Laboratory Assessment of Leaching Potential Coal Tar at MGP Sites

Technical Report

Laboratory Assessment of Leaching Potential of Coal Tar at MGP Sites

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REPORT SUMMARY

Non-aqueous phase liquids (NAPL) are highly immiscible in water, and their presence in the environment continues to spark interest in the regulatory community. When considering NAPL mobility in the subsurface, it is often classified as free product or residual product. Free product or free-phase NAPL exists in the subsurface with a positive pressure such that it can flow into a well. DNAPL will typically flow in this manner until all NAPL is trapped within soil pores by capillary forces. NAPL concentration in soil at which capillary forces overcome gravity and hydraulic forces is called the residual saturation concentration. At concentrations at or below residual saturation, NAPL is immobile and is called residual product. This project focused on a specific NAPL coal tar, which is a byproduct of the manufactured gas process.

Background

Coal tar is dense nonaqueous phase liquid (DNAPL) that is composed of a large number of different monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs). Due to past practices, coal tar is often found in the subsurface at former manufactured gas plants (MGPs). Coal tar in the subsurface, whether above or below residual saturation, can act as a long-term source of groundwater contamination due to dissolution of coal tar constituents into the water. Some practitioners have considered groundwater systems containing coal tar to be in thermodynamic equilibrium, which allows prediction of concentrations in groundwater based solely on thermodynamics. However, many fate and transport processes may prevent these systems from reaching thermodynamic equilibrium. Some important fate and transport processes include advection of groundwater, dissolution of coal tar constituents into groundwater, sorption of constituents onto aquifer solids, and biodegradation of aqueous coal tar constituents by indigenous microorganisms. Rather than being at thermodynamic equilibrium, these systems will typically reach a kinetic equilibrium where the contaminant source rates (for example, dissolution) and loss rates (for example, biodegradation) equilibrate. When these rates are equal, the system is said to be at steady state. At kinetic equilibrium, concentrations of coal tar constituents in groundwater can be significantly lower than those predicted solely by thermodynamics. For this reason, it is important to understand the fate and transport processes when evaluating coal-tar-contaminated sites.

Objectives

To evaluate key fate and transport properties of PAHs and MAHs from MGP sites with coal tar present at concentrations at or below the residual saturation.

Approach

Project teams obtained eleven sets of coal tar and soil (contaminated and uncontaminated) samples from former MGP sites. This study focused on determining representative values for coefficients that are used to model the fate and transport of coal tar constituents in groundwater

systems from these soil and coal tar samples. These coefficients include (1) average coal tar molecular weight, which is required to calculate equilibrium aqueous concentrations based on the Raoult's Law relationship; (2) soil-water partition coefficients, which define the partitioning of constituents between water and soil and strongly influence chemical transport through groundwater systems; and, (3) the mass transfer rate, which defines how quickly coal tar constituents will dissolve into water. Additional parameters include (4) soil physical properties (particle size, water content, specific gravity, and fraction organic carbon); (5) coal tar physical properties (viscosity and specific gravity); and, (6) coal tar and contaminated soil chemical properties (MAH and PAH concentrations).

The teams used subsets of the collected samples to determine these coefficients. Two-phase (coal tar/water) experiments were used to determine coal tar molecular weights from a Raoult's-Law-based technique developed for this study. Three-phase (coal tar/water/soil) experiments were used to determine the aqueous partitioning relationship between coal tar constituents and soil. Relationships between the soil organic carbon partition coefficient (Koc) and the octanol partition coefficient (Kow) were developed. Five column tests were conducted on contaminated soil samples with coal tar present below residual saturation. These column tests were run until steady-state aqueous effluent concentrations were achieved, and bulk mass transfer rates for the BTEX compounds eluting from contaminated soil samples were calculated.

Results

Two-phase test results showed that coal tar molecular weight increases with increasing viscosity. There also is a high correlation between molecular weight and total concentration of one- and two-ring aromatic hydrocarbons. Analysis of experimental data from the three-phase tests showed that sorption of coal tar constituents to soil increases the effective organic carbon content of soil and enhances partitioning of coal tar constituents. This is important for low organic carbon content soils because applying literature Log(Koc)-Log(Kow) relationships without considering the effects of the sorbed hydrocarbon mass on soil organic carbon content may under-predict sorption. Additionally, variation in mass transfer coefficients between samples highlights their site-specificity.

EPRI Perspective

The report provides a new experimental method for determining the average molecular weight of coal tar, based on application of Raoult's law. This method provides a consistent definition of coal tar average molecular weight in line with its intended application. Second, the report finds that predicting partition coefficients with soil organic carbon-based relationships in the literature will under-predict sorption when coal tar is present (relationships are presented to allow calculation of partition coefficients). Finally, mass transfer coefficients are provided for the elution of BTEX compounds from contaminated soil samples, and their large variation between sites highlights their site-specificity and uncertainty. Field-scale studies on mass transfer rates are needed in the future to fully understand *in situ* dissociation of coal tar constituents.

Keywords

Coal tar
Residual saturation
Molecular weight
Partition coefficient
Mass transfer rate

ABSTRACT

Non-aqueous phase liquids (NAPL) are liquids that are highly immiscible in water, and their presence in the environment continues to spark interest in the regulatory community. When considering NAPL mobility in the subsurface, it is often classified as free product or residual product. *Free product* or free-phase NAPL exists in the subsurface with a positive pressure such that it can flow into a well. If they are not trapped into a pool, free-phased NAPLs that are denser than water (DNAPLs) will flow vertically through an aquifer, or laterally down sloping fine-grained stratigraphic units, until all the NAPL is trapped within the soil pores by capillary forces. The NAPL concentration in the soil at which capillary forces overcome gravity and hydraulic forces is called the *residual saturation* concentration. At concentrations at or below residual saturation, the NAPL is immobile and is called *residual product*.

This project focused on a specific NAPL coal tar, which is a byproduct of the manufactured gas process. Coal tar is DNAPL that is composed of a large number of different monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs). Due to past practices, coal tar is often found in the subsurface at former manufactured gas plants (MGPs). Coal tar in the subsurface, whether above or below residual saturation, can act as a long-term source of groundwater contamination due to dissolution of the coal tar constituents into the water.

This research was conducted to evaluate the aqueous phase release and transport of MAHs and PAHs from MGP sites with coal tar present at concentrations at or below the residual saturation. This study focused on determining representative values for coefficients that are used to model the fate and transport of coal tar constituents in groundwater systems from these soil and coal tar samples, including the average coal tar molecular weight, which is required to calculate equilibrium aqueous concentrations based on the Raoult's Law relationship; the mass transfer rate, which defines how quickly coal tar constituents will dissolve into water; and the soil-water partition coefficients, which define the partitioning of constituents between the water and soil, and strongly influence chemical transport through groundwater systems.

Eleven sets of coal tar and soil (contaminated and uncontaminated) samples from former MGP sites were obtained for this study, and subsets of these samples were used to determine the coefficients described above. Two- and three-phase batch equilibrium tests were conducted on coal tar and soil samples from the MGP sites. The two-phase (coal tar/water) experiments were used to determine the coal tar molecular weights from a Raoult's Law-based technique developed for this study. This technique provides an experimental definition of molecular weight consistent with its intended application, and removes interferences that may occur with more commonly used techniques. The results showed that coal tar molecular weight increases with increasing viscosity, and the relationship is well represented by the Mark-Houwink equation. There is also a high correlation between the molecular weight and the total concentration one- and two-ring aromatic hydrocarbons. The three-phase (coal tar/water/soil) experiments were used to determine the aqueous partitioning relationship between coal tar constituents and soil, and relationships between the soil organic carbon partition coefficient (K_{oc}) and the octanol partition coefficient (K_{ow}) were developed. Through analysis of the experimental data, it has been shown that sorption of coal tar constituents to the soil increases the effective organic carbon content of the soil and enhances the partitioning of coal tar constituents. This is an important consideration for low organic carbon content soils, as application of literature $\text{Log}(K_{oc})$-$\text{Log}(K_{ow})$ relationships without consideration of the effects of the sorbed hydrocarbon mass on the soil organic carbon content may under-predict the sorption. Finally, five column tests were conducted on contaminated soil samples with coal tar present below residual saturation. These column tests were run until steady-state aqueous effluent concentrations were achieved, and bulk mass transfer rates for the BTEX compounds eluting from contaminated soil samples were calculated. While the mass transfer coefficients obtained from the disturbed soil samples provided for this study are expected to differ from those observed in the field, they may be thought of as an upper limit for the field values. Additionally, the variation in mass transfer coefficients between samples highlights their site-specificity.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION

1.1 Background

Non-aqueous phase liquids (NAPL) are liquids that are highly immiscible in water, and their presence in the environment continues to spark interest in the regulatory community. When considering NAPL mobility in the subsurface, it is often classified as free product or residual product. *Free product* or free-phase NAPL exists in the subsurface with a positive pressure such that it can flow into a well. If they are not trapped into a pool, free-phased NAPLs that are denser than water (DNAPLs) will flow vertically through an aquifer, or laterally down sloping fine-grained stratigraphic units, until all the NAPL is trapped within the soil pores by capillary forces. The NAPL concentration in the soil at which capillary forces overcome gravity and hydraulic forces is called the *residual saturation* concentration. At concentrations at or below residual saturation, the NAPL is immobile and is called *residual product*.

This project focused on a specific NAPL called coal tar, which is a byproduct of the manufactured gas process. Coal tar is DNAPL that is composed of a large number of different monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs). Due to past practices, coal tar is often found in the subsurface at former manufactured gas plants (MGPs). Coal tar in the subsurface, whether above or below residual saturation, can act as a long-term source of groundwater contamination due to dissolution of the coal tar constituents into the water.

Some practitioners have considered groundwater systems containing coal tar to be in thermodynamic equilibrium, which allows prediction of concentrations in the groundwater based on solely on thermodynamics. However, many fate and transport processes may prevent these systems from reaching thermodynamic equilibrium. Some important fate and transport processes include advection of the groundwater, dissolution of the coal tar constituents into the groundwater, sorption of the constituents onto aquifer solids, and biodegradation of aqueous coal tar constituents by indigenous microorganisms. Rather than being at thermodynamic equilibrium, these systems will typically reach a kinetic equilibrium, where the contaminant source rates (e.g. dissolution) and loss rates (e.g., biodegradation) equilibrate. When these rates are equal, the system is said to be at steady-state. This is the key difference between thermodynamic equilibrium and kinetic equilibrium. At kinetic equilibrium, the concentrations of the coal tar constituents in the groundwater can be significantly lower than those predicted solely by thermodynamics. For this reason, it is important to understand the fate and transport processes when evaluating coal tar-contaminated sites.

MAHs and PAHs are sparingly soluble in water, and as such, their fate and transport in groundwater is a strong function of their dissolution rate from the coal tar into the water and their interactions with the aquifer solids. The fate and transport of coal tar constituents in the subsurface can be modeled via the advection-dispersion equation, which is a differential equation in space and time that accounts for travel of dissolved contaminant with the flowing groundwater (advection) and mixing of the groundwater due to the tortuous flow paths through porous media (dispersion). For the simple case of one-dimensional (1D) transport in the x-direction, the advection-dispersion equation can be written as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + \text{sources} - \text{sinks} \qquad \textbf{Eq. 1-1}$$

where C is the aqueous concentration of the chemical of concern (mass/volume); D_x is the dispersion coefficient (length^2/time); v_x is the groundwater velocity (length/time); and t is time. The source/sink terms are placeholders for including additional processes such as sorption, dissolution, biodegradation, etc.

A key fate and transport process that governs the transport of MAHs and PAHs in the subsurface is sorption. Sorption is the process of an aqueous contaminant either adsorbing or absorbing onto a solid particle. *Adsorption* occurs when a contaminant adheres to the surface of the solid, whereas *absorption* occurs when the contaminant penetrates into the interior of the solid. From a practical standpoint, these processes cannot be readily distinguished, and are typically lumped together as sorption. In its simplest form, sorption is often quantified as the ratio of the aqueous contaminant concentration (C) to the sorbed contaminant concentration (S) under equilibrium:

$$K_d = \frac{S}{C} \qquad \textbf{Eq. 1-2}$$

With this relationship, K_d is called the *linear partition coefficient*. When C is in units of mg/L and S_c in units of mg per kg of soil, k_d has units of L/kg. When considering contaminant transport through groundwater and sorption to aquifer solids, the 1D advection-dispersion equation can be written as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{\rho_b}{\theta}\frac{\partial S}{\partial t} \qquad \textbf{Eq. 1-3}$$

where ρ_b is the bulk density of the soil (mass/volume) and θ is the soil porosity. Substituting Equation 1-2 into Equation 1-1 results in the standard form of the advection-dispersion equation with equilibrium sorption

$$\left(1 + \frac{\rho_b}{\theta} K_d\right)\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \textbf{Eq. 1-4}$$

The term in parentheses is called the *retardation coefficient*, R. If we consider a scaled time, t_R = t/R, then Equation 1-4 can be written as

$$\frac{\partial C}{\partial t_R} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \textbf{Eq. 1-5}$$

In this manner, it is seen that sorption retards the migration of the contaminant, resulting in the apparent velocity of the contaminant being slower than that of the groundwater. For example, if groundwater contains a contaminant that has a retardation coefficient of 50, and the groundwater travels 100 meters in one year, the contaminant will have traveled only two meters during that year. This is a very important process for contaminant transport, as contaminants with large partition coefficients will travel very slowly through groundwater, while those with small partition coefficients are more mobile.

When a sparingly soluble NAPL, such as coal tar, is in contact with groundwater, the NAPL will slowly dissolve into the water. This dissolution process is typically modeled using a mass transfer relationship:

$$\left.\frac{\partial C}{\partial t}\right|_{\text{dissolution}} = -\frac{\rho_b}{\theta}\frac{\partial C^N}{\partial t} = k_{La}\left(C^{eq} - C\right) \qquad \textbf{Eq. 1-6}$$

where C^N is the concentration of NAPL in the subsurface (e.g., mg/kg soil); k_{La} is the mass transfer coefficient (time^{-1}); and C^{eq} is the equilibrium concentration of the contaminant. As written here, the mass transfer coefficient is a function of many variables, including the interfacial area between the coal tar and water; the presence of any films on the coal tar surface, such as a biofilm layer or interfacial skin (Luthy et al., 1993); the chemical composition of the coal tar, which affects the diffusion of individual constituents within the coal tar; and the structure of the porous media, which controls the flow of water past the coal tar interface and affects the diffusion of dissolved components at the interface into the bulk water. Because of these effects, mass transfer coefficients are highly site-specific, and can vary spatially over a site due to changes in subsurface conditions.

When the NAPL consists of a single component, such as with TCE, then C^{eq} is equal to the aqueous solubility of the pure component, C_s. However, when the NAPL is a mixture of chemicals, such as with coal tar, then C^{eq} is not equal to the aqueous solubility, but rather the Raoult's law effective solubility. Raoult's law is used to relate the concentration of a compound within a NAPL mixture to its aqueous concentration at equilibrium with the NAPL mixture (Peters and Luthy 1993; Peters, Knightes, and Brown 1999; Brown, Knightes, and Peters 1999):

$$C^{eq} = \chi \frac{C_s}{FR} \qquad \textbf{Eq. 1-7}$$

Here, C^{eq} is the effective aqueous solubility of the compound of interest in equilibrium with the NAPL; χ is the mole fraction of the compound within the NAPL (moles of compound per mole NAPL); and FR is the solid/liquid reference fugacity ratio for the compound, which is readily available in the literature for many chemicals (Mackay, Shiu, and Ma 1992). The overall result is that the effective aqueous solubility of a compound in equilibrium with a complex mixture is lower than its pure compound aqueous solubility.

The mole fraction of a compound within the coal tar can be calculated from the following equation

$$\chi = \frac{MW_{ct}}{MW} C_{ct} \qquad \textbf{Eq. 1-8}$$

where C_{ct} is the concentration of the compound of interest in the coal tar (g/g coal tar), MW_{ct} is the average molecular weight of the coal tar, and MW is the molecular weight of the compound of interest. Incorporation of Equation's 1-6 to 1-8 into the one-dimensional advection-dispersion equation with sorption gives

$$\left(1 + \frac{\rho_b}{\theta} k_d\right) \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + k_{La}\left(\frac{MW_{ct}}{MW} \frac{C_s}{FR} C_{ct} - C\right) \qquad \textbf{Eq. 1-9}$$

Three key terms in this equation are the partition coefficient (k_d), mass transfer rate (k_{La}) and coal tar average molecular weight (MW_{ct}). The first two terms are specific for each compound within the coal tar (e.g., benzene, naphthalene, phenanthrene, etc.), while the latter term is a bulk term for the coal tar itself. Thus, Equation 1-9 would be applied individually for each compound of interest in the coal tar, and all the equations would be tied together through the terms MW_{ct} and C_{ct}, which will change as compounds dissolve from the coal tar into the flowing water. The changing MW_{ct} and C_{ct} over time is an important consideration, because as they change, the mass transfer rate for the compound will decrease or increase correspondingly.

It is important to note that systems can be significantly more complex that that described by Equation 1-9. For example, biodegradation of the various coal tar constituents may be occurring, which is often modeled using either Monod kinetics or a first-order degradation kinetics. Also, desorption of strongly sorbed coal tar constituents from the soil may be rate limited, resulting in a mass transfer-limited desorption for a fraction of the sorbed constituents. This combination of equilibrium and rate-limited sorption is often modeled using a two-site sorption model (Brown, Guha and Jaffé, 1999). Finally, with coal tar-contaminated soil, it is difficult to differentiate between mass transfer of the components from the coal tar and mass transfer from the components strongly sorbed to the soil, and as such, a lumped mass transfer term is often used.

1.2 Objectives

Previous Electric Power Research Institute (EPRI) reports aimed to develop information and predictive tools to estimate the release potential of PAHs (EPRI, 1996; EPRI, 1998). These previous reports focused on estimating the maximum release concentration of PAHs from MGP soils that were contaminated by direct contact with coal tar or through year of contact with contaminated groundwater. In addition, laboratory procedures were developed to estimate release of MAHs and PAHs from coal tars and contaminated soils at MGP sites.

The objectives of this research were to evaluate key fate and transport properties of PAHs and MAHs from MGP sites with coal tar present at saturations at or below the residual saturation. This study focused on determining representative values for coefficients that are used to model the fate and transport of coal tar constituents in groundwater systems from these soil and coal tar samples. These coefficients include:

1. The average coal tar molecular weight, which is required to calculate equilibrium aqueous concentrations based on the Raoult's Law relationship;

2. The mass transfer rate, which defines how quickly coal tar constituents will dissolve into water; and

3. The soil-water partition coefficients, which define the partitioning of constituents between the water and soil, and strongly influence chemical transport through groundwater systems.

Additional parameters determined in this study include:

4. The soil physical properties (particle size, water content, specific gravity, and fraction organic carbon);

5. The coal tar physical properties (viscosity and specific gravity); and

6. The coal tar and contaminated soil chemical properties (MAH and PAH concentrations).

1.3 Approach

Eleven sets of coal tar and soil (contaminated and uncontaminated) samples from former MGP sites were obtained for this study, and subsets of these samples were used to determine the coefficients described above. Chemical properties of the contaminated soil and coal tar samples were determined by META Environmental, Inc. All other laboratory tests were conducted by Lehigh University. Two-phase (coal tar/water) and three-phase (coal tar/water/soil) batch tests were conducted to determine the coal tar average molecular weight and equilibrium distribution of contaminants between soil and water. Column tests were conducted on the contaminated soil samples to determine the mass transfer coefficients.

Two research teams worked on this project. The principal investigators were Dr. Horace Moo-Young and Dr. Derick Brown of Lehigh University (LU). The residual saturation values of the coal tars were determined at Georgia Institute of Technology. The soil analysis, batch and column tests of the MGP site samples were performed at LU, and the results are summarized in this report. Figure 1-1 illustrates the laboratory protocols utilized in this study.

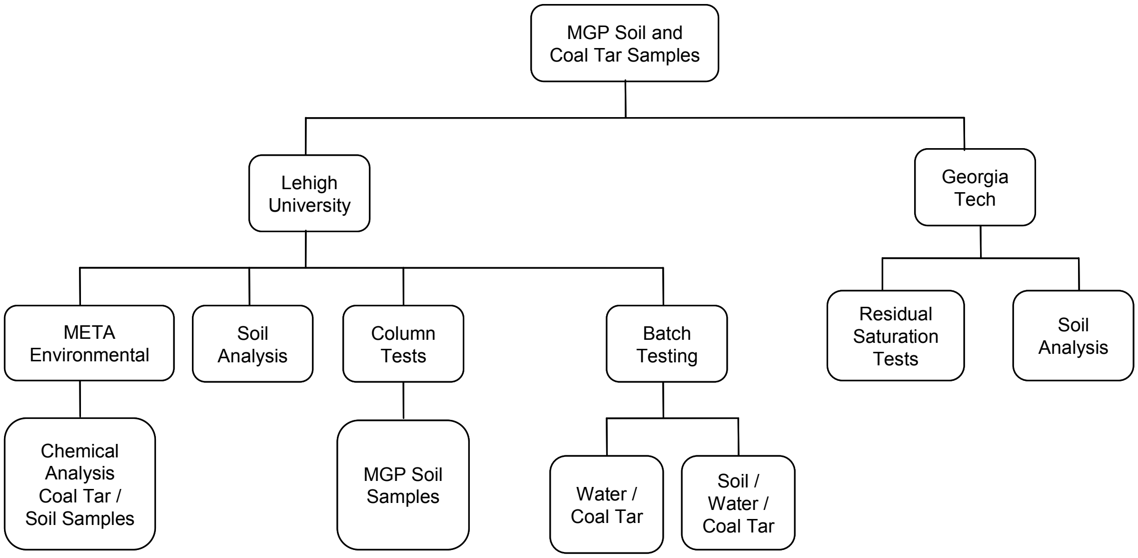


Figure 1-1
Laboratory Protocol

2
METHODS AND MATERIALS

2.1 Introduction

Participating MGP sites were requested to provide the researchers with a 1-gallon sample of coal tar from the site and uncontaminated soil and contaminated samples that are representative of the site. A contaminated sample was defined as a soil containing MGP residuals (tar-like-material, oil-like-material, black staining, malodorous). An uncontaminated soil sample was one defined as "clean" and free of any MGP residuals. Table 2-1 shows the list of samples received by Lehigh University from MGP sites. Large particles of gravel, wood branches, and brick pieces were removed from all samples. In addition, each soil sample was homogenized by mixing in a stainless steel bowl. After homogenization, all these samples were sealed in a jar, and stored at 4°C.

Lehigh University conducted the following tests: 1) soil properties analysis on each uncontaminated soil sample, 2) long term leaching tests on contaminated soil samples, and 3) batch tests on uncontaminated soils and coal tar samples. In addition, for chemical analysis, 20-ml of coal tar and 200-g of contaminated soil samples were sent to META Environmental, Inc., Watertown, MA., for chemical analysis.

Table 2-1
Samples Received from MGP Sites

MGP Site	Uncontaminated Soils	Contaminated Soils	Coal Tar
1	×	×	×
2	×	×	×
3	×	×	×
4	×	×	** × (2)
5	* ×	×	×
6	×	×	×
7		×	×
8	×	×	×
9	×	** × (2)	×
10	×	×	×
11	×	×	** × (2)

* Contains a small amount of coal tar

** Two different type samples

2.2 Soils and Coal Tars

2.2.1 Soil Analysis

Soil properties including particle size, specific gravity, water content, and organic content were analyzed using American Society for Testing and Materials (ASTM) methods. Table 2-2 is summary of the test methods for this analysis. ASTM D421 and D422 were used to determine the grain size distribution curves of soils. The water content was determined by ASTM 2216, and the organic content was determined by ASTM D 2974. ASTM D 854 was used for determination the specific gravity. These tests were conducted in duplicate. Soil particles having larger than 4.75-mm were excluded in water content, organic content and specific gravity tests.

Table 2-2
Test Methods for Analyzing Soil Properties

Parameter	Methods
Grain Size Analysis	ASTM D421, D422
Water Content	ASTM D2216
Organic Content	ASTM D2974
Specific Gravity	ASTM D854
Soil Classification	ASTM D 2478

2.2.2 Viscosity of Coal Tar

The viscosity of the coal tar samples was measured at various temperatures using a rotary viscometer (Model MV 2000 manufactured by Cannon Instrument Company). This device was calibrated by measuring the viscosity of a known standard (Cannon certified viscosity standard: RT12500) at a known temperature. The measured value for viscosity was compared with the known value to produce a correction constant, expressed as a ratio of the actual to measured value. The constant was used as multiplier for measured values of other samples.

2.3 Chemical Analysis

The contaminated soil and coal tar samples were analyzed by META Environmental, Inc., Watertown, MA. Samples were prepared by solvent extraction using dichloromethane (DCM) following Environmental Protection Agency (EAP) method 3570 (for contaminated soils) and EPA method 3580 (for coal tar), respectively. A portion of each extract of contaminated soils and coal tars was exchanged to pentane and fractionated on a silica gel column (EPA method 3650). The extracts and fractions were spiked with internal standard and analyzed by Gas Chromatography (GC)/Flame Ionization Detection (FID) and Gas Chromatography with Mass Spectrometry in Selected Ion Monitoring (GC/MS/SIM). A second aliquot of the soil samples were prepared by solvent extraction using DCM (EPA method 3570) and analyzed gravimetrically for Total Extractable Hydrocarbons (TEH) (MET method 7002). The purpose of conducting the chemical analysis is to determine the MAH and PAH constituent concentrations in the coal tar and contaminated soil samples. This provides the background concentrations in the sample. Table 2-3 provides a summary of chemical properties of common coal tar constituents, including the chemical formula, molecular weight, solubility, log octanol-water partitioning coefficient (Log K_{ow}), and the solid-liquid reference fugacity ratio.

Table 2-3
Physical-Chemical Properties of MAHs and PAHs

Compound	Chemical Formula	Molecular Weight	Aqueous Solubility (mg/L)[a,b]	Log(K_{ow})[a,c]	Fugacity Ratio[a,b]
Benzene	C_6H_5	78	1780	2.13	1
Toluene	$C_6H_5CH_3$	92	515[c]	2.73	1[c]
Ethylbenzene	$C_6H_5C_2H_5$	106	153[c]	3.15	1[c]
o-Xylene	$C_6H_4(CH_3)_2$	106	130[c]	3.12	1[c]
Naphthalene	$C_{10}H_8$	128	31	3.30	0.31
2-methylnaphthalene	$C_{11}H_{10}$	142	25	3.86	0.86
1-methylnaphthalene	$C_{11}H_{10}$	142	28	3.87	1
Acenaphthylene	$C_{12}H_8$	152	3.9	3.74	0.22
Acenaphthene	$C_{12}H_{10}$	154	3.8	3.92	0.20
Fluorene	$C_{13}H_{10}$	166	1.9	4.18	0.16
Anthracene	$C_{14}H_{10}$	178	0.05	4.45	0.01
Phenanthrene	$C_{14}H_{10}$	178	1.1	4.46	0.28
Fluoranthene	$C_{16}H_{10}$	202	0.26	4.90	0.21
Pyrene	$C_{16}H_{10}$	202	0.13	4.88	0.11
Benz(a)Anthracene	$C_{18}H_{12}$	228	0.011	5.61	0.04
Chrysene	$C_{18}H_{12}$	228	0.002	5.61	0.01
Benzo(b)Fluoranthene	$C_{20}H_{12}$	252	0.0015	6.57	0.039
Benzo(k)Fluoranthene	$C_{20}H_{12}$	252	0.008	6.84	0.013
Benzo(a)Pyrene	$C_{20}H_{12}$	252	0.004	5.97	0.030
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278	0.005	6.5	0.004
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276	0.003	7.23	0.003
Ideno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276	0.062	7.66	0.045

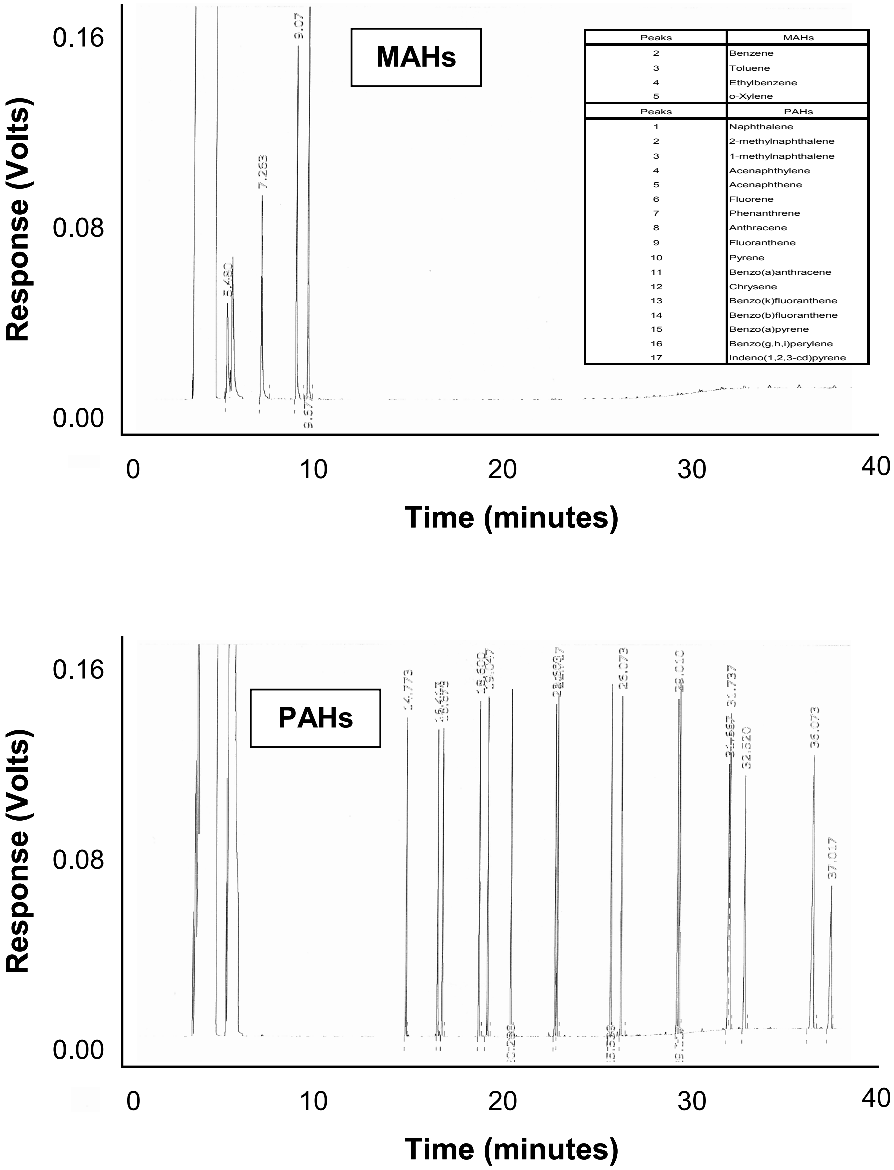
a. All data at 25°C

b. Brown, Knightes and Peters (1999), unless otherwise specified

c. Mackay Shiu and Ma (1992)

Water Samples obtained from the batch and column experiments described below were analyzed at Lehigh University for MAHs and PAHs. Samples were prepared by solvent extraction using a technique based on META Environmental, Inc. method MET2005. This extraction procedure is described in detail in Appendix A. The extracts were analyzed by Gas Chromatography (GC)/Flame Ionization Detector (FID). The GC column was a fused silica capillary column having 30m x 0.32mm with a 0.5mm film thickness. This column was chemically bonded 5% phenyl methyl polysiloxane (DB-5). The detailed test procedures are described in Appendix A.

Figure 2-1 shows a GC/FID chromatogram of a calibration standard combining MAHs and PAHs. Figure 2-2 presents a chromatogram obtained from a batch test, showing the large number of compounds present in coal tar contaminated water. Figures 2-1 and 2-2 represent the retention time of the various hydrocarbon compounds, and the area of the respective compounds.



Peaks	MAHs
2	Benzene
3	Toluene
4	Ethylbenzene
5	o-Xylene
Peaks	**PAHs**
1	Naphthalene
2	2-methylnaphthalene
3	1-methylnaphthalene
4	Acenaphthylene
5	Acenaphthene
6	Fluorene
7	Phenanthrene
8	Anthracene
9	Fluoranthene
10	Pyrene
11	Benzo(a)anthracene
12	Chrysene
13	Benzo(k)fluoranthene
14	Benzo(b)fluoranthene
15	Benzo(a)pyrene
16	Benzo(g,h,i)perylene
17	Indeno(1,2,3-cd)pyrene

Figure 2-1
Chromatogram of Calibration Standard of MAHs and PAHs Analyzed by GC/FID

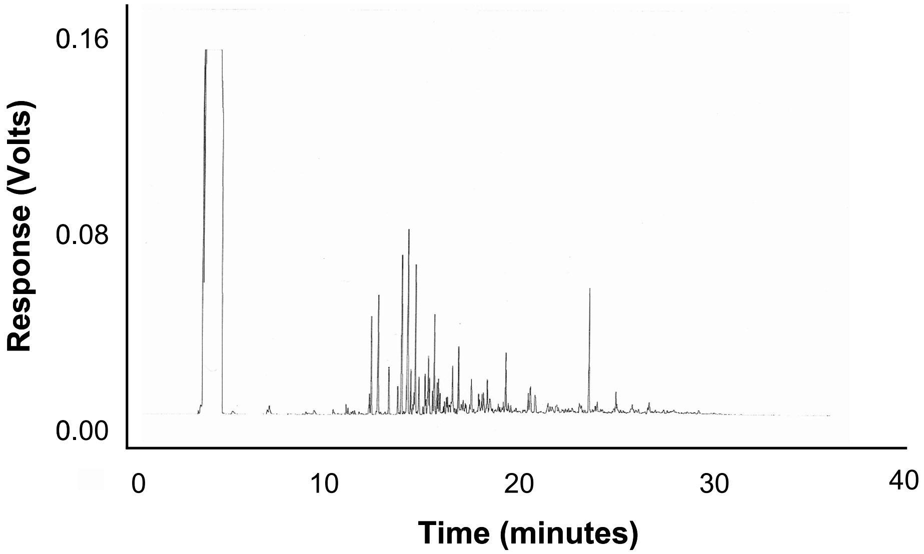


Figure 2-2
Example Chromatogram of MAHs and PAHs Obtained from Batch Test for Site 1

2.4 Batch Experiments

Batch experiments were conducted to determine (a) coal tar average molecular weight (two-phase coal tar/water experiments), and (b) sorption of the coal tar constituents to soil (three-phase coal tar/soil/water experiments). The procedures for each of these experiments are outlined below.

2.4.1 Numerical Analysis of Molecular Weight

The coal tar average molecular weight is commonly determined through a technique called Vapor Pressure Osmometry (VPO). The VPO technique examines the partitioning of a solvent into a droplet of the sample being analyzed, and determines the change in temperature of the droplet during this process. This process was developed for determining the average molecular weight of polymer mixes, and is often applied to coal tars and asphaltenes due to its simplicity. However, a key interference with this technique is the presence of additional solvents in the sample (Glover, 1975). As coal tar contains many solvents, such as benzene, toluene, ethyl-benzene and xylene, the VPO technique may provide erroneous results when applied to coal tars. In addition, while coal tar molecular weights have only been reported with the VPO technique, there is an ongoing disagreement over determination of average molecular weight of asphaletenes, with reported molecular weights spanning over an order of magnitude, depending on the experimental technique employed (Buch et al., 2003; Eser et al., 2003; Groenzin and Mullins, 2003, 2000; Stubington et al., 1995).

For this study, the coal tar average molecular weight was determined with coal tar/water partitioning data through application of Raoult's law. This provides an experimental definition of molecular weight consistent with its intended application, and removes interferences that may occur with more commonly used techniques, such as vapor pressure osmometry. For a system where coal tar is in contact with water, Raoult's law can be used to relate the aqueous concentration of compound *i* at equilibrium to its mole fraction in the coal tar.

$$C^i_{aq} = \frac{\chi_i}{FR_i} C^i_s$$ **Eq. 2-1**

where:

χ_i = mole fraction of the compound i in the coal tar;

FR_i = solid/liquid reference fugacity ratio of compound *i* in coal tar;

C^i_s = aqueous solubility of pure compound *i*; and

C^i_{aq} = Concentration of compound *i* in aqueous phase.

The mole fraction of compound *i* in the coal tar can be calculated through the equation

$$\chi_i = \frac{C^i_{ct} MW_{ct}}{MW_i}$$ **Eq. 2-2**

where:

C^i_{ct} = concentration of compound *i* in coal tar;

MW_{ct} = average molecular weight of the coal tar

MW_i = molecular weight of compound *i* in coal tar

Substitution of Equation 2-1 into Equation 2-2 gives the relationship.

$$C^i_{aq} = \frac{C^i_s}{FR_i} \cdot \frac{MW_{ct}}{MW_i} C^i_{ct} = G_i MW_{ct}$$ **Eq. 2-3**

where:

$$G_i = \left[\frac{C^i_s}{FR_i} \cdot \frac{C^i_{ct}}{MW_i} \right]$$ **Eq. 2-4**

In this form, Equation's 2-3 and 2-4 assume that C^i_{ct}, which is obtained from the known coal tar chemical analysis, does not change appreciably upon equilibration with water. This assumption can be removed by accounting for the coal tar mass and composition changes via the following equation:

$$C_{ct}^{i} = \frac{\left[C_{ct}^{i} m_{ct}\right]_{t=0} - V_{aq} C_{aq}^{i}}{\left[m_{ct}\right]_{t=0} - V_{aq} \sum_{i} C_{aq}^{i}} \qquad \textbf{Eq. 2-5}$$

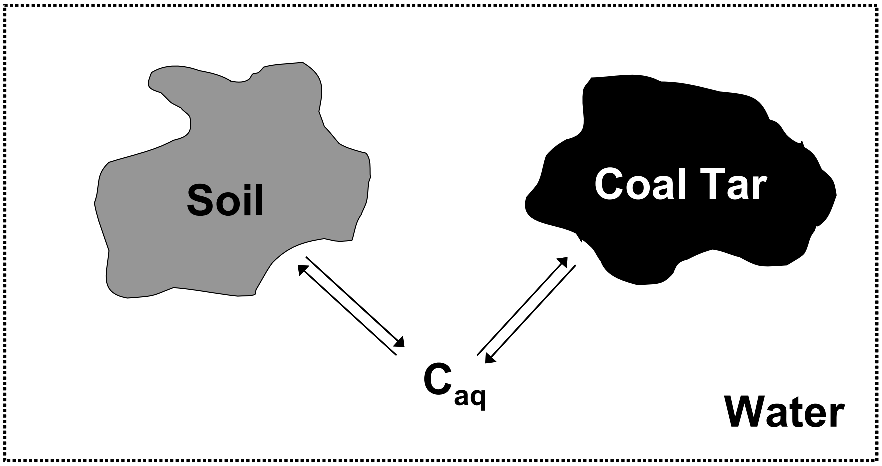


Figure 2-3
Three-Phase Coal Tar/Soil/Water System for Determination of Soil-Water Partition Coefficient with Free-Phase Coal Tar Present

where

$\left[C_{ct}^{i} m_{ct}\right]_{t=0}$ = Initial mass of compound i in the coal tar;

$\left[m_{ct}\right]_{t=0}$ = Initial mass of coal tar; and

V_{aq} = volume of water in the system.

In Equation 2-5, the numerator is the mass of compound i in the coal tar after equilibrium and the denominator is an estimate of the mass of the coal tar after equilibrium, adjusted by the mass of measured constituents in the water that have dissolved from the coal tar.

Assuming the coal tar molecular weight does not significantly change upon equilibrium with water, a plot of C_{aq}^{i} versus G_i for each coal tar should yield a straight line, with the slope being equal to the average molecular weight of the coal tar (this assumption can be qualified through application of Equation 2-5). The only unknown in this system is the coal tar average molecular weight. Given C_{aq}^{i} from the batch equilibrium experiments and C_{ct}^{i} from the coal tar chemical analysis, the molecular weight of each coal tar can be determined through application of Equation’s 2-3 to 2-5.

2.4.2 Numerical Analysis of Partition Coefficient

Prior EPRI studies have developed partitioning relationships between aqueous coal tar constituents and soil for two-phase systems (soil and water) (EPRI, 1996; EPRI 1998; EPRI 1999). The purpose of this experiment was to determine these relationships for a system where the constituents are present in three phases – coal tar, soil, and water. The system being considered is shown in Figure 2-3, where the aqueous chemical concentration of compound i (C^i_{aq}) is in equilibrium with both the coal tar and soil phases. A mass balance on each coal tar constituent provides the following equation

$$m^i_{tot} = V_{aq}C^i_{aq} + m_{soil}C^i_{soil} + m_{ct}C^i_{ct} \qquad \textbf{Eq. 2-6}$$

where

m^i_{tot} = total mass of compound i in the system;

m_{soil} = mass of soil in the system

C^i_{soil} = concentration of compound i sorbed to the soil (mass i/mass soil)

m_{ct} = mass of coal tar in the system

This equation can be written in terms of the aqueous concentration of compound i. First, Equation 2-3 can be rearranged to give

$$C^i_{ct} = \frac{FR_i}{C^i_s}\frac{MW_i}{MW_{ct}}C^i_{aq} \qquad \textbf{Eq. 2-7}$$

Next, assuming equilibrium partitioning between compound i and the soil, the concentration of compound i sorbed to the soil can be written as

$$C^i_{soil} = K^i_d C^i_{aq} \qquad \textbf{Eq. 2-8}$$

where k^i_d is the linear partition coefficient for compound i and the soil being examined. Substitution of Equation’s 2-7 and 2-8 into Equation 2-6 gives

$$m^i_{tot} = \left[V_{aq} + m_{soil}K^i_d + m_{ct}\frac{FR_i}{C^i_s}\frac{MW_i}{MW_{ct}}\right]C^i_{aq} \qquad \textbf{Eq. 2-9}$$

Similar to the molecular weight analysis, the initial mass of compound in the coal tar is related to the total coal tar mass added to the system and the initial concentration of compound i in the coal tar via

$$m^i_{tot} = \left[C^i_{ct}m_{ct}\right]_{t=0} \qquad \textbf{Eq. 2-10}$$

At equilibrium, the mass of the coal tar will be lower than the initial mass due to partitioning of some of the coal tar constituent mass onto the soil, and in the process, the concentrations of the coal tar constituents in the coal tar will change. The coal tar mass at equilibrium is then estimated to be the initial mass minus the sum of the sorbed and aqueous masses of the coal tar constituents:

$$m_{ct}^{eq} = [m_{ct}]_{t=0} - V_{aq} \sum_i C_{aq}^i - m_{soil} \sum_i C_{aq}^i K_d^i \qquad \textbf{Eq. 2-11}$$

Now, substitution of Equation 2-10 into Equation 2-9, and accounting for change in the coal tar mass via Equation 2-11, gives

$$C_{aq}^i = \frac{\left[C_{ct}^i m_{ct}\right]_{t=0}}{V_{aq} + m_{soil} K_d^i + m_{ct}^{eq} \dfrac{FR_i}{C_s^i} \dfrac{MW_i}{MW_{ct}}} \qquad \textbf{Eq. 2-12}$$

The only unknown in this system of equations is the partition coefficient, K_d^i. Given C_{aq}^i from batch equilibrium experiments, the partition coefficient can be determined through application of Equation's 2-11 and 2-12.

2.4.3 Batch Experimental Methods

For the molecular weight experiments, two-phase coal tar/water batch tests were conducted. In these experiments, one gram of coal tar was added to 20 mL of deionized water in a crimp-sealed vial. After five days, 16 mL of the liquid sample was collected after centrifuge separation, extracted using method MET 2005 (Appendix A) and analyzed via GC/FID. Initial experiments were conducted for durations of 2 to 7 days, and the results showed that 5 days was sufficient to achieve equilibrium.

For the partition experiments, three-phase coal tar/soil/water tests were conducted. For each coal tar/soil combination, five individual tests were conducted, each with two grams of uncontaminated soil and one of five different coal tar masses (0.5 to 2.5 grams) added to 20 mL of deionized water in a crimp-sealed vial. Soil particles larger than 1 mm were removed from the soils before being added to the vial. After six days, 16 mL of the liquid sample was collected by centrifuge separation, extracted using method MET 2005 (Appendix A) and analyzed via GC/FID.

2.5 Column Experiments

2.5.1 Numerical Analysis of Mass Transfer Rate

The mass transfer coefficient for coal tar dissolution from contaminated soils was determined by applying Equation 1-11 to data from a laboratory column packed with the contaminated soil. The analysis can be simplified by passing water through the column until a steady-state effluent concentration is reached, resulting in dC/dt = 0 in Equation 1-11. Also, for short columns, dispersion is negligible. Given this, Equation 1-11 can be written as

$$0 = -v_x \frac{dC}{dx} + k_{La}\left(C^{eq} - C\right) \qquad \textbf{Eq. 2-13}$$

This equation can be integrated via the method of separation of variables. First, the equation is rearranged to the form

$$\frac{dC}{\left(C^{eq}-C\right)}=\frac{k_{La}}{v_x}dx \qquad \textbf{Eq. 2-14}$$

Equation 2-14 then integrated from the column inlet to the outlet (i.e., integration limits of C_o to C_e for dC, where C_o is the influent concentration of the compound of interest entering the column and C_e is the concentration in the column effluent, and 0 to L for dx, where L is the column length), resulting in

$$\ln\left(C^{eq}-C_o\right)-\ln\left(C^{eq}-C_e\right)=\frac{k_{La}}{v_x}L \qquad \textbf{Eq. 2-15}$$

For this study, the columns were eluted with clean water, so that $C_o = 0$. Equation 2-15 can be rearranged to provide the mass transfer coefficient:

$$k_{La}=\ln\left(\frac{C^{eq}}{C^{eq}-C_e}\right)\frac{v_x}{L} \qquad \textbf{Eq. 2-16}$$

Using Equation 2-16, the mass transfer rates for the coal tar constituents dissolving from the coal tar into the pore water can be computed from the column steady-state effluent concentrations. Equation 2-16 was purposefully left written in terms of C^{eq}. If the compounds of interest are dissolving directly from coal tar into the water, then C^{eq} is calculated using Raoult’s law via Equation’s 1-9 and 1-10. However, if coal tar is not present, but rather the compounds are sorbed to the soil and are being slowly released, then C^{eq} is the aqueous solubility of the pure compound.

2.5.2 Column Experimental Method

Column tests were conducted on the contaminated soil samples obtained from the MGP sites to quantify the mass transfer (dissolution) rate of coal tar constituents into the water. Stainless steel columns were utilized in this study (Figure 2-4). The interior dimensions of the column were 1.89 inches in diameter and 4.65 inches in length. Glass filter discs (0.45 cm thickness) were installed on top and bottom of the soil column to provide uniform distribution of liquid and to prevent clogging by soil particles. A peristaltic pump with an adjustable flow rate (0.03 ~ 8.2 ml/min) was used to elute clean water through the sample, and the column was maintained at a temperature of 8°C to simulate subsurface conditions. The flow system is shown in Figures 2-5 and 2-6.

Uniform packing of the sample is vital to achieve consistent results with column experiments. Vibratory and constant tapping of the sample are generally adopted to achieve the required sample density. However, these methods were not suitable due to the moist nature of the MGP soils provided for this study. With this limitation, direct compaction of the moist soils was selected. A donut hammer on a slide was dropped through a specified height, imparting energy to the soil through a circular “foot” at the base of the compactor. The soil was compacted in four layers, and the number of blows per layer was varied according to the desired final density. Typically, the top of each soil layer (lift) was roughened before placement of the next lift in order to minimize the effects of the lift interfaces. Using these compaction procedures, it was possible to create uniform as well as repeatable specimens at consistent, predictable densities.

Chemical analysis was conducted on the pore water eluted from each sample. At specified times, 16 mL of the liquid sample was collected from the column outflow, extracted using method MET 2005 (Appendix A) and analyzed via GC/FID.

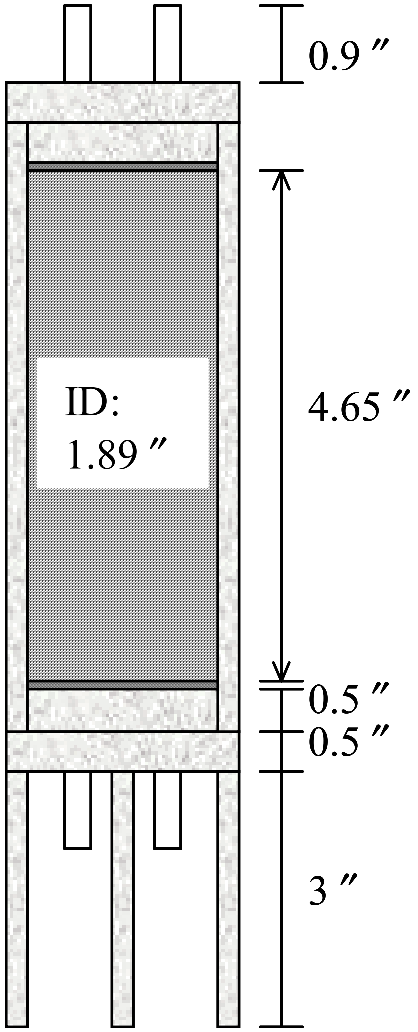


Figure 2-4
Schematic of Stainless Steel Column

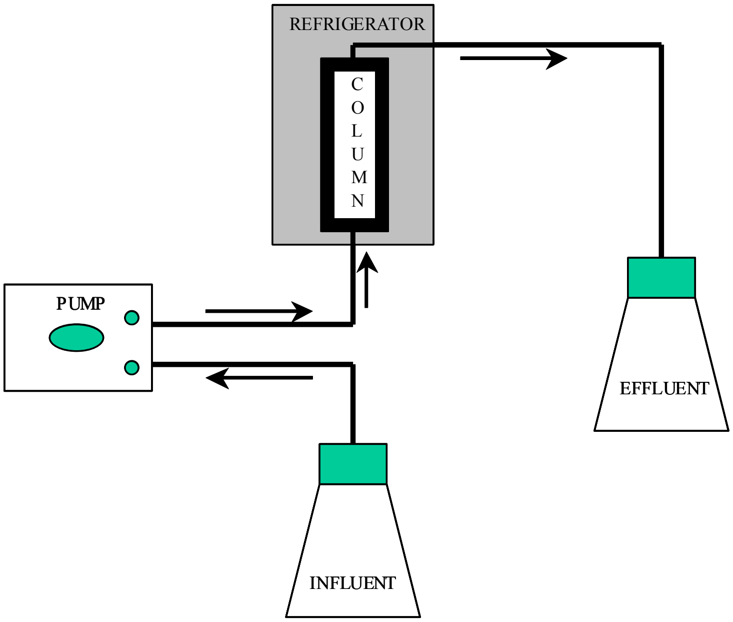


Figure 2-5
Schematic of Column Test Apparatus

Figure 2-6
Photograph of Column Test Apparatus

3

RESULTS

3.1 Physical Properties of Soils and Coal Tars

3.1.1 Soils

Table 3-1 summarizes the physical properties of the soils which include the soil classification, water content, organic content, and specific gravity from the ten sites. Soil types for each sample were determined by Unified Soil Classification System (USCS) and ranged from sands to clayey sands. Water content ranges from 5.47% (site 3) to 20.51% (site 9). Organic content ranges from 0.47% (site 9) up to 6.2% (site 6). The high organic content of site 6 soil samples was also detected by visual observation. Specific gravity determined by ASTM D854 ranges from 2.47 (site 6) to 2.72 (site 3).

Table 3-1
Soil Properties of MGP Site Soils

Site	Soil Type (USCS)	Water Content (%)[1]	Organic Content (%)[1]	Specific Gravity (G_s)[1]	Organic Content (%)[1,2]
1	SC	14.39	0.68	2.63	0.60
2	SP	16.89	1.19	2.60	0.62
3	SP	5.47	1.28	2.72	1.10
4	SC	14.88	0.92	2.71	1.09
5	SW-SM	18.17	1.31	2.66	–
6	SM	16.27	6.20	2.47	3.8
8	SC-SM	13.91	1.83	2.68	–
9	SP	20.51	0.47	2.66	0.21
10	SP-SM	12.95	1.81	2.64	2.65
11	SP	13.05	1.21	2.64	–

USCS = Unified Soil Classification System, SC = Clayey Sand, SM = Silty Sand,
SC-SM = Silty, Clayey Sand, SW = Well-graded Sand, SP = Poorly-graded Sand
1. Weight/weight
2. Data from Georgia Institute of Technology.

Figure 3-1 shows the particle size distribution curves for ten of the MGP site soils. From these curves, parameters such as D_{10}, D_{30}, D_{60} as well as C_c and C_u were measured and computed (Table 3-2). D_{10}, D_{30}, and D_{60} present the grain diameter at 10%, 30%, and 60% passing by mass in the particle size distribution curve. C_c and C_u present the coefficient of curvature and the coefficient of uniformity, respectively.

Thus, soil types for each soil sample were determined by Unified Soil Classification System (USCS) and ranged from sands to clayey sands.

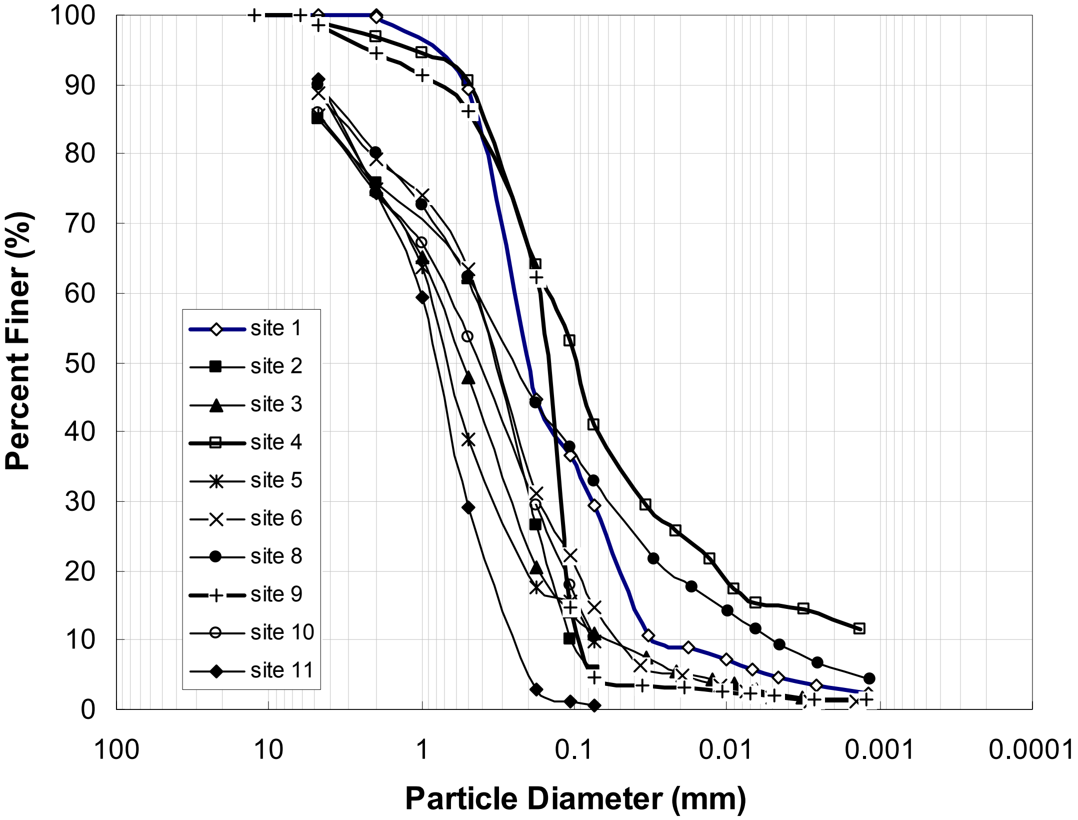


Figure 3-1
Particle Size Distribution Curves of MGP Site Soils

$$C_c = \frac{D_{30}^2}{D_{10} \times D_{60}}$$

Eq. 3-1

$$C_u = \frac{D_{60}}{D_{10}}$$

Table 3-2
Parameters from Particle Size Distribution Curves

Site	D_{10} Particle Diameter (10% passing)	D_{30} Particle Diameter (30% passing)	D_{60} Particle Diameter (60% passing)	Coefficient of Curvature C_c	Coefficient of Uniformity C_u
1	0.03	0.08	0.23	0.8	7.4
2	0.11	0.19	0.47	0.7	4.3
3	0.06	0.27	0.80	1.5	13.1
4	0.00	0.03	0.14	8.3	140.0
5	0.07	0.33	0.88	1.7	12.1
6	0.05	0.17	0.43	1.3	8.4
8	0.01	0.06	0.32	2.2	61.5
9	0.09	0.12	0.17	0.9	1.8
10	0.07	0.18	0.67	0.7	9.3
11	0.23	0.50	1.00	1.1	4.3

3.1.2 Coal Tars

Residual saturation tests were conducted by Georgia Institute of Technology (GIT) to determine the residual saturation states at which coal tars (or water) become discontinued and are immobilized by capillary forces. Table 3-3 shows the residual water content, θ_r and residual coal tar saturation (S_{Nr}) and coal tar concentrations within the soil at residual saturation (C_{Nr}) determined by GIT. Another concentration value (C_{TPH}) of total petroleum hydrocarbons in contaminated site samples, based on the data from META Environmental, is also presented in Table 3-3. Although C_{TPH} provides the total extractable hydrocarbons in the contaminated soils, whereas C_{Nr} is based on the total coal tar mass in the soil, the significant difference between C_{Nr} and C_{TPH} values indicates that the samples received from the MGP sites were all below the residual saturation values obtained by GIT.

Table 3-3
Results of Residual Saturation Tests

Site	Residual Water Content[1] θ_r	Residual Coal Tar Saturation[1] S_{Nr} (%)	Residual Coal Tar Concentration[1, 2] C_{Nr} (mg/kg)	Concentration of Site Samples[3] C_{TPH} (mg/kg)
1	0.19	15.9 (± 1.2)	48,081 (± 2,783)	690
2	0.12	22.6 (± 2.8)	71,569 (± 12710)	11,653
3	0.1	15.8 (± 0.8)	26,218 (± 470)	958
4	0.19	13.1 (± 4.2)	26,824 (± 8663)	4239
6	0.12	18.2 (± 1.3)	50,823 (± 2647)	289
9	0.1	19.2 (± 2.4)	52,821 (± 8,350)	3818

1. Data received from Georgia Tech.
2. Units of mg coal tar per kg soil.
3. Total Petroleum Hydrocarbon data received from META Environmental Inc., units of mg total measurable hydrocarbons per kg soil.

Viscosity tests were conducted on six tar samples. The remaining coal tar samples had too much debris present to perform viscosity tests. The viscosity results are shown in Figure 3-2. Coal tar samples show a very wide range in viscosity from 10 cp to 100,000 cp for different sites. The site 1 sample is the most viscous coal tar, which is almost solid at room temperature, whereas the site 9 sample has a viscosity comparable to water.

The data were analyzed by a regression analysis by performing a least-squares fit using a simple power function:

$$y = cx^b \qquad \textbf{Eq. 3-2}$$

where

y = viscosity (cp, centipoises)

x = temperature (°C)

c and b = constants.

The fitted curves are shown in Figure 3-2 and the regressions are presented in Table 3-4.

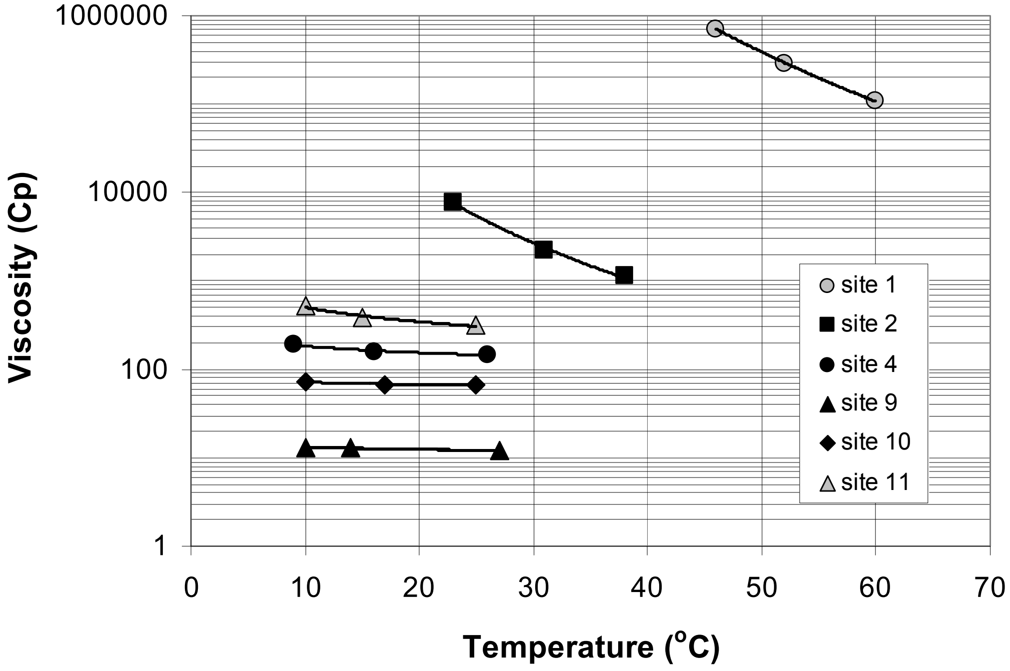


Figure 3-2
Results of Viscosity Tests: Viscosity (Cp) vs. Temperature (°C)

Table 3-4
Regression Equations of Viscosity as a Function of Temperature

Site	Equations	R^2
1	$y = 6.225 \bullet 10^{18} x^{-7.812}$	0.976
2	$y = 1.387 \bullet 10^{9} x^{-3.867}$	0.995
4	$y = 336.83x^{-0.2596}$	0.987
9	$y = 14.916x^{-0.0695}$	0.577
10	$y = 89.588x^{-0.0957}$	0.992
11	$y = 1802.0x^{-0.5489}$	0.969

3.2 Chemical Analysis for MAHs and PAHs

3.2.1 Coal Tars

The chemical compositions of coal tar samples 1 to 9 are shown in Table 3-5. Samples 10 and 11 arrived too late to be analyzed for this study. At seen in Table 3-5, the bulk of the analyzed compounds for all sites are in the naphthalenes and phenanthrene. As an example, this is shown in Figure 3-3, which presents the coal tar chemical composition for Site 4. All sites shown a similar distribution, but with varying magnitudes, as shown in Figure 3-4, where the distributions are plotted on the same scale.

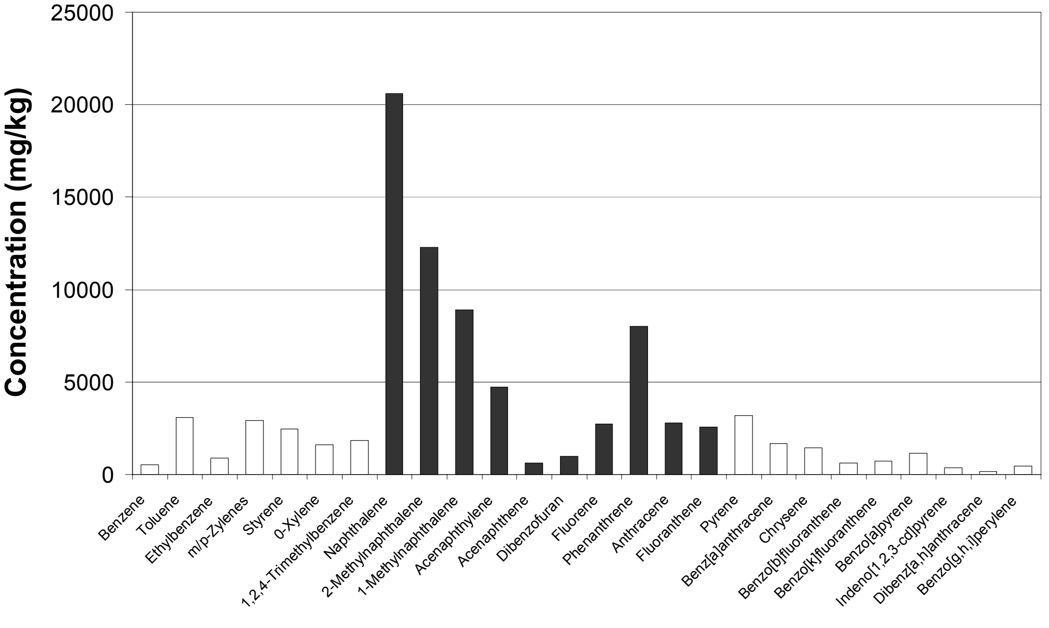


Figure 3-3
Coal Tar Chemical Composition of Site 4

Table 3-5
Coal Tar Chemical Compositions (mg/kg)

Compounds	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
Benzene	47.5	984	491	514	523	964	986	1690	1360
Toluene	210	3690	2020	3100	1000	3330	2840	6370	4270
Ethylbenzene	48.4	2920	1330	901	251	647	1760	2590	3790
m/p-Zylenes	284	3120	1720	2920	1160	3020	2100	4620	3400
Styrene	183	954	122	2450	467	508	1110	3410	337
0-Xylene	148	1610	728	1600	440	1620	1060	2180	1590
1, 2, 4-Trimethylbenzene	323	1950	884	1830	705	2650	1130	2710	2410
Naphthalene	10000	32700	7770	20600	27500	28800	13900	56100	68200
2-Methylnaphthalene	4660	19000	5270	12300	6860	27000	8620	24000	38300
1-Methylnaphthalene	2870	16200	3330	8900	3930	17400	5530	14000	24300
Acenaphthylene	1710	9520	567	4730	4050	6600	2430	8040	20000
Acenaphthene	430	1880	1150	612	928	1330	559	959	2300
Dibenzofuran	1520	1030	185	1000	5250	1040	180	421	2505
Fluorene	2420	6320	716	2730	2960	4540	1370	2540	9510
Phenanthrene	5570	17300	2160	8010	10400	14200	4080	9830	27200
Anthracene	1670	5170	634	2780	3090	4020	1210	2970	8310
Fluoranthene	2870	5240	572	2550	6220	2390	1330	3070	8690
Pyrene	2100	7150	762	3200	5110	4260	2200	4750	11400
Benz[a]anthracene	1110	3600	347	1680	2440	1210	1020	1950	4390
Chrysene	802	3930	339	1430	2250	1080	979	1840	3850
Benzo[b]fluoranthene	481	1170	136	638	1630	329	389	735	1930
Benzo[k]fluoranthene	695	1650	156	712	1780	413	419	1060	2420
Benzo[a]pyrene	678	2610	268	1150	2340	816	864	1960	4100
Indeno [1, 2, 3-cd] pyrene	311	797	85.4	371	1270	202	295	671	1530
Dibenz[a,h]anthracene	93.9	346	33.7	151	366	80.4	124	222	463
Benzo [g, h, i]perylene	351	1000	100	465	1400	251	487	898	1930

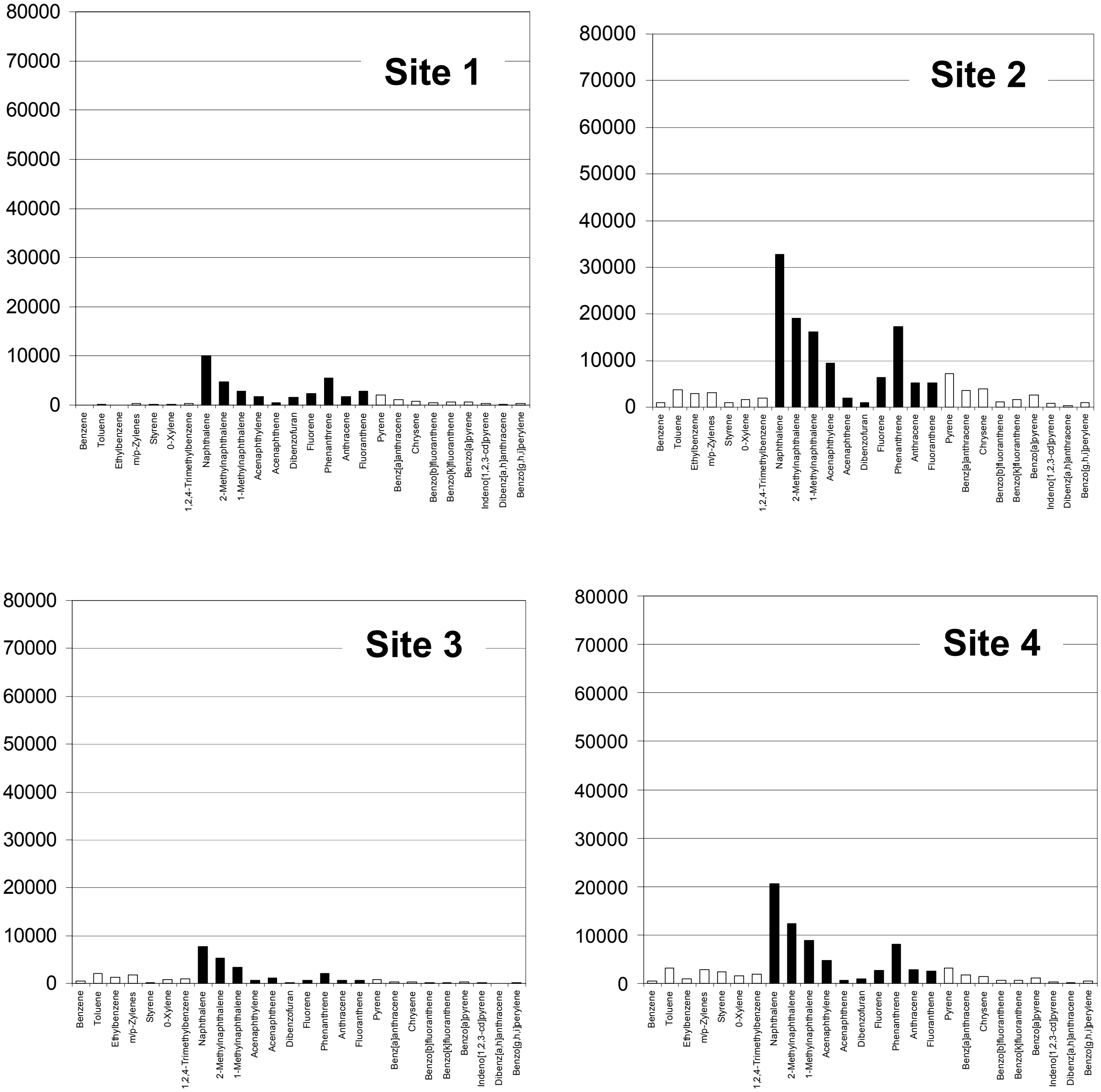


Figure 3-4
Coal Tar Chemical Distributions. See Figure 3-3 for Description of Axes

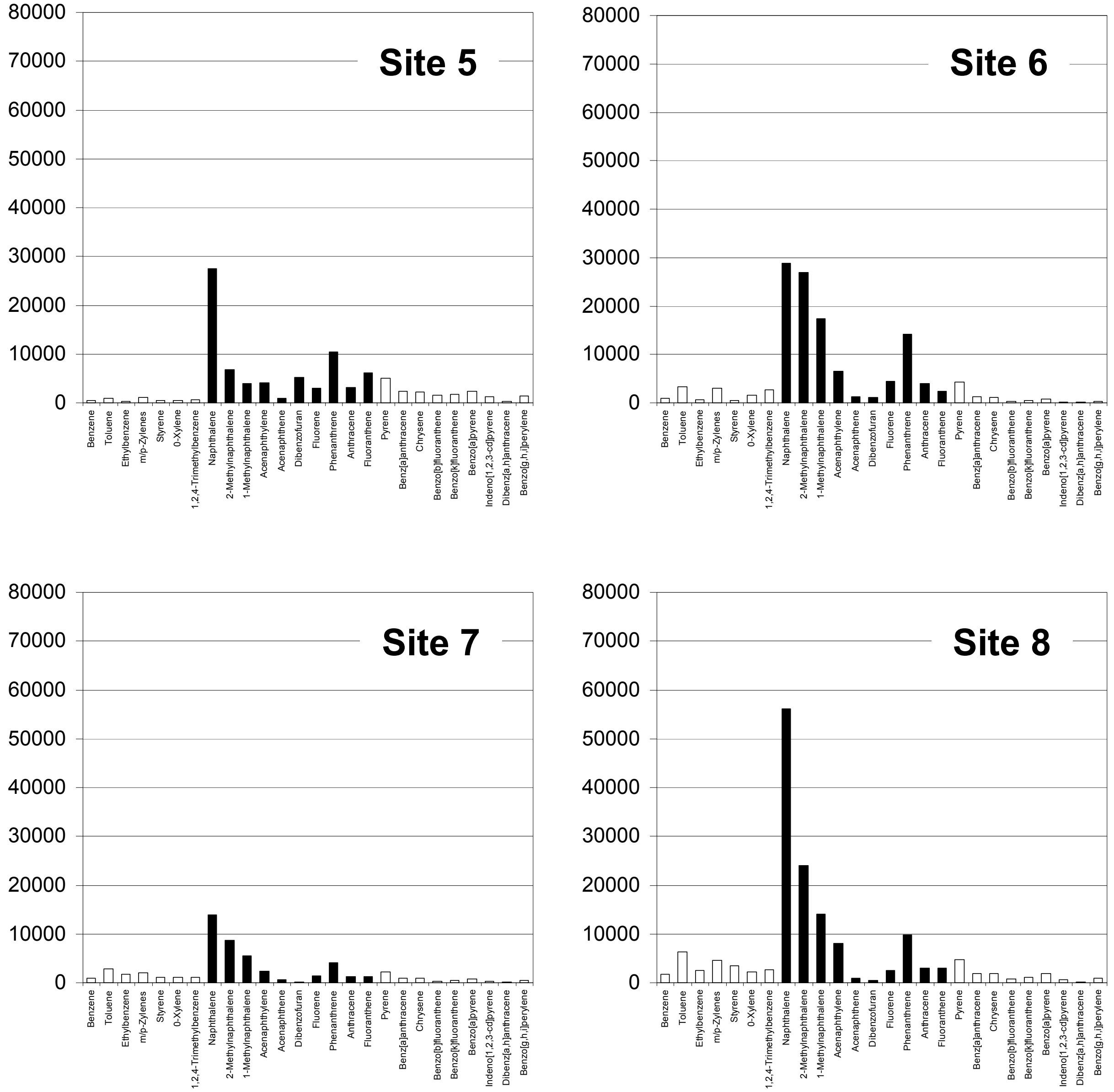


Figure 3-4
Coal Tar Chemical Distributions. See Figure 3-3 for Description of Axes (Continued)

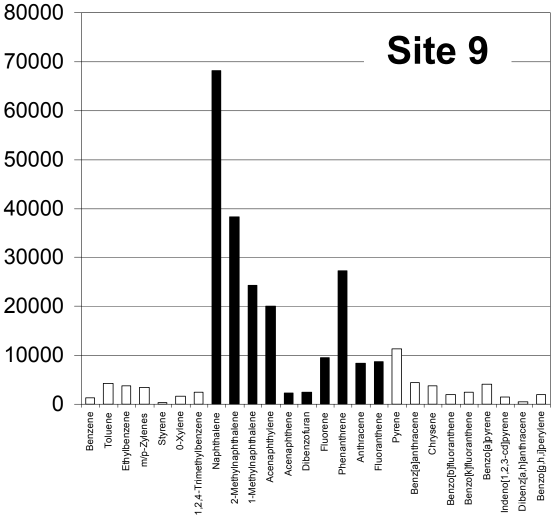


Figure 3-4
Coal Tar Chemical Distributions. See Figure 3-3 for Description of Axes (Continued)

3.2.2 Contaminated Soils

Chemical analysis of the contaminated soils is presented in Table 3-6 and the distributions are shown in Figure 3-5. The distributions in Figure 3-5 show that the trend of concentrations versus compounds of all site samples is very similar to the coal tar samples shown in Figure 3-3: the Naphthalenes and Phenanthrene show higher concentration level than the other compounds. In site 1, however, the high concentration occurs for the four or higher ring PAHs.

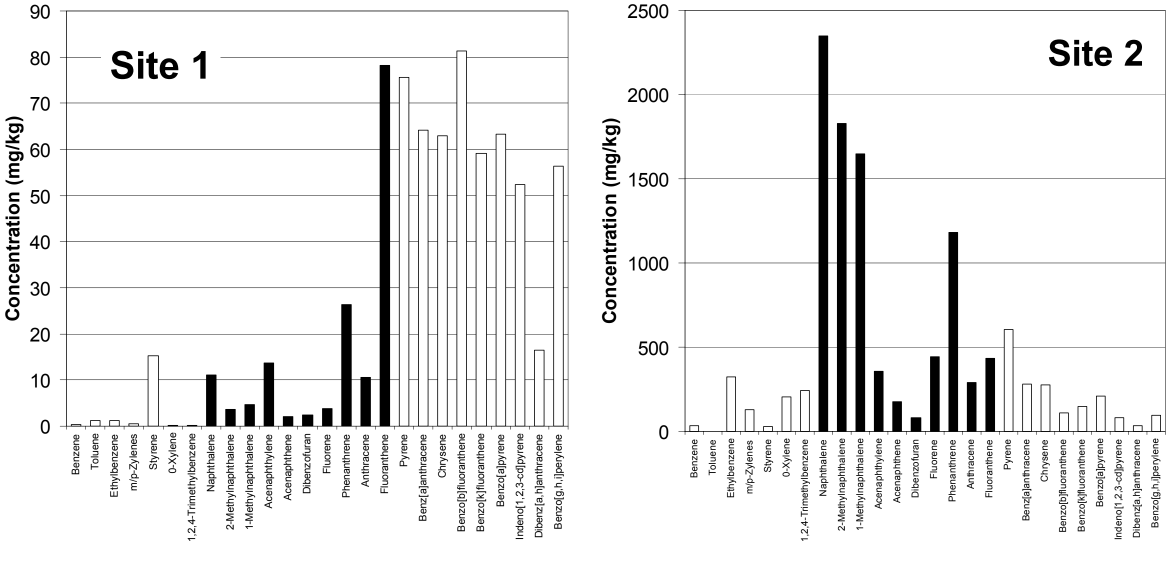


Figure 3-5
Chemical Composition of Coal Tar-Contaminated Soils

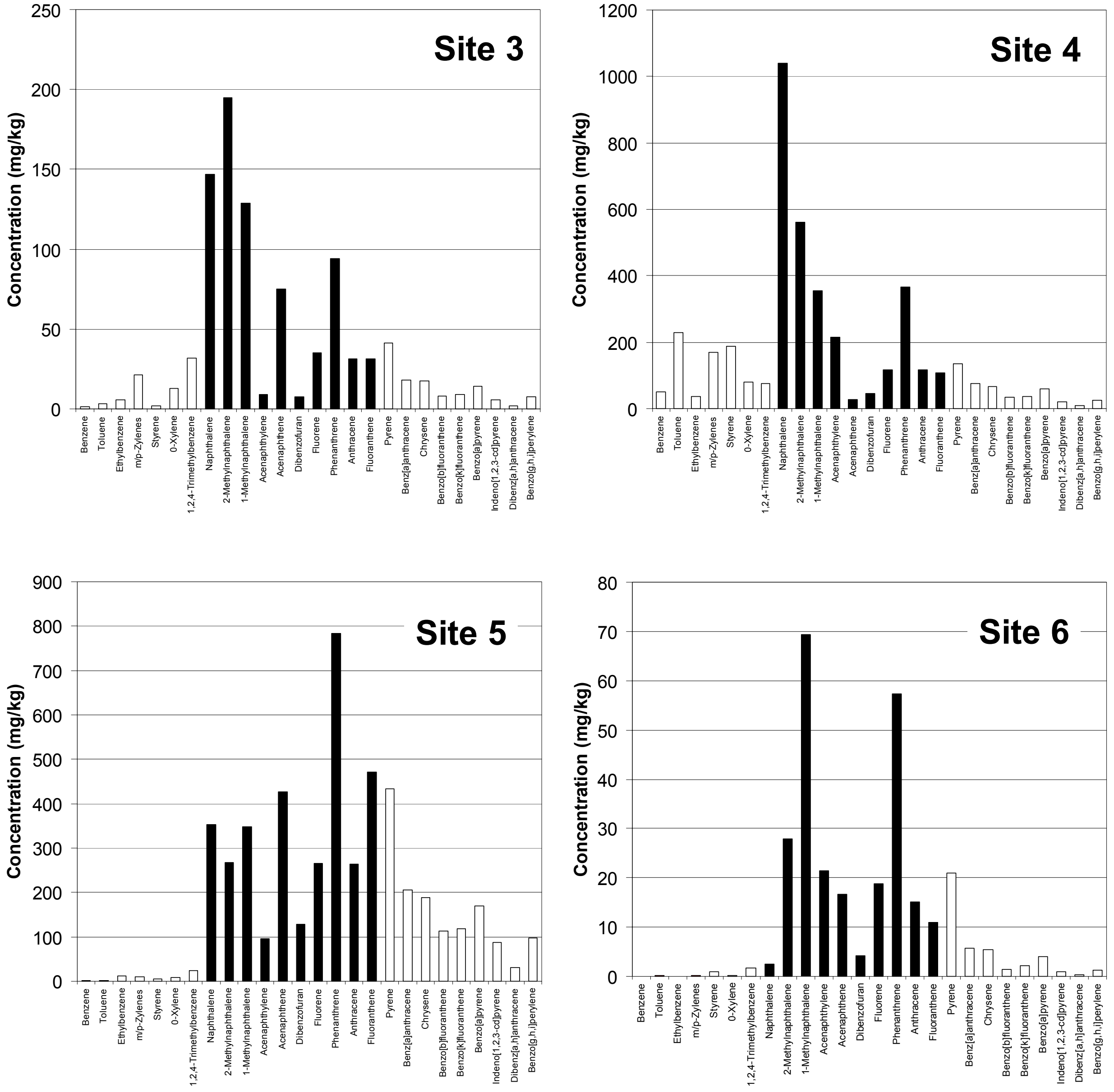


Figure 3-5
Chemical Composition of Coal Tar-Contaminated Soils (Continued)

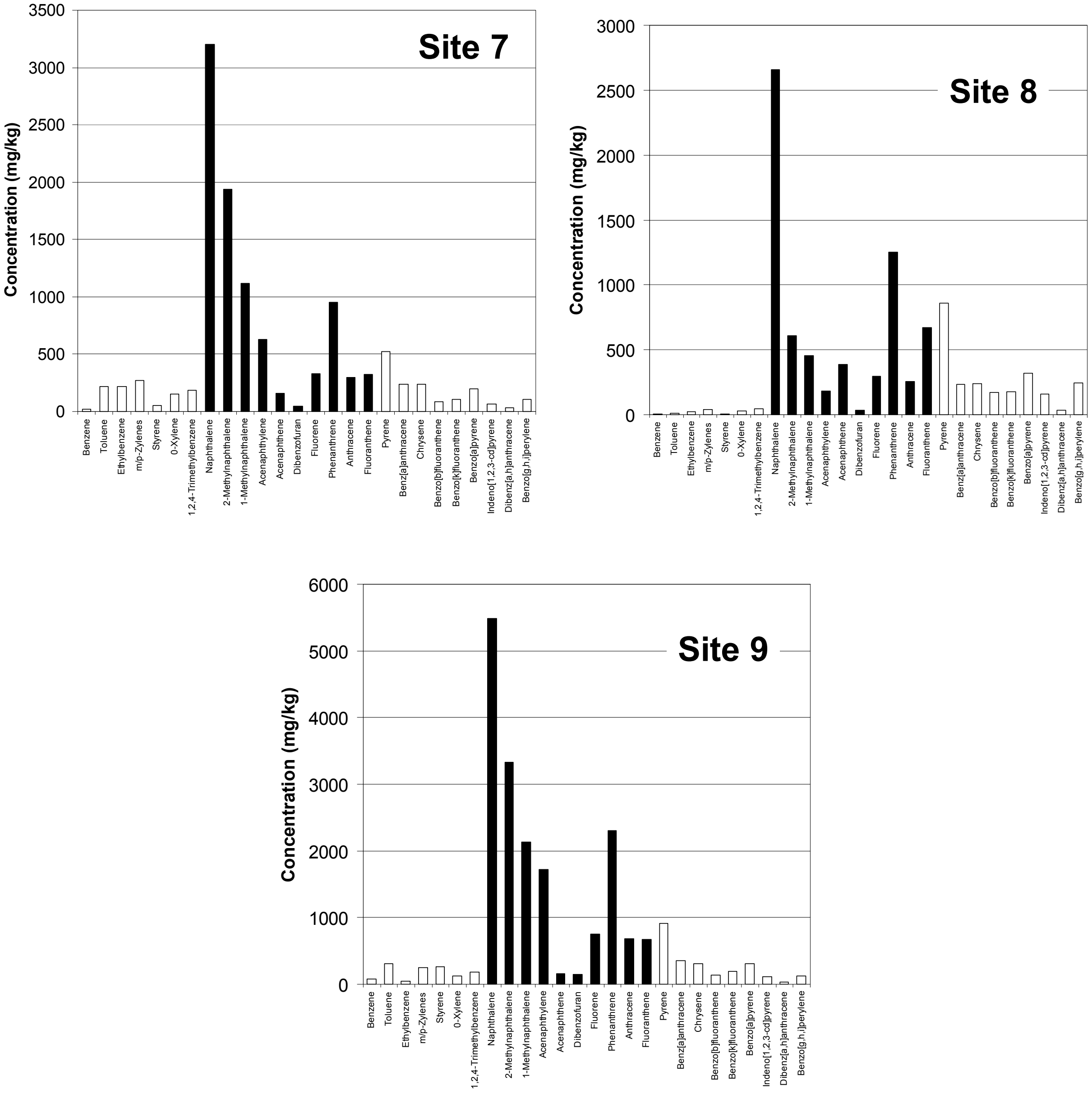


Figure 3-5
Chemical Composition of Coal Tar-Contaminated Soils (Continued)

Table 3-6
Contaminated Soil Component Concentrations (mg/kg)

Compounds	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9
Benzene	0.35	35.3	1.33	50	1.39	BD	22.7	7.98	2.75
Toluene	1.18	6.2.	3.51	229	2.2	0.21	217	9.25	11
Ethylbenzene	1.24	326	5.59	36.7	11.2	BD	221	23.6	38.3
m/p-Zylenes	0.47	129	21.6	169	10.1	0.08	274	37.1	51.6
Styrene	15.2	30.2	1.78	188	5.56	0.85	52.4	5.62	10.3
0-Xylene	0.24	206	12.7	81.2	8.97	0.15	153	29.9	24.3
1,2,4-Trimethylbenzene	0.24	242	32	74.9	24.4	1.77	183	46.4	43.9
Naphthalene	11.1	2350	147	1040	354	2.5	3200	2660	1030
2-Methylnaphthalene	3.64	1830	195	560	267	27.9	1940	607	668
1-Methylnaphthalene	4.67	1650	129	356	348	69.3	1120	453	438
Acenaphthylene	13.7	358	9.06	216	95.6	21.4	626	184	132
Acenaphthene	2.05	178	75.3	27	427	16.7	157	389	240
Dibenzofuran	2.5	78.6	7.63	45.8	129	4.17	47	33.5	27.8
Fluorene	3.88	445	35.3	116	266	18.8	330	295	155
Phenanthrene	26.3	1180	94.2	367	784	57.4	950	1250	446
Anthracene	10.5	292	31.5	117	264	15.1	301	258	139
Fluoranthene	78.2	431	31.2	107	471	10.9	321	670	124
Pyrene	75.6	603	41.4	134	434	20.9	522	862	166
Benz[a]anthracene	64.1	281	18	74.7	205	5.71	241	236	68
Chrysene	62.9	274	17.5	67.2	188	5.32	235	240	60.6
Benzo[b]fluoranthene	81.3	108	8.19	33.7	114	1.35	84.7	169	29.6
Benzo[k]fluoranthene	59.2	148	9.26	35.6	119	2.18	104	179	37.4
Benzo[a]pyrene	63.3	211	14.3	59.6	170	4.07	199	316	61.1
Indeno[1, 2, 3-cd]pyrene	52.4	79.9	5.85	20.4	88.1	0.95	64.5	160	22.9
Dibenz[a,h]anthracene	16.4	31.9	2.03	8.52	31.1	0.33	30.7	34.3	7.65
Benzo[g, h, i]perylene	56.3	93	7.42	24.9	97.1	1.23	106	243	26.4

BD = Below detection limit

3.3 Batch Analysis

3.3.1 Coal Tar Molecular Weight

Figure 3-6 presents the results of the molecular weight analysis, showing the linear trend with C_{eq} and G, predicted by Equation 2-3. The data is presented for compounds from benzene to fluoranthene in Table 2-3. The curve fits to the data are presented in Table 3-7. These curve fits were obtained by fitting the data in log space, and then converting the slope back to normal space.

Table 3-7
Summary of Molecular Weights of MGP Coal Tars

Site	Average Molecular Weight [g/mole]	R^2
1	6992	0.878
2	764	0.919
5	2962	0.915
6	983	0.967
7	1668	0.937
9	474	0.986

The molecular weight of a chemical mixture can be related to the viscosity through the Mark-Houwink relationship, which relates the intrinsic viscosity to the molecular weight (Cooper, 1989):

$$\eta = K \cdot MW^{a} \qquad \textbf{Eq. 3-3}$$

Here η is the viscosity, MW is the molecular weight, and K and a are fitted coefficients. Figure 3-7 plots the molecular weight versus viscosity at 40°C, along with data from an earlier EPRI study (EPRI, 1993).

It should be pointed out that, as is currently common practice, EPRI (1993) used vapor pressure osmometry (VPO) to determine the coal tar molecular weight. While the VPO technique has been extensively used in past studies to determine the average molecular weight of coal tars, there are interferences when used with coal tar, as described above in §2.4.1. As seen in Figure 3-7, the Raoult’s law-based technique developed here provides molecular weights two to three times greater than that from the VPO technique, with the difference increasing with average molecular weight. Similar variations have been observed with shale oil samples when comparing VPO-determined molecular weights to those from gel permeation chromatography (GPC) (Stubington et al., 1995). Additionally, a factor of two is considered to be in rough agreement, compared to the order-of-magnitude differences often observed between different measurement techniques (Groenzin and Mullins, 2000).

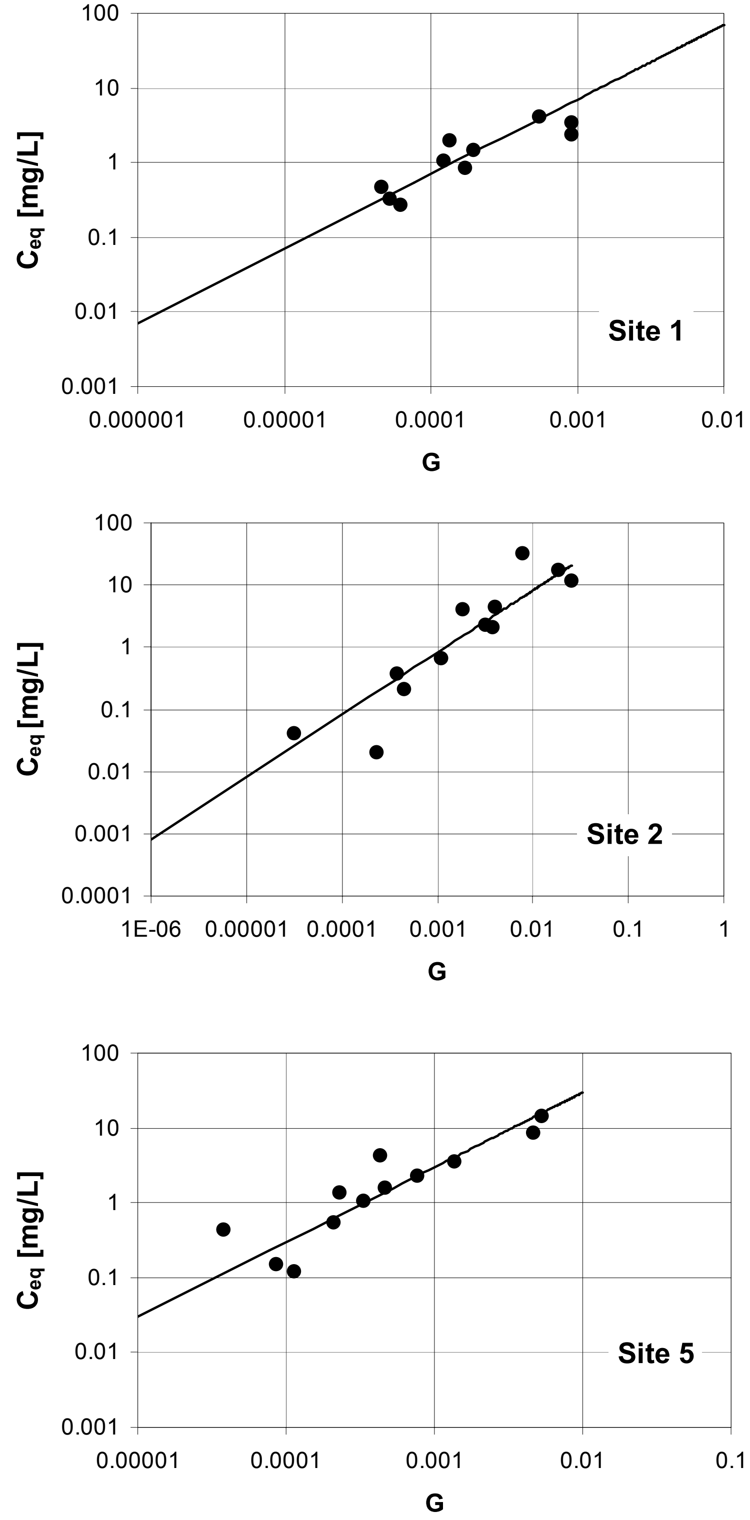
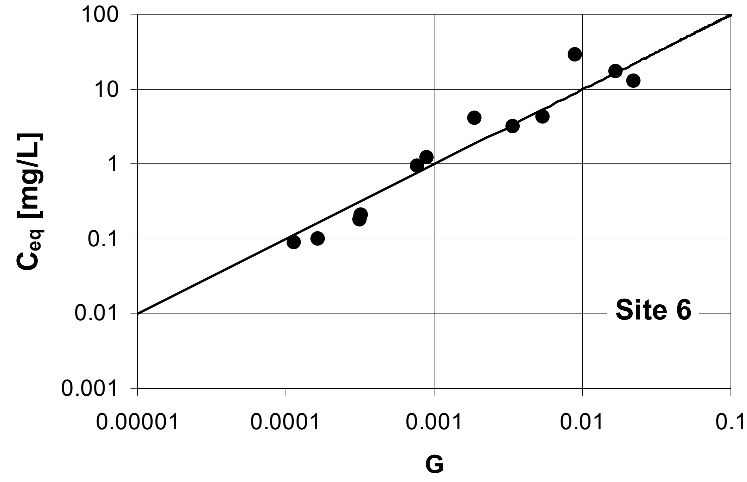
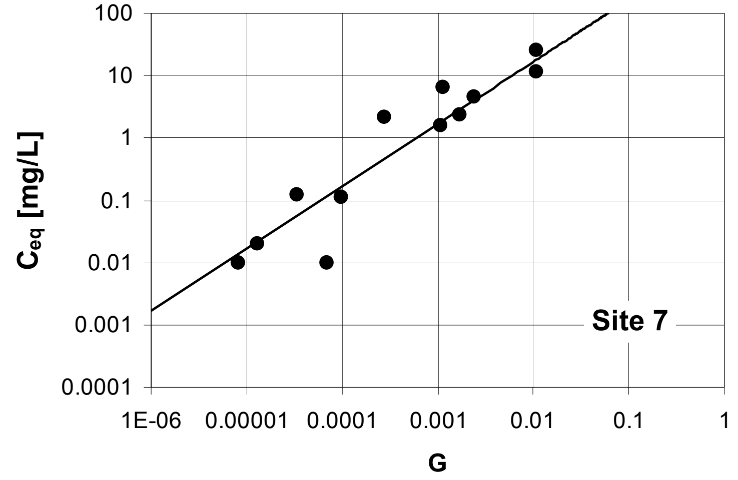


Figure 3-6
C_{eq} vs. G Plots for Determination of Coal Tar Average Molecular Weight





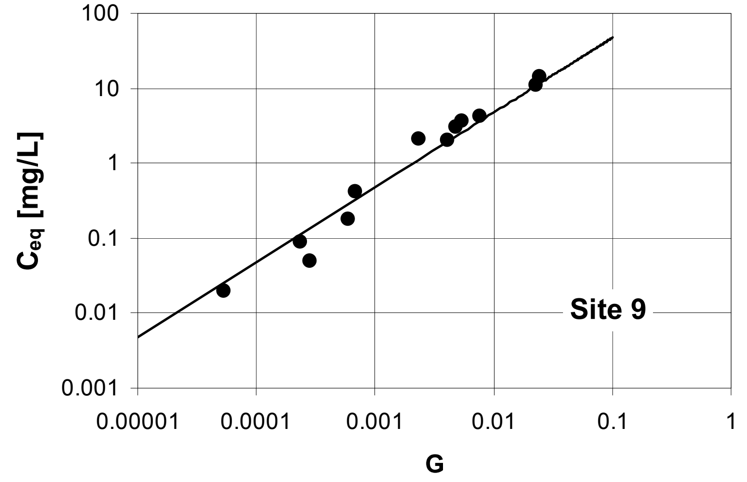


Figure 3-6
C_{eq} vs. G Plots for Determination of Coal Tar Average Molecular Weight (Continued)

It is important to note that there can be significant differences in laboratory-determined molecular weights. For example, the molecular weight of asphaltenes and other petroleum products can vary over an order of magnitude, depending on the experimental technique used (Buch et al., 2003; Eser et al., 2003; Groenzin and Mullins, 2003, 2000; Stubington et al., 1995). These variations have been attributed to differences in measurement technique (e.g., VPO measures the boiling point change in the present of a solvent vapor, whereas GPC measures molecular sizes), to different extents of dissociation of solutes in different solvents, to differences in experimental temperatures, and to differences in the physical structure of the oil in the experimental apparatus (Stubington et al., 1995). Because of these effects, it is prudent to use a experimental technique that provides a molecular weight interpretation in-line with the intended use of that data. For environmental applications, the average coal tar molecular weight is used to determine effective aqueous solubilities of coal tar constituents through application of Raoult's law. Thus, the Raoult's law-based technique developed in this study provides a consistent definition of coal tar average molecular weight based on its intended use.

Finally, the relationship between coal tar average molecular weight and chemical composition is readily apparent when comparing the results in Table 3-7 to the coal tar compositions in Table 3-5 and Figure 3-4. This relationship can be quantified by taking the total concentration of the one- to two-ring aromatic hydrocarbons in Table 3-5 (benzene to 1-methylnaphthalene) and plotting this value against the coal tar average molecular weight. The results, presented in Figure 3-8, show a high correlation between these two values.

3.3.2 Soil-Water Partition Coefficients

Soil-water partition coefficients were determined for four soil/coal tar combinations, using the numerical and experimental techniques outlined in §2.4.2 and §2.4.3, respectively. The partition coefficients for these four sites are presented in Table 3-8, along with prior results determined by EPRI (1999). In the EPRI study, a solvent extract technique was used to estimate the soil-water partition coefficients for coal tar-contaminated soil, and this data is provided in Table 3-8 for comparison.

It is often assumed that organic chemical sorb to the organic fraction of soil particles (Chiou, 2002). One means often used to represent this is to normalize the soil-water partition coefficient by the organic fraction of the soil. This normalized partition coefficient, K_{oc}, is defined as concentration of chemical adsorbed to the organic carbon content of the soil divided by the concentration in water. K_{oc} can be calculated from the soil-water coefficient as follows:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \textbf{Eq. 3-4}$$

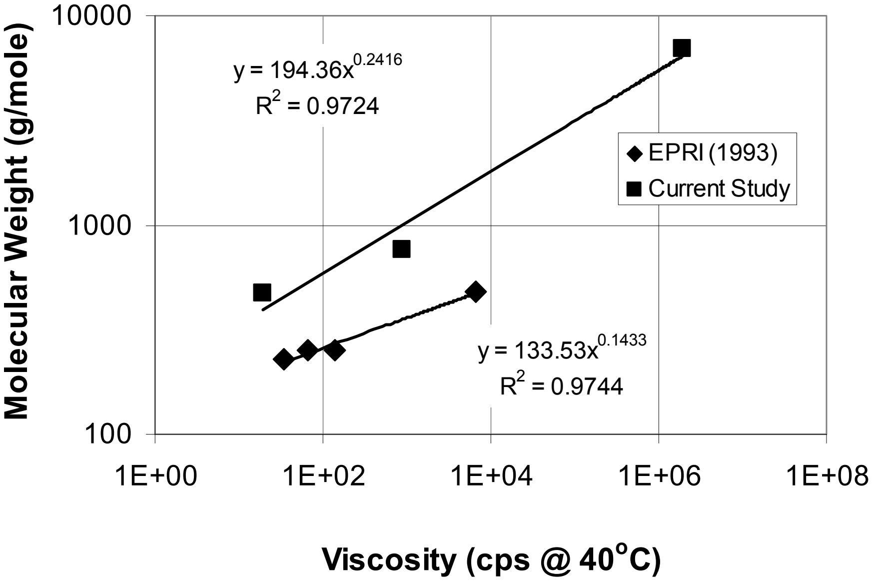


Figure 3-7
Coal Tar Average Molecular Weight versus Viscosity. Current Study uses a Raoult's Law-Based Technique, while EPRI (1993) used Vapor Pressure Osmometry

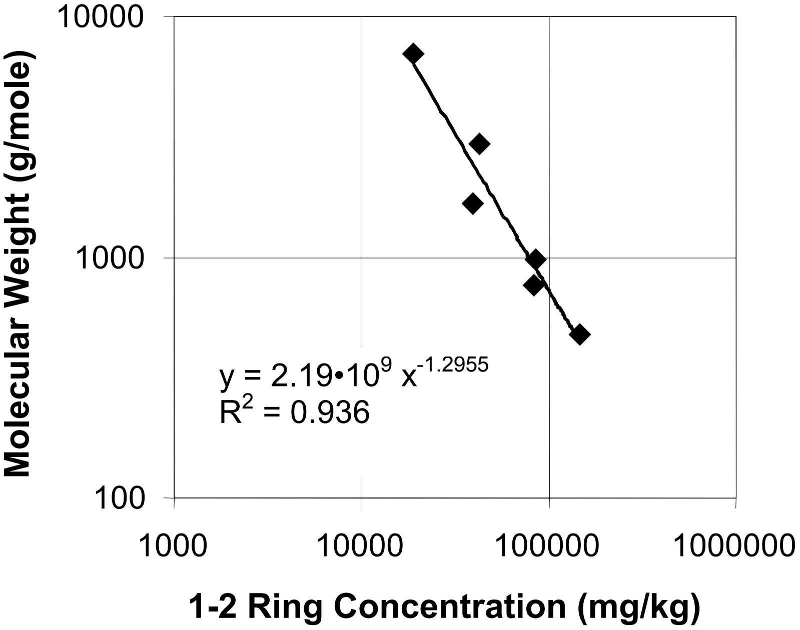


Figure 3-8
Coal Tar Average Molecular Weight versus Total Concentration of One- and Two-Ring Aromatic Hydrocarbons

Table 3-8
Soil Water Distribution Coefficient for MGP Soils from Batch Test Data

	Log (Kd) [L/kg]				
Compound	**Site 1**	**Site 2**	**Site 6**	**Site 9**	**EPRI (1999)**
Benzene	0.82	2.12	2.71	2.07	
Toluene	1.81	2.64	2.81	2.69	
Ethylbenzene	2.28	3.26	3.48	3.34	
o-Xylene	0.69	2.23	2.85	3.27	
Naphthalene	2.57	3.56	3.66	3.77	1.84-3.98
2-Methylnaphthalene	3.03	4.05	4.13	5.43	2.51-4.72
1-Methylnaphthalene	3.39	3.99	4.20	4.22	2.41-3.07
Acenaphthylene	3.79	5.70	4.98	-	2.56-3.31
Acenaphthene	-	4.58	3.82	4.59	2.42-3.47
Fluorene	3.40	4.97	5.07	-	2.58-3.72
Phenanthrene	3.92	4.91	4.85	5.28	2.86-4.18
Anthracene	-	-	4.17	4.75	3.03-4.50
Fluoranthene	3.47	-	-	4.62	3.45-5.02

where f_{oc} is the fraction of organic carbon (w/w). An excellent discussion on the applicability of K_{oc} is provided in EPRI (1996). This partition coefficient is typically plotted against the octanol-water partition coefficient (K_{ow}), which is easily determined in the laboratory and is available in the literature for a wide range of organic compounds. A plot of Log(K_{oc}) versus Log(K_{ow}) is typically a straight line, and the first Log(K_{oc})-Log(K_{ow}) relationship reported in the literature was based on sorption of a number of organic contaminants, including PAHs, to sediments (Karrichoff 1980, 1984):

$$\log(K_{oc}) = 1.00 \cdot \log(K_{ow}) - 0.21 \qquad \textbf{Eq. 3-5}$$

Since this time, a number of studies have developed a wide array of different Log(K_{oc}) versus Log(K_{ow}) relationships for PAH sorption to soil and sediment organic matter (Karickhoff, 1980, 1984;, Chiou 2002, 1998; EPRI 1996, 1998, 1999). All these studies were based on two-phase soil/water experiments, where a separate NAPL phase was not present.

Figure 3-9 shows plots of the Log(K_{oc})-Log(K_{ow}) relationships for the three-phase coal tar/soil/water data in Table 3-8, and the regressions are summarized in Table 3-9. Theoretically, the normalization process in Equation 3-4 should remove most soil influences, and Log(K_{oc})-Log(K_{ow}) relationship should be the same when applied to different soils; however, examination of Figure 3-10 shows a wide separation between the data in Figure 3-9. Similar variations have been found in other MGP studies (EPRI, 1996).

The key assumption here is that the organic fraction is responsible for the bulk of the contaminant sorption to the solids. However, for materials with very low organic fractions, other sorption processes dominate, and the Log(K_{oc})-Log(K_{ow}) relationships will under-predict the sorption coefficient (Chiou 2002). Since the soils used this study have low organic carbon contents (Table 3-1), this provides a plausible explanation for the variation between relationships in Figure 3-10.

In an attempt to correct for this discrepancy, it was assumed that mineral interactions will be important for these low organic carbon content soils, ultimately resulting in interactions between aqueous hydrocarbons and hydrocarbons sorbed to the mineral surface. This effect can be modeled as an increase in the soil organic carbon content due to the sorbed hydrocarbons, an approach which has been previously used to model sorption enhancements due to sorbed surfactants (Edwards et al., 1992). For this analysis, the organic carbon due to the sorbed hydrocarbons, which is readily calculated from the experimental sorption data and chemical structure of each hydrocarbon, is added to the organic carbon initial present on the soil, and the K_{oc} value is calculated as in Equation 3-4.

Table 3-9
Correlations Between K_{ow} and K_{oc} for PAH and MAH Compounds

Sites	Soil f_{oc}	Modified f_{oc}
1	Log(K_{oc}) = 1.167Log(K_{ow}) + 0.967	Log(K_{oc}) = 1.170Log(K_{ow}) + 0.380
2	Log(K_{oc}) = 1.276Log(K_{ow}) + 1.560	Log(K_{oc}) = 1.278Log(K_{ow}) + 0.552
6	Log(K_{oc}) = 1.047Log(K_{ow}) + 1.490	Log(K_{oc}) = 1.051Log(K_{ow}) + 1.120
9	Log(K_{oc}) = 1.250Log(K_{ow}) + 2.648	Log(K_{oc}) = 1.250Log(K_{ow}) + 0.542
Average	Log(K_{oc}) = 1.180Log(K_{ow}) + 1.745	Log(K_{oc}) = 1.276Log(K_{ow}) + 0.434

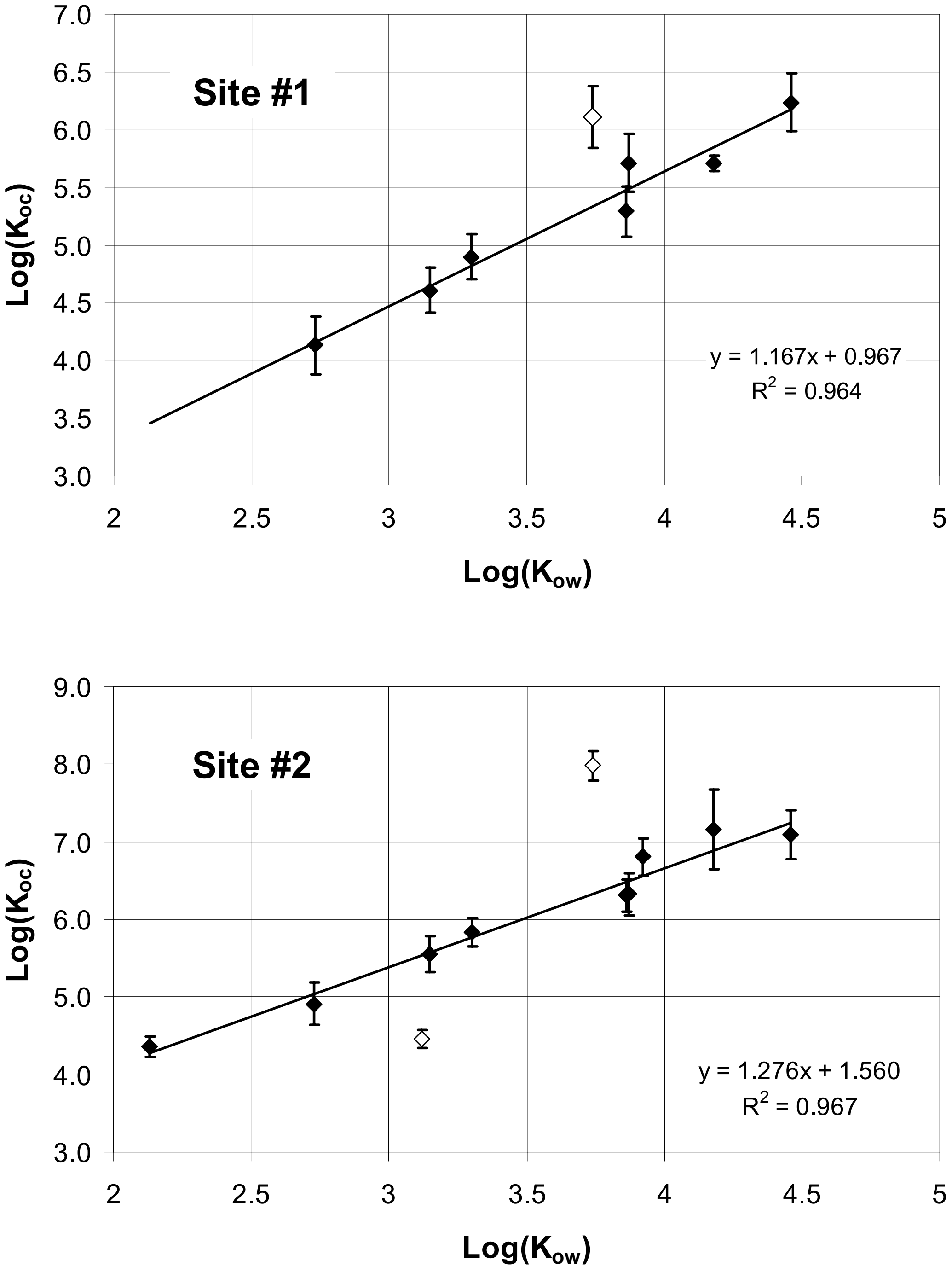
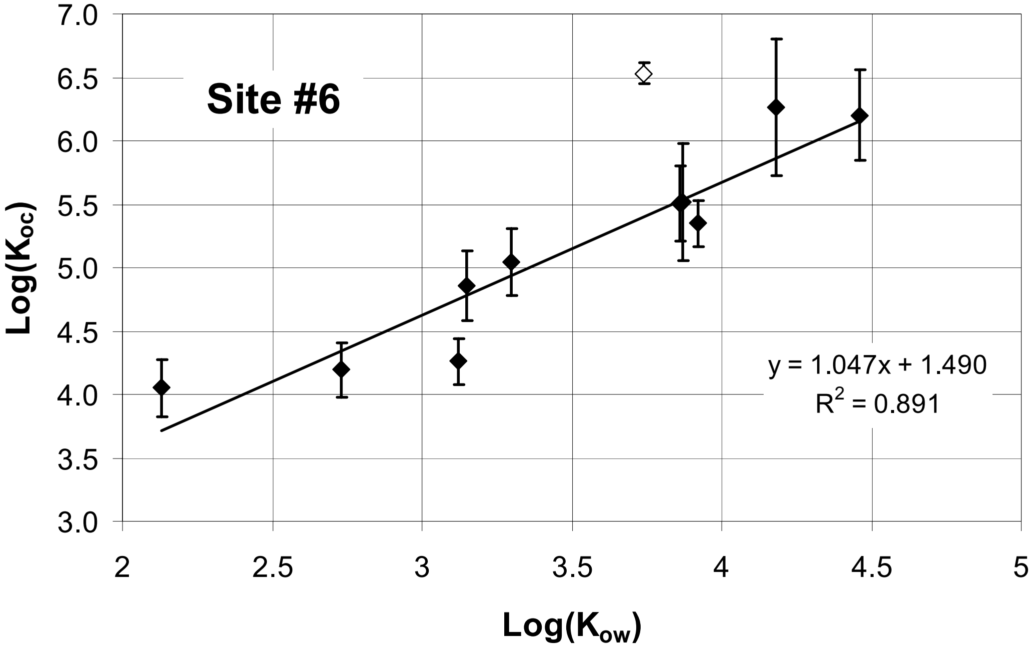


Figure 3-9
Relationship of Log(K_{oc}) vs. Log(K_{ow}) for Soils in this Study. Hollow Symbols are Outliers not Included in the Regression



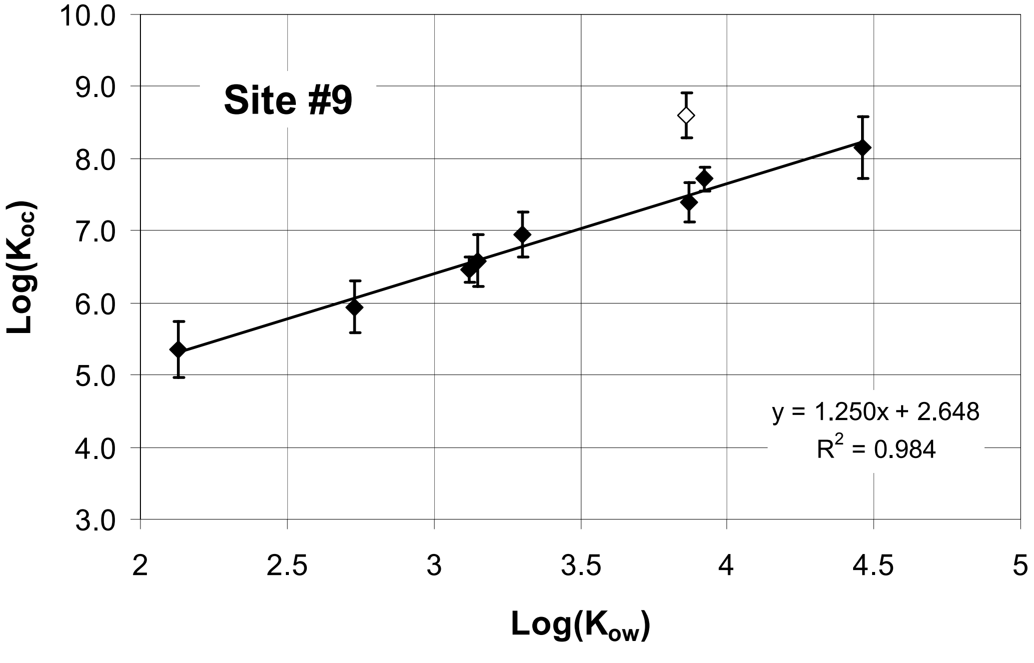


Figure 3-9
Relationship of Log(K_{oc}) vs. Log(K_{ow}) for Soils in this Study. Hollow Symbols are Outliers not Included in the Regression (Continued)

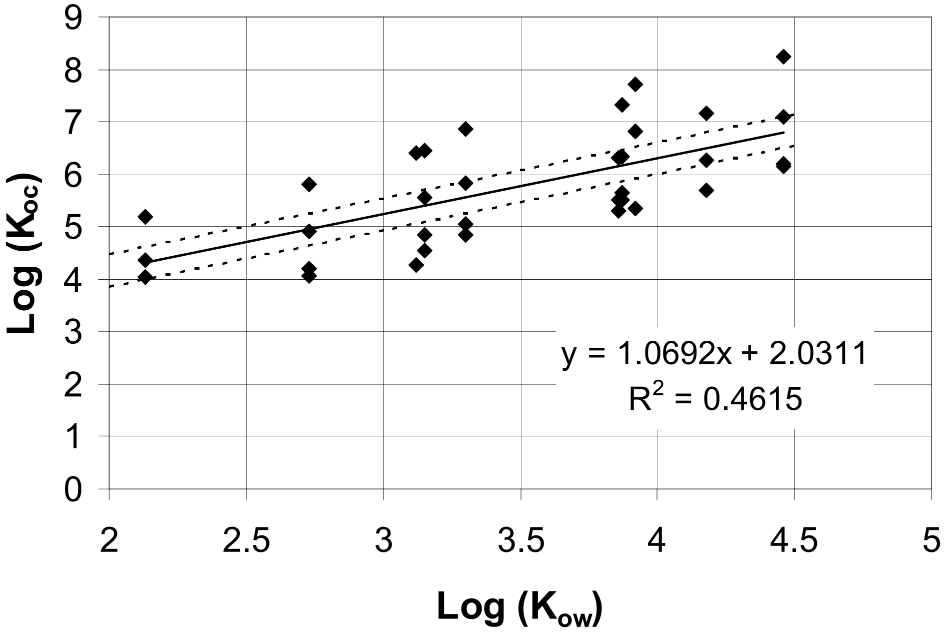


Figure 3-10
Summary Plot of Data for All Four Sites in Figure 3-9. The Dashed Lines Show a Factor of Two Error Bar about K_{oc} for the Regression Line

Table 3-9 and Figure 3-11 show the results using the modified organic fraction, and it is seen that there is a significant improvement in the fit relationship to the data, supporting the hypothesis that hydrocarbons sorbed on the mineral surface will “condition” the surface and enhance further sorption. It is important to note that the majority of Log(K_{oc})-Log(K_{ow}) relationships in the literature were calculated for two-phase systems, where the total hydrocarbon mass is low. For these systems, the alteration of the soil organic fraction by the sorbed hydrocarbons will be small, and Log(K_{oc})-Log(K_{ow}) relationships based on the soil organic fraction will be applicable. However, for sites where coal tar is present as a NAPL, this will not be the case, and application of literature Log(K_{oc})-Log(K_{ow}) relationships will under-predict the sorption. The application of general Log(K_{oc})-Log(K_{ow}) relationships to coal tar-contaminated soils must account for changes in the total soil organic carbon content due to sorption of the coal tar constituents to the soil, otherwise incorrect sorption parameters may be calculated.

3.4 Column Analysis

Column tests were performed on contaminated soils from Sites 1, 2, 5, 6 and 9. The operating parameters for each of the columns are presented in Table 3-10. The columns were run until they reached and maintained steady-state effluent concentrations, with durations ranging from 50 to 120 days. Figures 3-12 to 3-16 show the aqueous concentrations of benzene, toluene, ethylbenzene, o-xylene and naphthalene from each of the columns over time. The higher molecular weight compounds are not shown, as they were at extremely low concentrations and their peaks were within the noise on the chromatogram. In addition to the five contaminated soil samples, four soil samples from the Georgia Tech residual saturation experiments were placed into columns for long term leaching experiments.

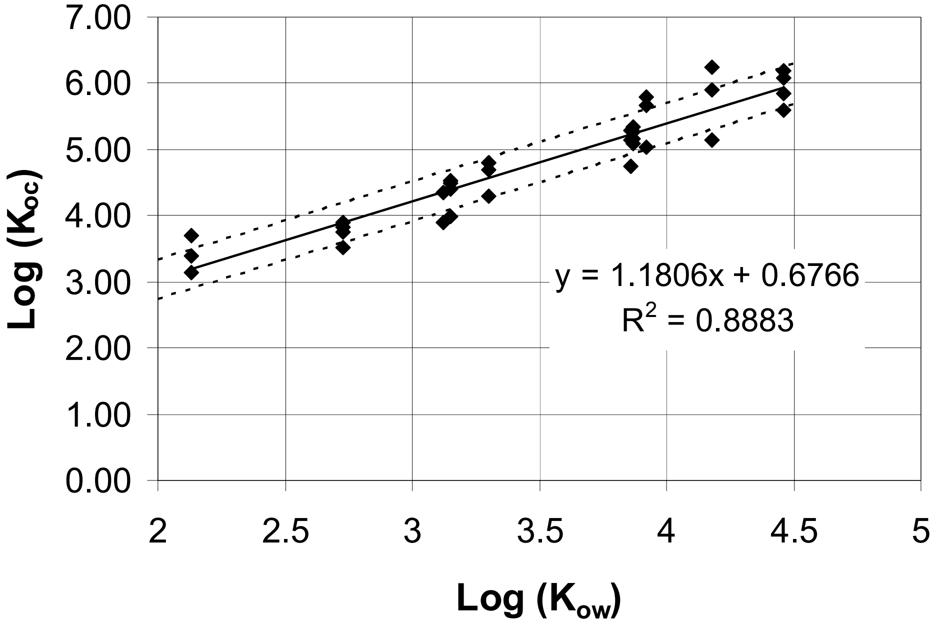


Figure 3-11
Summary Plot of Data for all Four Sites in Figure 3-9, using the Modified Soil Organic Carbon Fraction. The Dashed Lines Show a Factor of Two Error Bar about K_{oc} for the Regression Line

Table 3-10
Columns Tested on Contaminated Soils and Operating Parameters

Site	Porosity (%)	Bulk Density (g/cm^3)	Soil Density (g/cm^3)	Flow Rate (ml/min)	Flow (m/day)
1	39.10	1.83	2.63	0.51	1.04
2	52.68	1.44	2.60	0.46	0.69
5	33.81	2.08	2.66	0.47	1.12
6	32.82	1.93	2.47	0.52	1.30
9	39.58	1.94	2.66	0.50	1.04

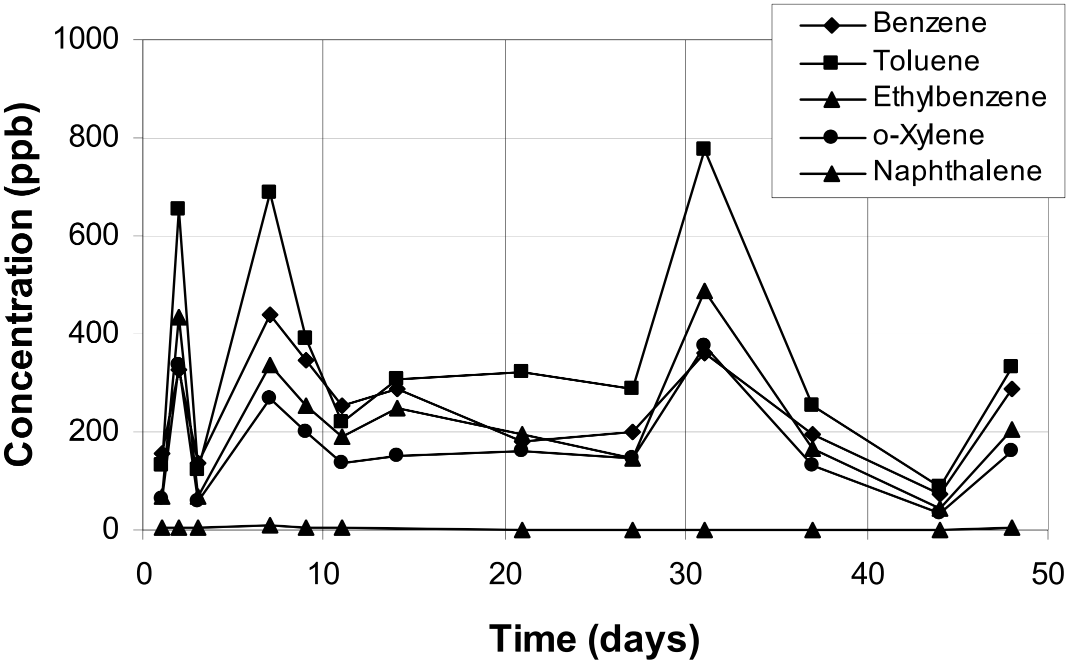


Figure 3-12
Column Effluent Concentrations for Site 1

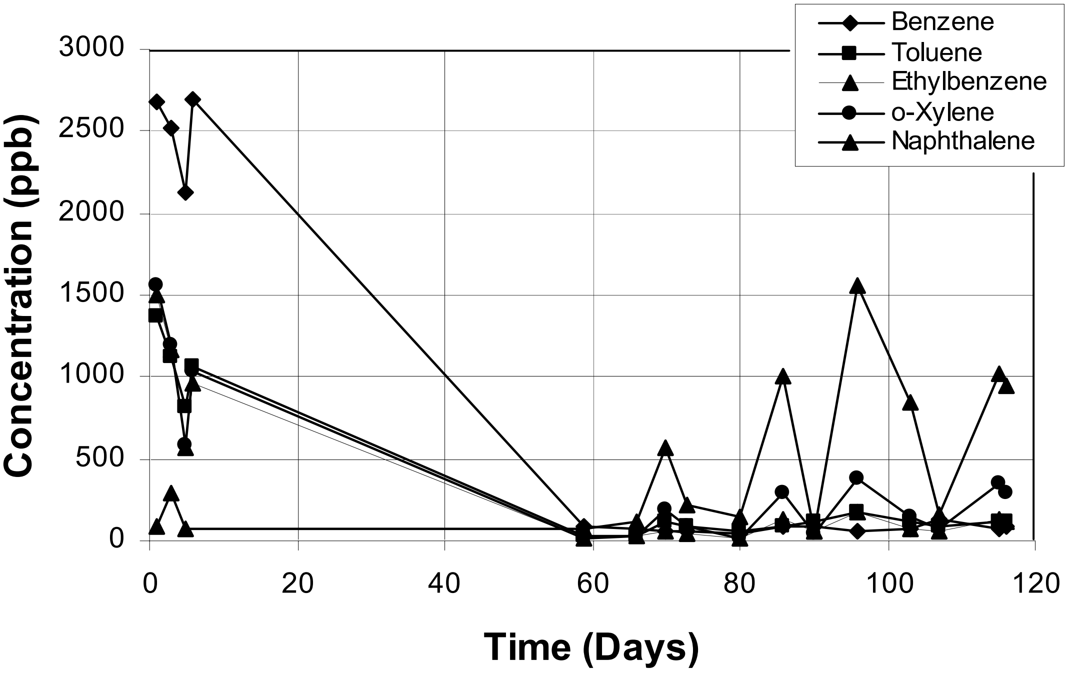


Figure 3-13
Column Effluent Concentrations for Site 2

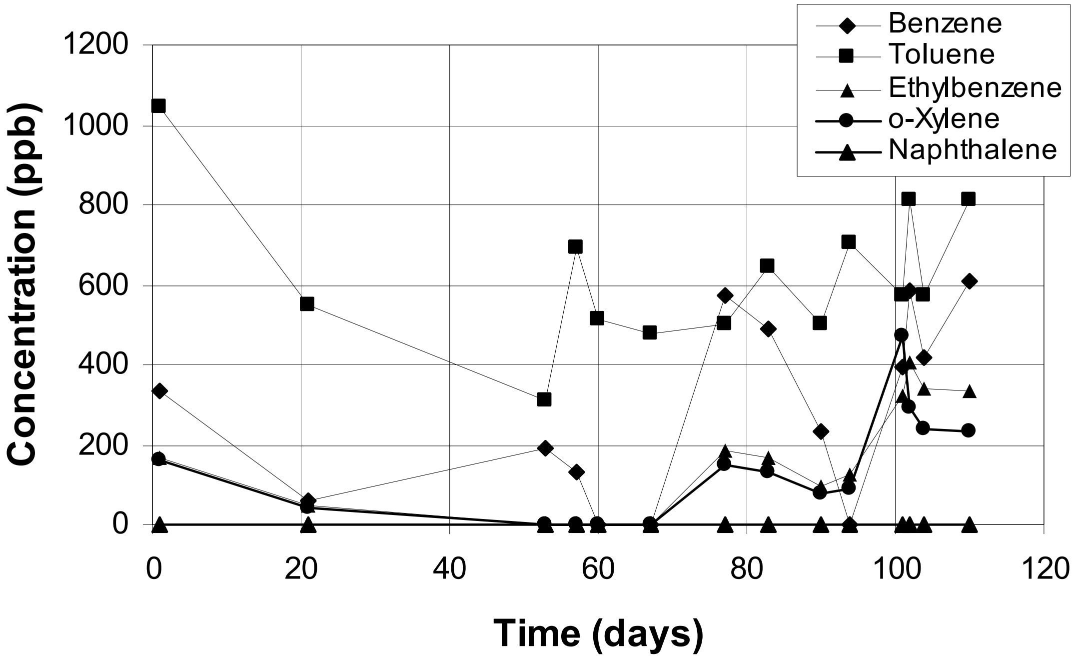


Figure 3-14
Column Effluent Concentrations for Site 5

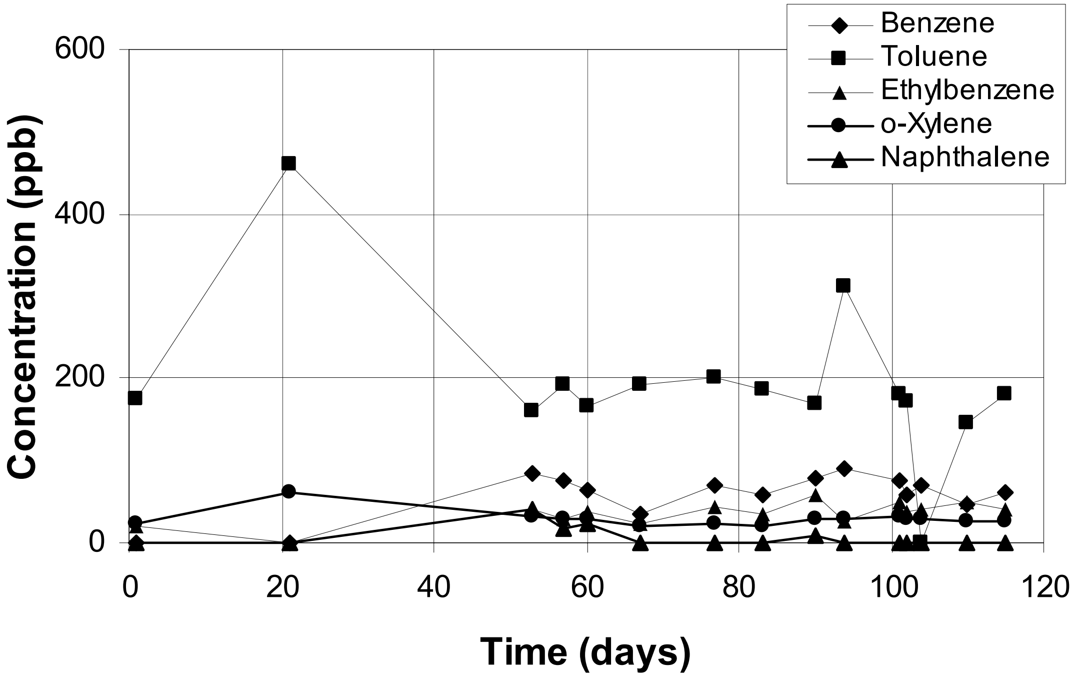


Figure 3-15
Column Effluent Concentrations for Site 6

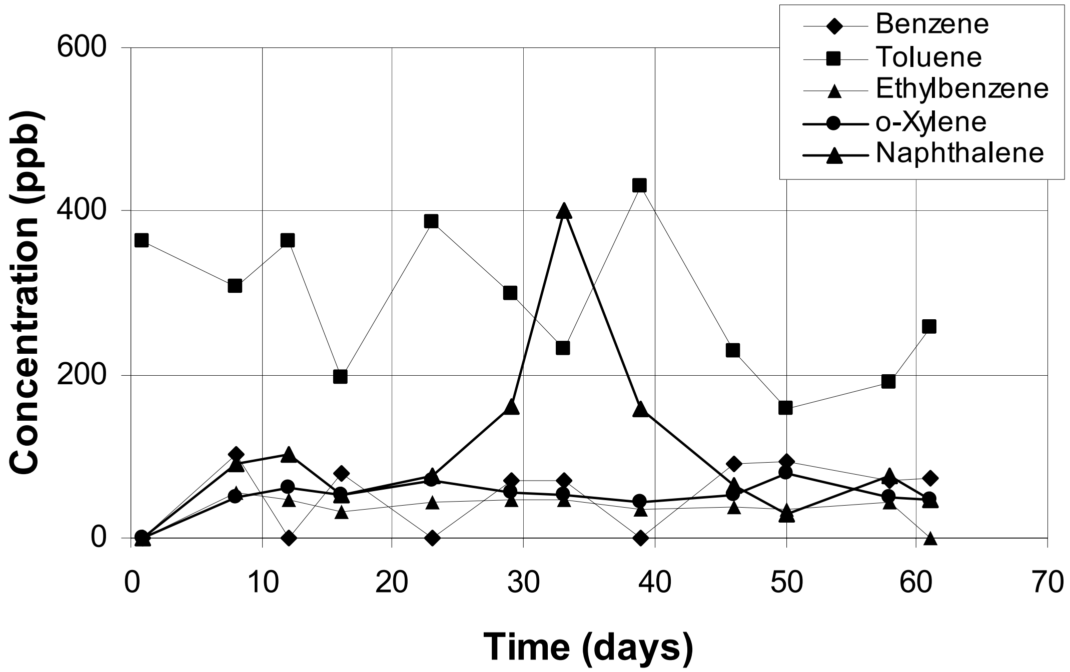


Figure 3-16
Column Effluent Concentrations for Site 9

Examination of these plots show that the BETX compounds are eluting from the columns at measurable concentrations of 100 ppb or greater, while naphthalene is not observed in the effluent for columns 1, 5 and 6. In addition, there is occasionally significant noise in the data, most likely due to interference on the GC via overlap of multiple peaks. With the exception of column 2, toluene is the dominant compound in the column effluent.

The steady-state effluent concentrations for the mass transfer analysis were determined as the mean and standard deviation of the measured effluent concentrations beyond 30 days, with the exception of site 1, which used the concentrations beyond 10 days. These values are provided in Table 3-11. The mean values in Table 3-11 were used to perform a mass balance on the mass of each BTEX compound leaving the column and their initial masses in the column. The results of this mass balance, shown in Table 3-12, are for the most part greater than one, indicating that more mass has left the column than was apparently in the column at the start of the experiment. This discrepancy may be due to a number of factors. First, while the soil samples were homogenized prior to the start of the experiments, there may have been portions of the soil samples with significantly higher BETX concentrations. These portions may have not been in the small sample volumes sent to META Environmental for chemical analysis, but may have been included in the larger sample volumes used to pack the columns. Second, the large number of peaks on the GC chromatograms combined with the low aqueous BTEX concentrations in the column effluent may have resulted in overlap of small peaks on the chromatograms, ultimately resulting in the GC predicting higher aqueous concentrations. The first issue won’t affect the mass transfer calculations, as they are the true aqueous concentrations. However, the second issue will affect the mass transfer calculations, as the aqueous concentrations are over-predicted. Unfortunately, this second issue cannot be removed from the analysis, as it is an inherent uncertainty when working with complex mixtures, such as coal tar, at low aqueous concentrations.

Table 3-11
Steady-State Effluent Concentrations from Column Experiments

	C_e [ppb] ± 95% Confidence Intervals				
	Site 1	**Site 2**	**Site 5**	**Site 6**	**Site 9**
Benzene	242 ± 90	75 ± 23	502 ± 110	66 ± 16	82 ± 11
Toluene	330 ± 187	93 ± 42	640 ± 126	193 ± 41	284 ± 87
Ethylbenzene	216 ± 119	77 ± 50	248 ± 116	39 ± 10	41 ± 5
o-Xylene	166 ± 91	162 ± 135	211 ± 130	28 ± 4	56 ± 11

Table 3-12
Ratio of Mass Leached to Initial Mass

Compounds	Site 1	Site 2	Site 5	Site 6	Site 9
Benzene	62	0.42	72	NC	3.4
Toluene	25	3.0	58	208	2.9
Ethylbenzene	16	0.047	4.4	NC	0.12
0-Xylene	62	0.16	4.7	42	0.26

NC – Not calculated, as the mass in the contaminated soil was below the detection limit (Table 3-6)

The mass transfer coefficients for the BTEX compounds were determined using the numerical procedure outlined in §2.5.1. In order to calculate the mass transfer coefficients, the value C^{eq} in Equation 2-16 must be defined appropriately. For a system with a significant volume of coal tar NAPL present, the coal tar is the dominant source of the solubilized constituents, and C^{eq} is equal to the Raoult's law effective solubility, as defined by Equation 1-9. If coal tar NAPL is not present, but rather the coal tar constituents are slowly desorbing from the soil, then C^{eq} in Equation 2-16 is appropriately defined as the aqueous solubility of each of the compounds being examined. For systems having both mass transfer-limited desorption and coal tar NAPL dissolution, both processes can be modeled simultaneously by accounting for changes in sorbed and coal tar masses and the coal tar chemical composition. However, this requires *a priori* knowledge of the mass of coal tar NAPL present in the system. When this information is not available, a lumped mass transfer coefficient is determined, and its definition is based on whether C^{eq} is defined as the Raoult's law solubility or the pure compound aqueous solubility.

While the contaminated soils used in this study contained MAHs and PAHs, from both visual observations and the data in Table 3-3 it was not readily apparent that there was coal tar NAPL present in the soils. Because of this uncertainty, bulk mass transfer coefficients were calculated for both definitions of C^{eq}. The results for C^{eq} based on Raoult's law are presented in Table 3-13 and Figure 3-17, and for $C^{eq} = C_s$ are presented in Table 3-14 and Figure 3-18. The Raoult's law-based calculations assume that the chemical composition of the coal tar NAPL in the contaminated soil is the same as the chemical composition of the bulk coal tar NAPL sample. As seen in these figures and tables, there is a difference of approximately two orders-of-magnitude in the mass transfer coefficients, depending on the definition of C^{eq}.

As discussed above in §1.1, mass transfer coefficients are highly site specific and can vary spatially over a site due to variations in subsurface conditions. In addition, it is important to note that mass transfer coefficients determined in the lab are not directly portable to the field. Laboratory analysis usually involves use of disturbed soil samples, which can alter the physical architecture of the soil and coal tar, and thus, can alter the mass transfer coefficient. It is typically assumed that these alterations will result in higher mass transfer rates that those in the field, due to the exposure of fresh soil and coal tar surfaces in the laboratory-packed columns. For this study, disturbed soil samples were provided from the different MGP sites. As such, the mass transfer coefficients will differ from those observed in the field. However, the mass transfer coefficients in Tables 3-13 and 3-14 may be thought of as an upper limit for the field values, and the variations between samples highlights the site-specificity of the mass transfer coefficients.

Table 3-13
Mass Transfer Coefficients for the BTEX Compounds Based on the Raoult's Law Effective Solubility

	Mass Transfer Coefficient, K_{La} [min^{-1}]				
	Site 1	Site 2	Site 5	Site 6	Site 9
Benzene	8.636×10^{-5}	7.715×10^{-6}	4.089×10^{-5}	1.020×10^{-5}	1.487×10^{-5}
Toluene	1.089×10^{-4}	1.041×10^{-5}	1.126×10^{-4}	3.519×10^{-5}	6.748×10^{-5}
Ethylbenzene	1.553×10^{-3}	4.253×10^{-5}	7.519×10^{-4}	1.459×10^{-4}	4.275×10^{-5}
o-Xylene	3.722×10^{-4}	2.001×10^{-4}	4.048×10^{-4}	4.718×10^{-5}	1.657×10^{-4}

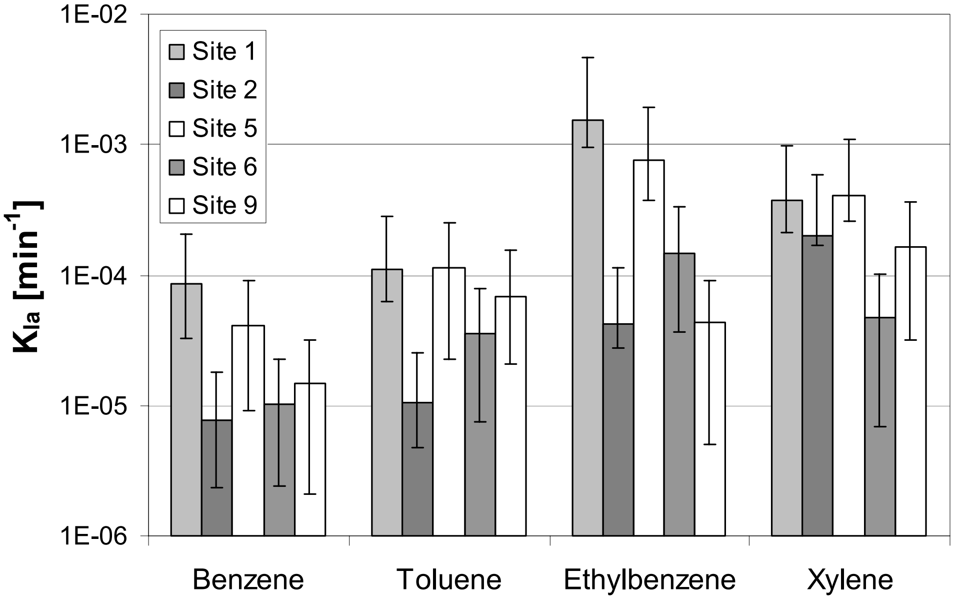


Figure 3-17
Mass Transfer Coefficients Based on the Raoult's Law Effective Solubility. Error Bars shown 95% Confidence Intervals

Table 3-14
Mass Transfer Coefficients for the BTEX Compounds Based on the Aqueous Solubility of the Pure Compounds

	Mass Transfer Coefficient, K_{La} [min^{-1}]				
	Site 1	**Site 2**	**Site 5**	**Site 6**	**Site 9**
Benzene	3.618×10^{-7}	7.419×10^{-8}	8.064×10^{-7}	1.237×10^{-7}	1.226×10^{-7}
Toluene	1.704×10^{-6}	3.179×10^{-7}	3.556×10^{-6}	1.246×10^{-6}	1.466×10^{-6}
Ethylbenzene	3.758×10^{-6}	8.846×10^{-7}	4.641×10^{-6}	8.566×10^{-7}	7.188×10^{-7}
o-Xylene	3.393×10^{-6}	2.196×10^{-6}	4.644×10^{-6}	7.039×10^{-7}	1.142×10^{-6}

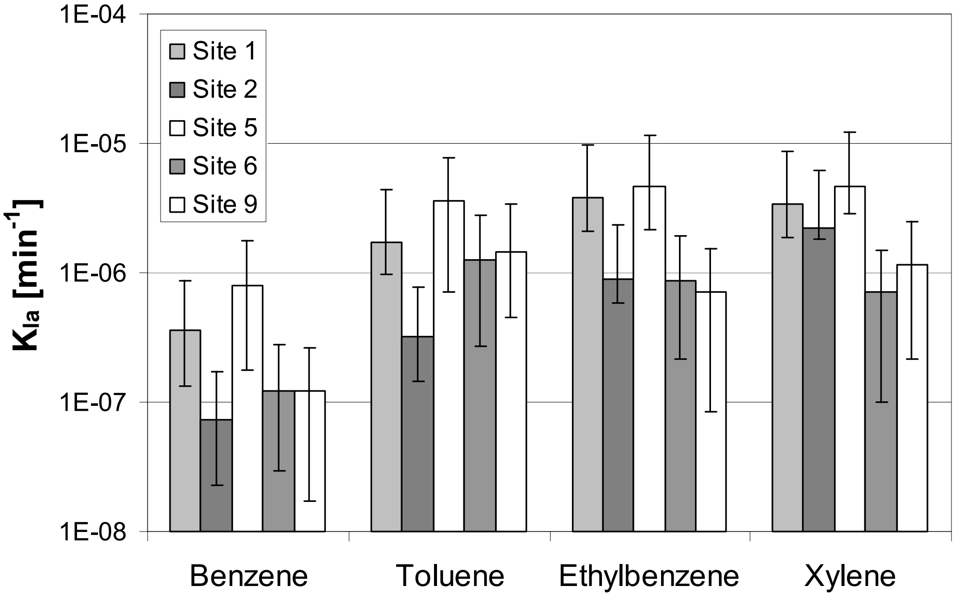


Figure 3-18
Mass Transfer Coefficients Based on Pure Compound Aqueous Solubility. Error Bars shown 95% Confidence Intervals

4

CONCLUSIONS

Batch and column experiments were conducted to determine three key fate and transport properties of coal tars and soils from former manufactured gas plant sites. These properties include the soil-water partition coefficient, coal tar molecular weight, and mass transfer coefficients. Key results are:

1. A method has been developed to determine the coal tar average molecular weight from two-phase coal tar/water batch experiments through application of Raoult's law. This provides an experimental definition of molecular weight consistent with its intended application, and removes interferences that may occur with more commonly used techniques. In addition, it has been shown that there is a strong correlation between the concentration of one- and two-ring compounds in the coal tar and the average molecular weight.

2. Soil-water partition coefficients have been determined through three-phase coal tar/soil/water batch experiments, and $\mathrm{Log}(K_{oc})$-$\mathrm{Log}(K_{ow})$ relationships have been developed. Through analysis of the experimental data, it has been shown that sorption of coal tar constituents to the soil increases the effective organic carbon content of the soil and enhances the partitioning of coal tar constituents. This is an important consideration for low organic carbon content soils, as application of literature $\mathrm{Log}(K_{oc})$-$\mathrm{Log}(K_{ow})$ relationships without consideration of the effects of the sorbed hydrocarbon mass on the soil organic carbon content will under-predict the sorption.

3. Bulk mass transfer rates for the BTEX compounds eluting from contaminated soil samples were calculated. While the mass transfer coefficients obtained from the disturbed soil samples provided for this study are expected to differ from those observed in the field, they may be thought of as an upper limit for the field values. Additionally, the variation in mass transfer coefficients between samples highlights their site-specificity.

5

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A
EXPERIMENTAL PROTOCOLS

A.1 Batch Tests

Coal Tar/Water Equilibration

1. Prepare four different amounts of coal tar samples such as 0.05, 0.1, 0.5, and 1.0g in 20 ml vial.
2. Add 20 ml de-ionized water to prepare coal tar/water batch.
3. Seal vial tightly with Teflon septa cap.
4. Wrap samples to minimize contact with light.
5. Equilibrate for 2, 5, and 7days on an end-over-end rotator.
6. Centrifuge (300 RCF) for 15 minutes.
7. Collect 16 ml of aqueous portion.
8. Extract the collected aqueous portion, final extract volume being 0.5 ml. (see Extraction procedure).
9. Inject 2 µl in GC (see GC operation).

Soil/Coal tar/Water Equilibration

1. Put 2g of soils in 40 ml vial. Soils were dried 48 hours at room temperature (25 degrees).
2. Add 0.5, 1.0, 1.5, 2.0, 2.5g of coal tars in this vial and shake well.
3. Add 20 ml de-ionized water into this vial.
4. Seal vial tightly with Teflon lined screw cap.
5. Wrap samples to minimize contact with light.
6. Equilibrate for 6 days on an end-over-end rotator.
7. Centrifuge (300 RCF) for 15 minutes.

8. Collect 16 ml of aqueous portion.

9. Extract the collected aqueous portion, final extract volume being 0.5 ml. (see Extraction procedure).

10. Inject 2 µl in GC (see GC operation).

A.2 Column Tests

1. Weigh stainless column (dimension of column are 1.875 inches in diameter and 6 inches in length) on a balance (2 decimal places).

2. Place glass filter disc (0.45 cm thickness) on the bottom of the specimen in column.

3. Compact soil samples in four layers. Top of each lift is roughened before placement of the next lift in order to minimize the effects of the lift interfaces.

4. Place glass filter disc on the top of the specimen.

5. Reweigh column included soil samples.

6. Connect inlet and outlet tubing on column.

7. Upon completion of the leaching test, a tracer solution ($CaCl_2$ = 0.01 M) will be eluted through the column. Column was placed in the refrigerator at 8 degree to simulate the ground condition. Sample–collection beakers were placed outside refrigerator at room temperature.

8. Collect 16 ml of effluent for analysis of MAHs and PAHs.

9. Extract the sample collected, final extract volume being 0.5 ml. (see Extraction procedure).

10. Inject 2 µl in GC (see GC operation).

A.3 Extraction Procedure of PAHs and MAHs from Aqueous Phase

1. Make sure all field and quality control (QC) samples are chilled to at least 4°C before proceeding. Prior to the extraction, prepare enough weigh boats with approximately 5.49 g NaCl for each ample and QC in the batch, and clean a 10 µl, 50 µl, 1.0 µl and a 2.5 µl syringe. Have methanol, acetone and DCM rinse containers ready. Take 3 – 4 samples out of the refrigerator at a time.
2. Syringe exactly 1.0 ml of DCM into the 1.0 ml syringe and put aside. Take the balance.
3. Take 16 ml of the sample to be extracted.
4. Add exactly 1 ml of DCM and approximately 5.49 g of anhydrous sodium chloride and 4.57 µl of surrogate standard to the VOA vial.

5. Cap the vial and shake vigorously for 5 minutes. Make sure the sodium chloride has dissolved completely. Set the sample aside and prepare the other samples accordingly. Remember to add DCM to the 1.0 ml gastight syringe before removing the cap form the next sample.
6. Briefly allow the phases to settle, then centrifuge at 2500 rpm for a recommended 30 minutes.
7. Prepare enough 1.0 ml amber vials for all the samples and QC with a small layer of anhydrous sodium sulfate before transferring. Using a 1 ml gas tight syringe, transfer exactly 0.5 ml of the lower DCM layer to 1.0 ml vial with a Teflon lined screw cap.
8. Prior to analysis, add 4.57 µl of the internal standard to the 0.5 ml of extract.
9. Discard the remaining contents of the VOA vial.
10. Analysis by Gas Chromatography with Flame Ionization Detection (GC/FID).
11. Keep in mind that although there is only 0.5 ml of extract in the screw top vial, the final volume of the extract must take into account the solvent remaining in the VOA vial for the purposes of calculating the sample results.

A.4 GC Operating Conditions

Samples were analyzed by capillary column GC/FID operated in the splitless injection mode.

The following GC conditions apply:

Column:	30 m×0.32 mm fused silica capillary with 0.25 micrometer film (SPB-5) thickness.
Injector:	2 mm splitless liner with glass wool plug

Inlet purge valve open after 0.25 minutes

Oven: 2.0 minutes at 30°C

Ramp at 10 degree C/minute to 310°C

Hold for 10 minutes

Pressure:	2.0 minutes at 30.0 psi
	Ramp at 0.7 psi/minute to 51.0 psi
	Hold at constant flow for 10min.
Inlet:	295°C
Detector:	320°C

2 µl samples were injected.

Program:
MGP Site Management

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