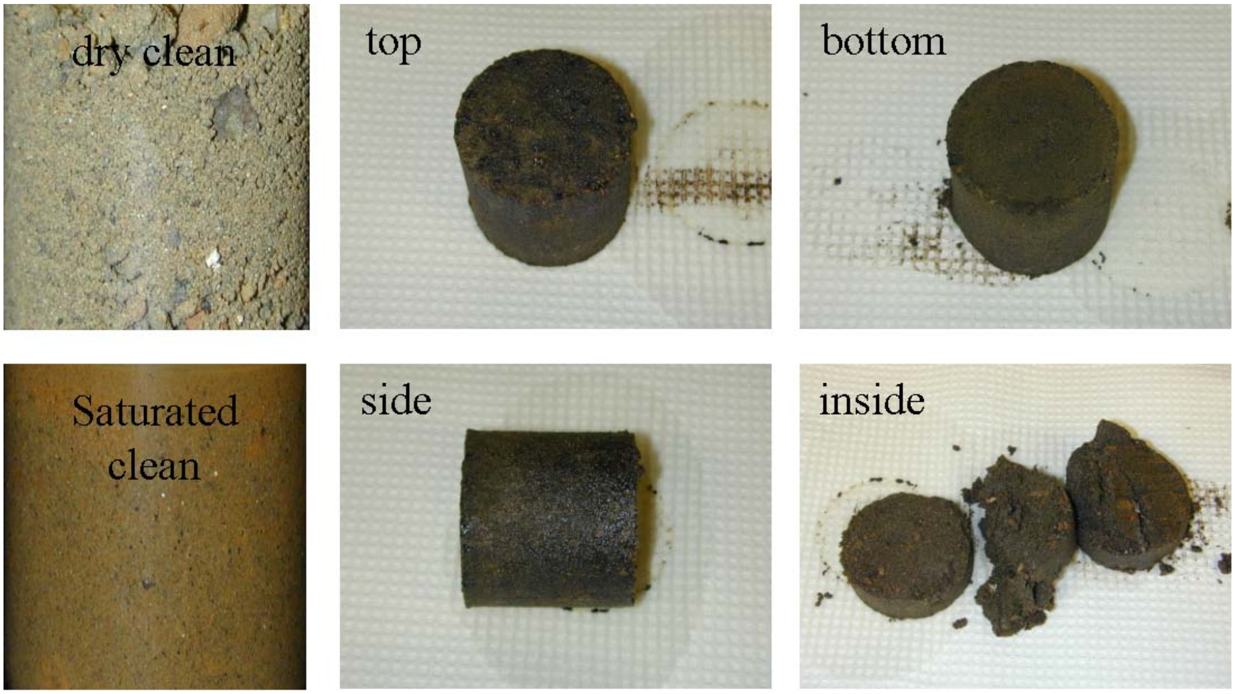

Figure 3-11
Images of Air-Dry and Water-Saturated Soil Sample from Site No. 2 (Clean), and the Extruded Soil Core at Residual Coal Tar Saturation

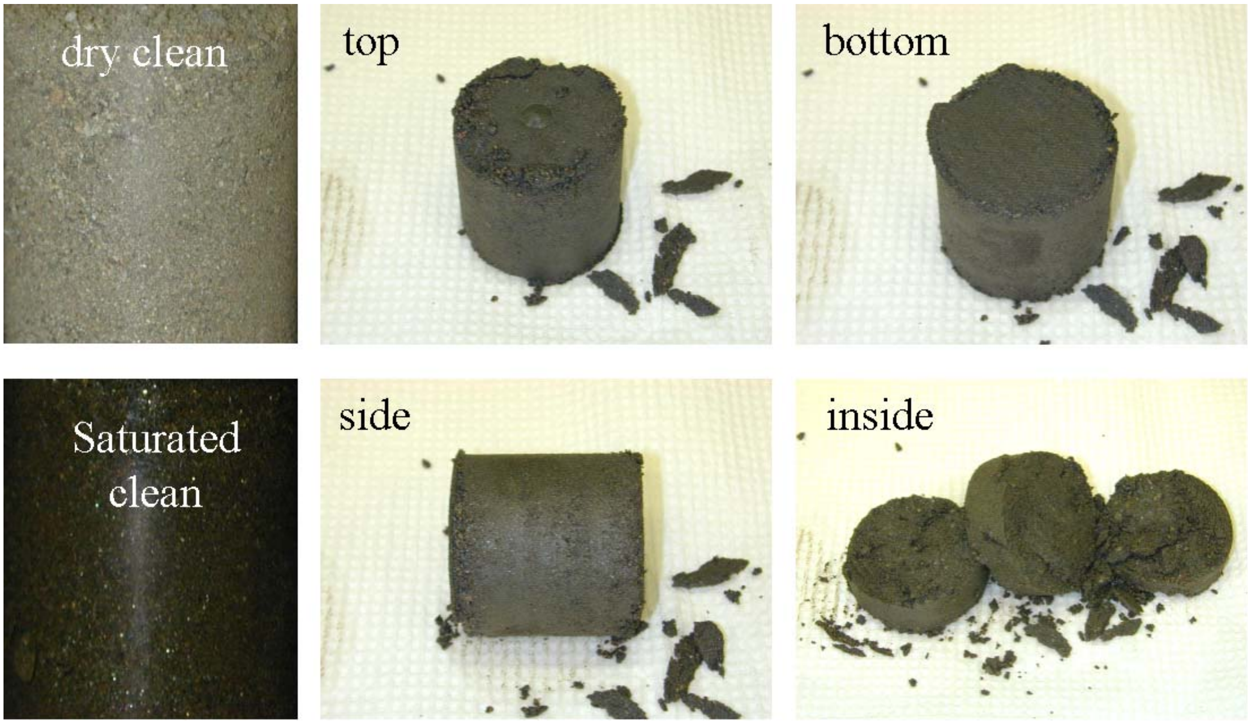

Figure 3-12
Images of Air-Dry and Water-Saturated Soil Sample from Site No. 6 (Clean), and the Extruded Soil Core at Residual Coal Tar Saturation

(Note: Coal Tar from Site No. 7 was used for Residual Saturation Test)

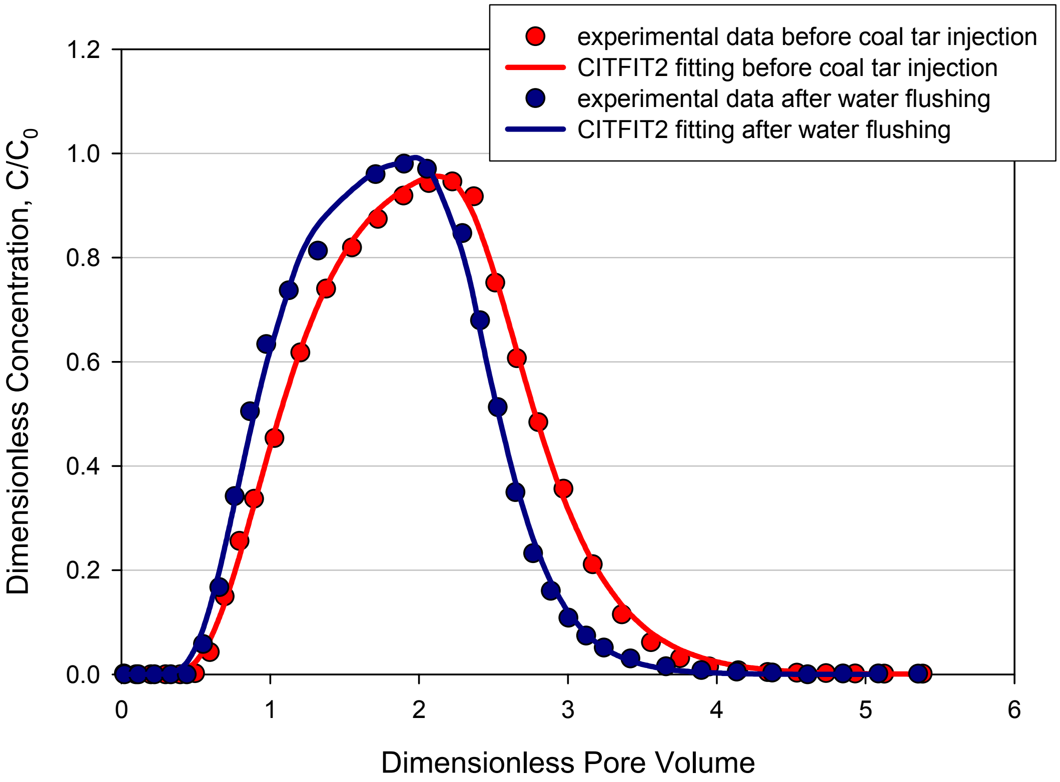

Figure 3-13
Examples of Measured and Fitted Non-Reactive Tracer (KI) Breakthrough Curves Before and After the Establishment of Residual Coal Tar Saturation

Table 3-5
Summary of Coal Tar Residual Saturation Measurements in Two-Phase (Water + Tar) Systems

Site Identifier	Bulk Density (g/cm^3)	Porosity (cm^3/cm^3)	Tar Viscosity (cP)	Water Saturation (S_w)[‡] (cm^3/cm^3)	Residual Tar Saturation (S_{Nr}) (cm^3/cm^3)	Residual Tar Concentration (C_{Nr}) (mg/kg)
1	1.497 (±0.022)	0.420 (±0.008)	63.6 (±0.1)	0.841 (±0.012)	0.159 (±0.012)	48,081 (±2,783)
2[•]	1.400 (±0.171)	0.435 (±0.25)	116.3 (±0.4)[§]	0.774 (±0.028)	0.226 (±0.028)	71,569 (±12,710)
3[†•]	1.928 (±0.020)	0.298 (±0.006)	32.0 (±0.1)	0.841 (±0.012)	0.158 (±0.008)	26,218 (± 470)
4[•]	1.795 (±0.009)	0.343 (±0.001)	144.6 (±0.8)	0.869 (±0.041)	0.131 (±0.042)	26,824 (±8,663)
6[†]	1.526 (±0.011)	0.396 (±0.004)	32.0 (±0.1)	0.818 (±0.012)	0.182 (±0.013)	50,823 (±2,647)
7	1.278 (±0.005)	0.451 (±0.003)	32.0 (±0.1)	0.844 (±0.048)	0.156 (±0.026)	59,389 (±10,124)
8[†]	1.766 (±0.006)	0.342 (±0.001)	32.0 (±0.1)	0.841 (±0.012)	0.122 (±0.014)	25,268 (±2,950)
9[•]	1.628 (±0.113)	0.383 (±0.004)	51.0 (±0.1)	0.808 (±0.024)	0.192 (±0.024)	50,588 (±8,323)
10	1.227 (±0.016)	0.530 (±0.006)	62.9 (±1.4)	0.923 (±0.008)	0.077 (±0.008)	34,732 (±3,778)

[*] Standard deviation (s.d. = $s/\sqrt{n-1}$)

[•] Soil core outsourced on behalf of one company for coal tar dissolution studies.

[†] Residual saturation data for soils from Site No. 3, 6 and 8 were obtained using Site No. 7 coal tar.

[‡] In a two-phase (water + tar) system, the sum of the water saturation and tar saturation must equal unity.

[§] Viscosity of Site No. 2B coal tar measured at 40°C; column was heated to 40°C to allow water to displace coal tar.

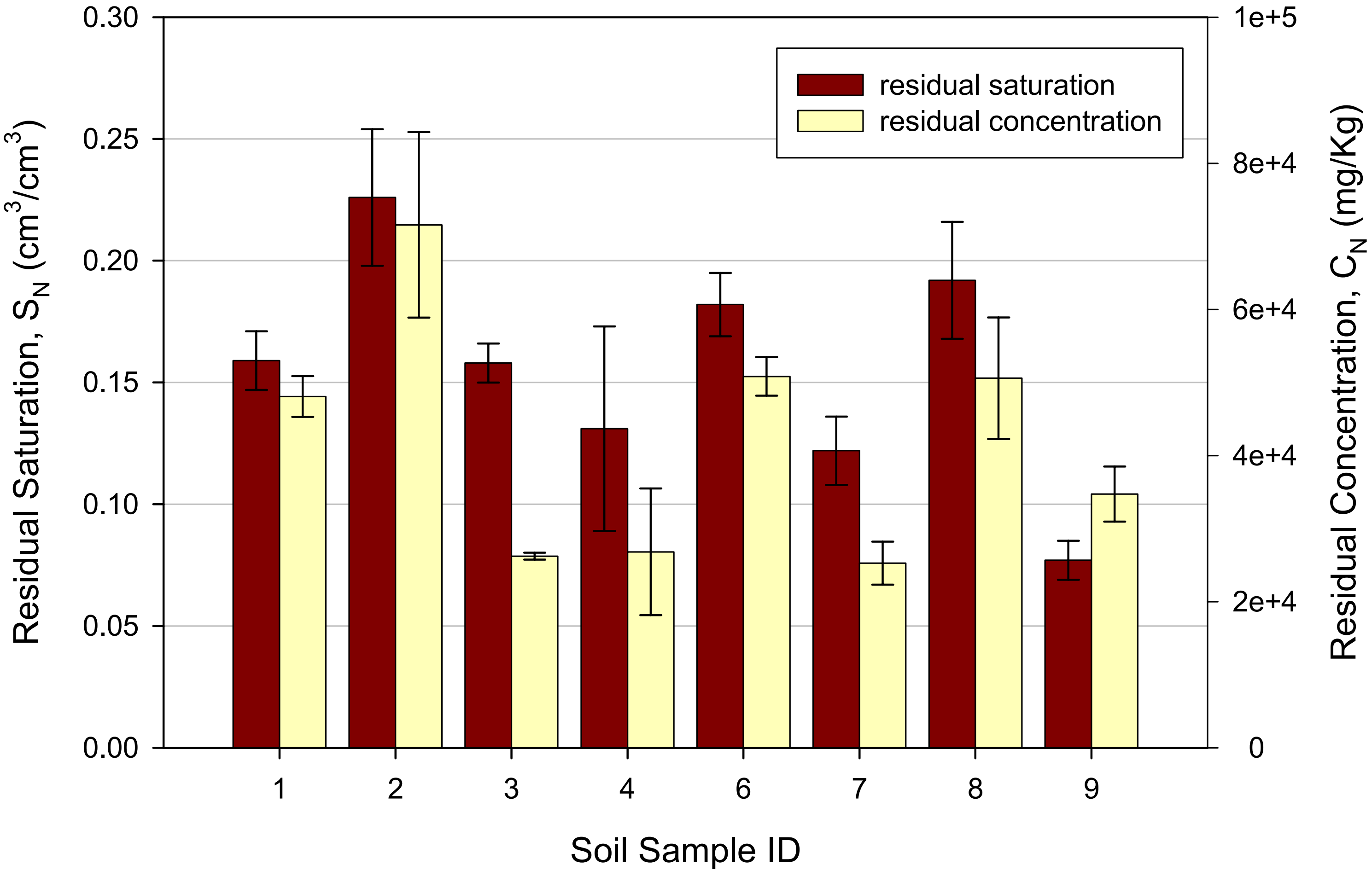

Figure 3-14
Comparison of Coal Tar Residual Saturation (S_{Nr}) and Residual Concentration (C_{Nr}) for Nine MGP Sites

Table 3-6
Properties of Coal Tar Contaminated Soil Cores

Soil Identifier	Bulk Density (g/cm^3)	Porosity (cm^3/cm^3)	Tar Viscosity (cP)	Water Saturation (S_w) (cm^3/cm^3)	Residual Tar Saturation (S_o) (cm^3/cm^3)	Residual Tar Concentration (mg/kg)
2 (core #2)	1.279	0.453	116.3 (±0.4)[§]	0.754	0.246	80,557
3 (core #2)[†]	1.914	0.303	32.0 (±0.1)	0.848	0.152	25,886
4 (core #4)	1.783	0.344	144.6 (±0.8)	0.839	0.161	32,949
7 (core #1)	1.281	0.452	32.0 (±0.1)	0.758	0.242	92,086
8 (core #2)[†]	1.771	0.342	32.0 (±0.1)	0.888	0.112	23,182
9 (core #3)	1.636	0.380	51.0 (±0.1)	0.808	0.175	46,917

[*] Standard deviation (s.d. = $s/\sqrt{n-1}$)

[§] Viscosity of Site No. 2B coal tar at 40°C; column was heated to 40°C to allow water to displace coal tar.

[†] Residual saturation data for Site No. 3 and 8 soil cores obtained using Site No. 7 coal tar.

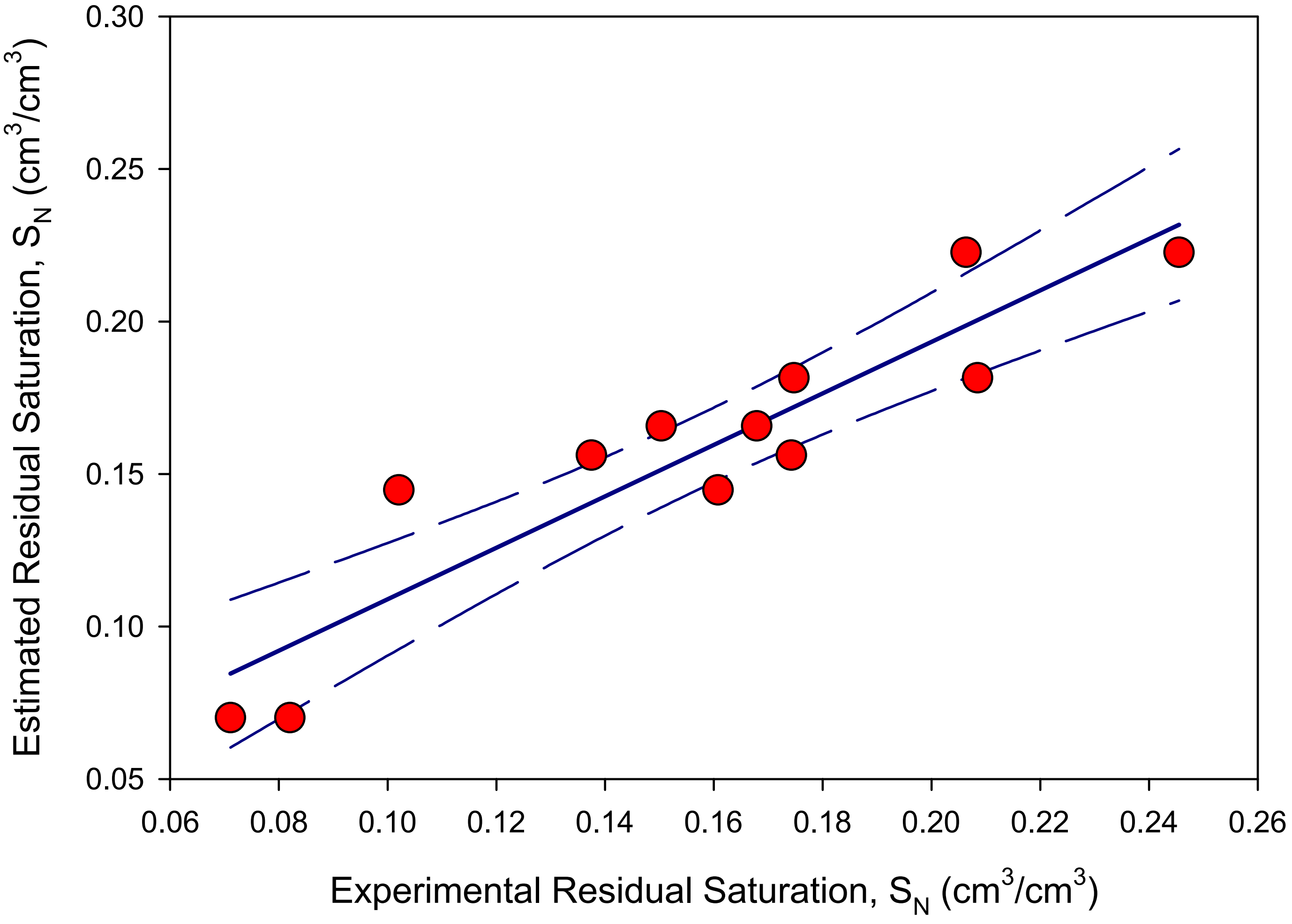

Figure 3-15
Best-Fit Correlation Obtained for Paired Soil and Tar Samples (from Site No. 2, 4, 8, 9, 10), Incorporating Two Soil Properties, Total Carbon (TC) and Median Grain Size (d_{50}), and Two Coal Tar Properties, Interfacial Tension (IFT) and Viscosity

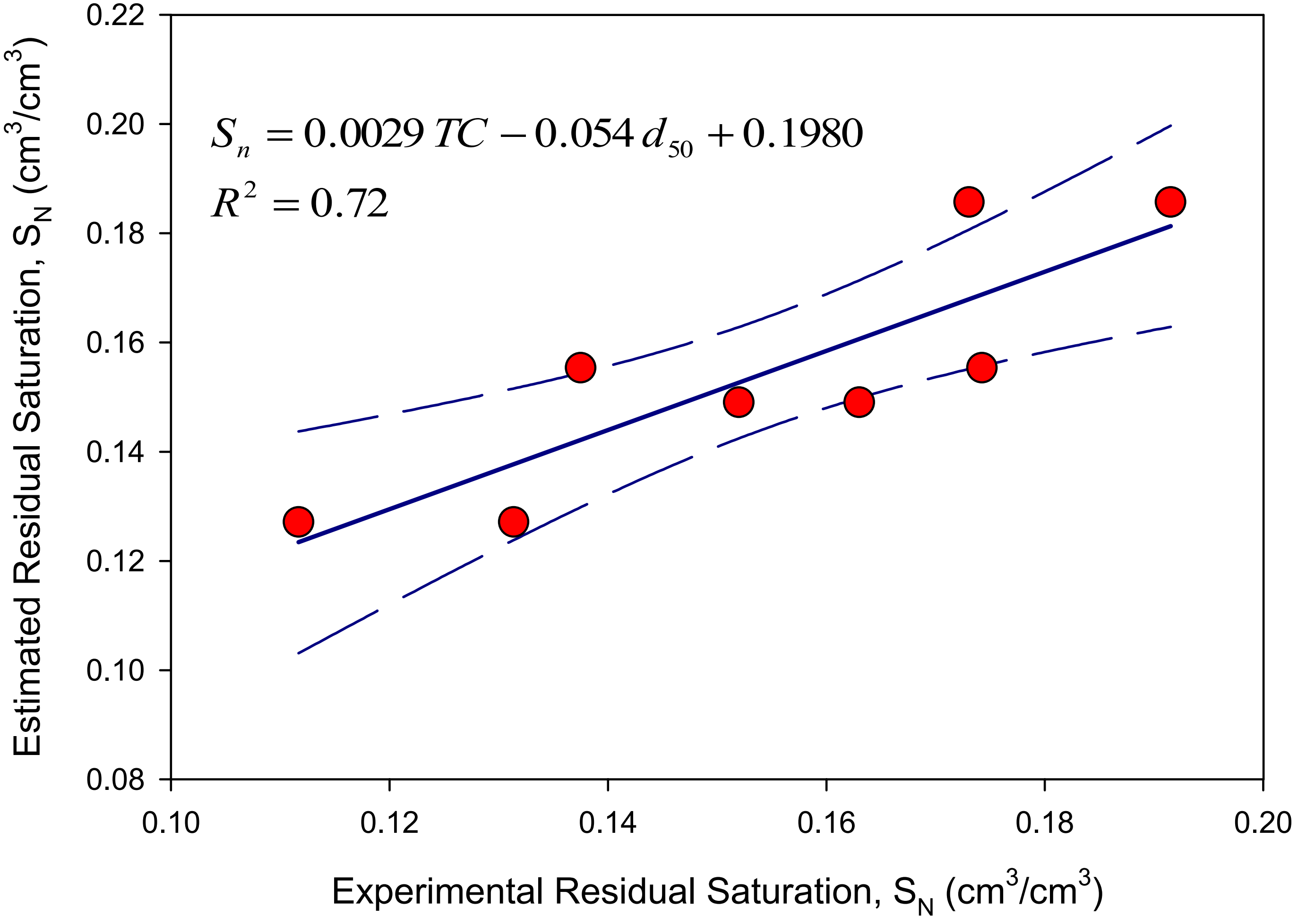

Figure 3-16
Best-Fit Correlation Obtained with Four Soils (from Site No. 3, 6, 7, 8) and a Single Tar Sample (Site No. 7), Incorporating Two Soil Properties, Total Carbon (TC) and Median Grain Size (d_{50})

Table 3-7
Calculated Concentrations (mg/Kg) of Individual MAH and PAH Compounds in Soil Containing Tar at Residual Saturation

Compound	Site 1	Site 2	Site 3	Site 4	Site 6	Site 7	Site 8	Site 9
1, 2, 4-Trimethylbenzene	112	276	156	169	302	353	150	142
Benzene	16	139	136	47	264	308	131	80
Ethylbenzene	17	413	243	83	471	550	234	223
M/p-Xylene	98	441	290	269	562	657	280	200
O-Xylene	51	228	146	147	284	331	141	93
Styrene	63	135	153	226	297	347	148	20
Toluene	73	522	392	286	760	888	378	251
Total MAH (mg/Kg)	431	2153	1517	1227	2940	3435	1462	1009
1-Methylnaphthalene	995	2291	763	820	1480	1729	736	1429
2-Methylnaphthalene	1616	2687	1190	1133	2307	2695	1147	2252
Acenaphthene	149	266	77	56	150	175	74	135
Acenaphthylene	593	1346	335	436	650	760	323	1176
Anthracene	579	731	167	256	324	378	161	489
Benz[a]anthracene	385	509	141	155	273	319	136	258
Benz[b]fluoranthene	167	165	54	59	104	122	52	113
Benz[k]fluoranthene	241	233	58	66	112	131	56	142
Benzo[a]pyrene	235	369	119	106	231	270	115	241
Benzo[g,h,I]perylene	122	141	67	43	130	152	65	113
Chrysene	278	556	135	132	262	306	130	226
Dibenz[a,h]anthracene	33	49	17	14	33	39	17	27
Dibenzofuran	527	146	25	92	48	56	24	121
Fluoranthene	995	741	184	235	356	416	177	511
Fluorene	839	894	189	252	367	428	182	559
Indeno[1,2,3-cd]pyrene	108	113	41	34	79	92	39	90
Naphthalene	3468	4624	1919	1898	3720	4347	1850	4010
Phenanthrene	1932	2446	563	738	1092	1276	543	1599
Pyrene	728	1011	304	295	589	688	293	670
Total PAH (mg/Kg)	13991	19317	6348	6820	12306	14380	6121	14163

4

DISCUSSION

Two-phase (water and coal tar) laboratory studies were completed for nine soils and six coal tars obtained from MGP sites. The resulting residual coal tar saturation values ranged from a low of 7.70 % to a high of 22.6 % on a volumetric basis (volume of coal tar per volume of pore space). The corresponding residual coal tar concentrations ranged from a low of 25,000 mg/kg to a high of 72,000 mg/kg on a weight basis (mass of coal tar per mass of solid). These results establish that a considerable amount of coal tar, on the order of 2.5 to 7.2 % (weight), can be retained in natural soils as residual NAPL. Both soil and coal tar properties were shown to play an important role in determining the residual coal tar saturation. A statistically significant correlation was observed between residual coal tar saturation and two soil properties (total carbon content and median grain size) and two coal tar properties (i.e., interfacial tension and viscosity), as illustrated in Figures 3-15 and 3-16. These statistical equations provide preliminary estimate of the amount of coal tar retained in soils as an immobile NAPL (residual product).

The laboratory studies successfully generated a comprehensive data set that included both paired experiments (six coal tars and soil samples from the same sites) and unpaired experiments (one coal tar and four soil samples). In addition, a reproducible method for measuring residual coal tar saturations in the laboratory was developed, which is based on non-reactive tracer tests conducted before and after the entrapment process. This approach provides for an independent measurement of the aqueous phase pore volume and corresponding volume of coal tar. In addition, the tracer approach also eliminates errors associated with methods that rely upon the measurement of small changes in column weight or measurements of the introduced and effluent coal tar volumes.

A possible extension of this work could be to systematically investigate the effect of temperature, pH, surfactants and/or co-solvents on relevant coal tar properties (e.g., viscosity and interfacial tension), coal tar displacement and recovery of free product, and residual coal tar saturation. Such work would require a combination of batch, column and tank experiments in order to accurately characterize fundamental relationships, and to properly assess remediation potential in a laboratory-scale pilot system.

5
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