

Coal Tar and Bedrock

A Summary of Coal Tar Properties, Fate and Transport Characteristics, and Investigation Methods in Bedrock

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REPORT SUMMARY

The characterization of bedrock groundwater and coal tar impacts is one of the most complicated tasks associated with managing manufactured gas plant (MGP) sites. This report provides an overview of the fate and transport of coal tar in bedrock and the methods available to investigate coal tar at particular sites and discusses how to develop a decision-making framework for coal tar investigations.

Background

The complex nature of groundwater migration in fractured bedrock and the complex chemical and physical properties of coal tar make it difficult to characterize groundwater aquifers in bedrock that may have been affected by a coal tar release. Some state and federal environmental protection agencies continue to monitor the literature to find definitive methods and solutions to contamination problems in bedrock aquifers, but only limited success has been realized in achieving groundwater protection goals established by numerical standards for drinking water protection. As a result, regulatory and professional focus has increasingly embraced a risk-based strategy that is based on establishing more realistic goals of groundwater resource protection. Advancements in characterization and mitigation technologies, coupled with more reasonable groundwater protection goals, provide an opportunity to address coal tar impacts in bedrock aquifers and ensure that resource protection goals can be achieved.

Objectives

- To provide an overview of the fate and transport of coal tar in bedrock
- To describe the methods available to investigate coal tar at particular sites
- To develop a decision-making framework for coal tar investigations.

Approach

The project team conducted a literature search on the fate and transport of coal tar in rock and the methods available to investigate coal tar at particular sites. They discussed the best ways to develop a technical decision making framework for investigating the state of the bedrock at MGP sites, including the creation of a conceptual site model (CSM), the selection and evaluation of investigative methods, and the use of decision support tools.

Results

This report presents an overview of the chemical and physical characteristics of coal tars and explains how coal tar chemical characteristics may affect the fate and transport of coal tar in fractured geologic media. The report discusses the transport and fate of coal tar, as well as the nature and extent of the associated groundwater plumes in bedrock.

One of the most challenging tasks associated with an MGP site investigation is how to address a coal tar release when coal tar is suspected to have entered into the underlying bedrock at a site. Investigating bedrock with invasive techniques, such as drilling, requires careful planning and execution. The introduction of physical stresses caused by drilling into bedrock can significantly change migration pathways, sometimes connecting previously disconnected fractures. Because of these risks and the technical limitations associated with the physical identification of coal tar, it is desirable to put an emphasis on characterizing the bedrock structural framework in order to increase the resolution of site maps and make adequate monitoring possible with less drilling and fewer monitoring wells. The use of conventional geologic mapping techniques, coupled with the application of improved geophysical methods, may provide all of the bedrock characterization data required to determine the location and number of monitoring wells necessary to achieve the resource protection goals. Site managers should develop appropriate project objectives and exercise extreme caution and technical judgment throughout the planning and execution of an investigation for suspected coal tar contamination in bedrock.

EPRI Perspective

The management and technical decisions associated with addressing bedrock groundwater issues at MGP sites require a great deal of technical and non-technical information to provide the basis for more informed decision making. The summary presented in this report provides a discussion of possible decision support activities that site owners may use to focus a bedrock investigation activity.

Keywords

Manufactured gas plant (MGP) Dense non-aqueous phase liquid (DNAPL) Fractures Coal tar Porosity Joints

ABSTRACT

Manufactured Gas Plant (MGP) sites often produced a complex mixture of organic compounds known as coal tar. Because of the potential adverse environmental and health affects that are associated with some of the chemical constituents in coal tars, MGP sites have increasingly been the focus of investigation and remediation efforts in the United States and internationally. Coal tar present in the subsurface at MGP sites can percolate through the soils and into the bedrock beneath a site, leading to contamination of bedrock groundwater aquifers. Although the tars produced at different MGP sites slightly differ with respect to their composition, MGP tars mostly share a common physical and chemical property range that supports the qualitative prediction of their fate and transport in bedrock.

Investigating the nature and extent of coal tar in bedrock can be difficult, costly, and highly uncertain as a result of the complex chemical characteristics of coal tar, the heterogeneous geologic framework and transport characteristics of bedrock, and the relatively limited number of methods available to identify coal tar and characterize the geologic framework. By systematically approaching a bedrock coal tar investigation, site managers can use a combination of available public information, gas production information, and geologic information to develop an effective investigation strategy. By considering a range of institutional, public, and site-specific information, a site manager increases the likelihood that a bedrock investigation for coal tar can be efficiently completed.

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1 INTRODUCTION

One of the most challenging tasks associated with an MGP site investigation is how to address a coal tar release when coal tar is suspected to have entered into the underlying bedrock at a site. Over time, coal tar that has been released at a site may have percolated through the soils and entered into the bedrock, potentially resulting in the contamination of groundwater in bedrock aquifers. Characterizing groundwater aquifers in bedrock that may have been affected by a coal tar release can be an extremely difficult, resource intensive task due to the complex nature of groundwater migration in fractured bedrock, and the complex chemical and physical properties of coal tar.

The difficulty in characterizing the vertical and horizontal extent of impacts to bedrock aquifers is not limited to MGP sites. Some state and federal environmental protection agencies continue to monitor the literature to find definitive methods and solutions to contamination problems in bedrock aquifers for decades, and have sponsored the development of interest groups and technical forums specifically to discuss how to best manage groundwater problems in bedrock and improve upon the technologies that can be employed to evaluate and manage bedrock groundwater issues. However, even as significant resources and professional interest has focused on resolving the technical problems associated with characterizing and managing bedrock groundwater contamination, limited success has been realized in achieving groundwater protection.

As a result, regulatory and professional focus has increasingly embraced a risk-based strategy that is based on establishing more realistic goals of groundwater resource protection. Even as these risk-based goals provide a less prescriptive standard to be achieved, bedrock site investigations continue to provide significant technical challenges to remediators due to the relatively limited technologies available for use and the low certainty associated with the available methods. Most commonly accepted investigation methods, such as installation of monitoring wells, involves high capital costs and relatively limited decision certainty. Finally, once contamination in bedrock has been determined to be adequately characterized, there may often be little that can be done to restore the bedrock aquifer.

Advancements in characterization and mitigation technologies, coupled with more reasonable groundwater protection goals, provide an opportunity to address coal tar impacts in bedrock aquifers and ensure that resource protection goals can be achieved. The U.S. EPA introduced the concept of technical impracticability (TI) in order to formally acknowledge that all contaminants identified in the subsurface may not be practically removable, and provides a mechanism for the appropriate adjustment of groundwater resource protection goals to achievable standards. As a result, MGP site managers have been able to satisfy regulatory requirements and complete the site investigation and remediation process without removing all coal tar from bedrock.

Introduction

Challenges Associated With a Coal Tar Investigation in Bedrock

Even as resource protection goals have been adjusted to more achievable endpoints, the difficulties associated with characterizing the complex fluid transport characteristics in bedrock, as well as the limited methods available to physically identify coal tar in bedrock, continue to present significant challenges to MGP site managers. Despite the various conventional and innovative technologies that are available to characterize the bedrock and identify chemical constituents in bedrock aquifers, there remains little to no direct means available to detect coal tar "in-situ". Because of the difficulty drilling into most types of bedrock, physical samples are difficult to obtain without driving the coal tar out of the sample before retrieving the sample at the surface. Thus, the most common way to identify coal tar in bedrock continues to be through the installation of bedrock monitoring wells. However, the probability that the installation of a bedrock well will intersect a fracture that contains coal tar is low.

Because of the challenge of physically identifying the source of coal tar contamination in bedrock, remediators often have little choice other than to use a "lines of evidence" approach to identify the presence and distribution of coal tar in fractured rock. The use of innovative coal tar identification methods, such as optical imaging techniques and partitioning interfacial tracer tests, offer improved opportunities to physically or qualitatively identify the presence and distribution of coal tar. However, methods to determine the spatial distribution of coal tar continue to be limited and subject to variable interpretation.

Because of the technical limitations associated with the physical identification of coal tar, placing increased effort in characterizing the bedrock structural framework, which defines the fate and transport pathway in bedrock, may increase the resolution of site characterization and lead to the installation of fewer groundwater monitoring wells. For example, the use of conventional geologic mapping techniques, coupled with the application of improved geophysical methods, may provide all of the bedrock characterization data required to determine the location and number of monitoring wells necessary to achieve the resource protection goals. Because these technologies do not require the disturbance of bedrock at the source area, the methods may also provide greater resource protection and lower the risk associated with advancing numerous boreholes within, or very close to, coal tar source areas.

Development of a Decision Making Framework

The characterization of bedrock groundwater and coal tar impacts is possibly one of the most complicated tasks associated with managing MGP sites, primarily as a result of the inherent uncertainties and data requirements that may not be practical to resolve. As such, management and technical decisions associated with addressing bedrock groundwater issues at MGP sites require a great deal of technical and non-technical information to provide the basis for more informed decision making. The summary presented in this report provides a discussion of possible decision support activities that site owners may use to focus a bedrock investigation activity. Emphasis is placed on the selection of technical methods, and how to select the most suitable method warranted by the degree of sensitivity to the bedrock fate and transport analysis.

2 OVERVIEW OF COAL TAR FATE AND TRANSPORT IN BEDROCK

The fate and transport of coal tar in bedrock is generally determined by the chemical nature of the coal tar present at a site and the characteristics of the bedrock geology. These two fundamental systems intrinsically determine where, and how, a particular coal tar will migrate and the rate it may attenuate. This means that a change in the conditions of either system will result in a change in the fate and transport conditions of the coal tar, which can then be observed in the spatial distribution of the coal tar and associated groundwater plumes.

Research regarding the behavior of coal tar dense non-aqueous phase liquid (DNAPL) in fractured geologic media has been relatively limited. Although there has been considerable research regarding the behavior of DNAPL in fractured rock, much of the published research has focused on the fate and transport of DNAPL associated with chlorinated solvents such as PCE and TCE. While the principle fate and transport processes are consistent from one type of DNAPL to another, the physical and chemical characteristics of coal tar DNAPLs are considerably different than those associated with other DNAPLs, such as chlorinated compounds. As a result, coal tar DNAPL exhibits unique fate and transport characteristics and chemical distribution patterns in fractured bedrock.

The integral relationship between the chemical properties of coal tar DNAPL and the physical and structural characteristics of a bedrock aquifer fundamentally determine the behavior of coal tar DNAPL in fractured bedrock. General and site-specific understanding of these two components is therefore necessary in order to identify and characterize the nature and extent of coal tar present in bedrock.

This report discusses the transport and fate of coal tar, as well as the nature and extent of the associated groundwater plumes in bedrock. Investigating bedrock with invasive techniques, such as drilling, requires careful planning and execution. The introduction of physical stresses caused by drilling into bedrock, as well as by the possible connecting previously disconnected fractures, can significantly change the migration pathway in bedrock. Site managers therefore should develop appropriate project objectives, and exercise extreme caution and technical judgment, throughout the planning and execution of an investigation for suspected coal tar contamination in bedrock.

This report also presents an overview of chemical and physical characteristics of coal tars, an overview of the geologic framework of consolidated materials, and how coal tar chemical characteristics may affect the fate and transport of coal tar DNAPL in fractured geologic media.

Chemical and Physical Characteristics of Coal Tar

Coal gasification, which resulted in the production of coal tar, was a common process used to manufacture gas from the mid-1800s through the mid-1950s, when manufactured gas was the primary source of gas used for lighting (illumination), heating, and cooking. Coal tars generally consist of a complex mixture of hydrocarbons that are produced as a result of the destructive distillation (carbonization) of coal or oil to produce gas (coal gasification) or coke. Coals tars are typically dense, non-aqueous phase liquids (DNAPL), with low solubility in water, high viscosity, and (relatively) low density (Kueper, et. al., 2003).

The chemical and physical complexity of coal tar provides unique challenges to the remediator when tasked to identify, characterize, and remediate coal tar present in the fractured bedrock environments. However, an understanding of the physical and chemical characteristics of the coal tar present at a site can provide a remediator with valuable information to estimate the location and extent of possible coal tar impacts in fractured rock. These data can aid the remediator in the development of appropriate management objectives and associated technical approach.

Tar Production

MGP sites generated tars as a by-product of the gas manufacturing process. There are three primary methods of gas production, including coal carbonization, water gas, and oil gas. A fourth method, rosin gas, which used rosin from Pine trees as the primary feedstock, was a method used at some smaller sites or early in the operational history of an MGP. The production methods generally produced tars with varying chemical and physical characteristics, and are often discussed in terms of their associated production method (e.g. water-gas tar, coal tar, oil gas tar). For example, water gas tars are generally known to be less viscous than a coal gas tar, although their elemental composition may be similar (EPRI, 1993). For discussion purposes, this technical update uses the term coal tar to encompass all of the different types of tar that may have been produced at an MGP since the focus of the update is on how tars from MGP sites behave in bedrock.

Many MGP sites used more than one method of gas production during its operational history, which can result in the generation of tars that have different physical and chemical properties. It is therefore not uncommon to identify more than one type of tar at a site. Being able to predict these different areas of possible tar handling and storage can enhance the efficiency of the site investigation and remediation process. It is therefore important to determine a plants operational history as early in the site management process as possible to provide important preliminary information to inform the site investigation process.

The following section presents a discussion of chemical and physical characteristics of coal tars, and how these characteristics may affect the distribution of coal tar at a given site.

The Chemistry of Coal Tar

Coal tar DNAPL is a complex mixture of hydrocarbons and is considered a "multi-component" DNAPL because it is composed of more than a single compound. The number of hydrocarbon compounds present in coal tar has been estimated to be anywhere from around 400 to several thousand individual constituents including light, middle, and heavy oil fractions (Environment Agency, 2003), and includes monocyclic aromatic hydrocarbons (MAHs), poly-aromatic hydrocarbons (PAHs), phenols, heterocyclic oxygen, nitrogen, sulphur, trapped (residual) water, organic carbon, ash, and debris such as sand and silt.

The chemical nature of coal tar generally depends on the temperature of the carbonization process and the source (type) of coal used in the gas manufacture operations at a particular site. As such, the chemical nature of the "virgin" coal tar produced at an MGP facility will vary as a result of changes in feedstock, operational enhancements of the MGP process facilities. Variations in chemical composition of the coal tar are also affected by the mechanism in which coal tar entered into the subsurface and other natural processes acting on the coal tar in the environment. Notwithstanding, the chemical constituents in coal tars from different sites are relatively consistent, while the concentrations of PAHs in tars form different sites may be highly variable (EPRI, 1993).

The predominant class of chemicals present in typical coal tar is PAHs, with naphthalene typically being the most prevalent compound. Research has demonstrated the chemical variability of coal tars generated at different MGP sites, and particularly between coal tar samples collected from the same site. MAHs, particularly benzene, toluene, ethylbenzene, and xylene, are typically present in coal tars at order of magnitude lower concentrations than the predominant PAH constituent fractions, although the relative distribution of MAHs and PAHs in coal tar samples are similar (Brown, et. al, 2006).

A significant fraction of constituents in coal tar cannot be quantified using common extraction and chromatographic techniques. This fraction, sometimes referred to as pitch, is related to the composition of the feedstock materials, and consists of aromatic compounds with high molecular weight and low aqueous solubility. While the pitch component of coal tar may not be a concern with respect to groundwater contamination, these components significantly influence the equilibrium portioning and the rate of release of the more soluble constituents such as benzene and naphthalene (Lee, et. al., 1992).

Coal Tar as a Complex Mixture

Coal tar DNAPLs are considered "complex mixtures" due to the number of chemical constituents present in coal tars. Contaminants composed of a single compound are known to behave "ideally", which removed some uncertainty when predicting their behavior in the subsurface. Because of the high number of chemical constituents found in coal tar, predicting or modeling changes in coal tar chemistry or behavior over time may be difficult and uncertain, although some evidence suggests that constituents in tars behave close to ideally (Peters, et. al., 1999, Eberhardt and Grathwohl, 2002).

Overview of Coal Tar Fate and Transport in Bedrock

Natural weathering and attenuation processes acting on the coal tar cause the chemical composition of coal tars to change over time, and can significantly alter the relative abundance of individual compounds present in the coal tar. The compositional changes over time are largely the result of the large differences in aqueous solubility of the chemical constituents present in coal tar, which favors the relative depletion of the lighter, more volatile fractions from the coal tar mass. Given relatively stable geochemical and hydrologic conditions, the changes in chemistry over time typically results in increased coal tar density, viscosity, and molecular weight, and a decrease in equilibrium partitioning of organic compounds from the coal tar mass into groundwater. This is due to the loss of the more soluble fractions.

Research efforts have shown that coal tars often behave similar to "ideal" solutions, suggesting that the equilibrium partitioning may be predicted using fundamental principles of chemistry and conventional modeling techniques (Peters, et. al., 1999, Eberhardt and Grathwohl, 2002, Kueper, et. al., 2003). Raoult's Law has been shown through laboratory and field-scale research efforts to be a reasonably accurate means for estimating aqueous concentrations of coal tar constituents (Lee, et. al., 1992). Specifically, it is generally accepted that the resulting concentrations of coal tar constituents present in groundwater are proportional to the mole-fraction of the individual constituents present in the coal tar mass (Kueper, et. al., 2003). Reasonable predictions can be made with respect to the concentrations of MAHs and PAHs in groundwater that is in contact with a source of coal tar (Lee, et. al., 1992).

An important factor to consider with respect to the possible dissolution of coal tar constituents from a coal tar mass into groundwater is the rate of dissolution. Because of the limited solubility of coal tar constituents and the chemical complexity of a coal tar mass, the dissolution processes acting on coal tar in fractured bedrock can be extremely slow, and therefore the extent of the associated groundwater plumes are limited by the dissolution kinetics.

There is a growing body of research that indicates the effective solubility of organic compounds is influenced by the presence of other organic compounds. For example, the solubility of PAH compounds has been shown to increase in the presence of naturally occurring organic compounds (Grundl, 1997).

Chemical Variations in Coal Tar Caused by Differential Weathering

Natural weathering (e.g. chemical decay, volatilization) and attenuation (e.g. dissolution, bioattenuation) processes can also affect the chemical nature and composition of coal tar that is exposed to the environment. The weathering processes acting on a coal tar mass may not uniformly affect the entire mass of coal tar, and will typically affect the more soluble and volatile fractions present in the coal tar. Thus, significant chemical variations may occur within the coal tar mass itself, and cause enrichment of certain NAPL-phase mole fractions (PAHs) to the point of their solubility limit. Because most PAHs are solids in their pure state at ambient temperatures, this enrichment may result in the formation of solid-phase within the coal tar mass (Peters, 1999).

Natural weathering processes may result in a significant stratification of chemical composition within a coal tar mass. For example, the associated weathering processes will readily act upon the outer portions of the coal tar mass that are directly exposed to the weathering force. In a

typical environmental setting, such as in a rock fracture where a coal tar mass may be present, the outer portion of the coal tar mass may be exposed to a weathering agent (e.g. oxygen or microorganism) that may volatilize or metabolize certain chemical constituents present in the coal tar. The weathering of the coal tar surface may cause a thin interfacial film which may alter the mass transfer and fluid mechanics of coal tar in fractured bedrock (Luthy, et. al., 1993, Nelson, et. al., 1996).

The chemical composition of coal tar, specifically the concentration of the MAH and PAH fractions, is therefore an important consideration particularly when identifying source areas, evaluating groundwater concentrations, and estimating the fate and transport of the resulting groundwater plume resulting from dissolution of chemicals present in a coal tar mass.

Physical Characteristics of Coal Tar

The physical characteristics of coal tar, which are directly related to the chemical composition of the coal tar, will play an important role in how the coal tar will enter into, and behave within, a fractured rock environment. This discussion will focus on physical properties of coal tars that play primary role in determining the spatial distribution of the coal tar and resulting groundwater plume, and include specific gravity (or relative density), viscosity, interfacial tension, capillary pressure, and wettability.

Typically, an investigation associated with coal tar in bedrock is predicated by the confirmation of a source of coal tar in the unconsolidated materials overlying the bedrock. In cases such as these, it can be useful to measure the physical properties of the coal tar sources identified in the unconsolidated "source" zone to develop preliminary understanding of possible coal tar migration scenarios and fate and transport with respect to the site conceptual model.

Coal Tar Density

Coal tars typically have densities that are slightly higher than that of water. The relative density, or specific gravity, of coal tars typically range from around 1.01 to 1.424 (EPRI, 1993, Environment Agency, 2003). Because coal tars are denser than water, their tendency is to sink when immersed in water. As a result, coal tar will generally migrate downward in saturated and unsaturated bedrock formations as a result of gravitational forces, given a *physical pathway* by which it can travel.

Because transport of coal tar is density-dependant, coal tar migration is not determined specifically by the direction of groundwater movement (as is typically the case with LNAPLs). However, coal tar migration can be influenced by groundwater flow as it migrates laterally and vertically. For example, if groundwater is flowing through rock fractures, and coal tar enters (from above) into the fracture, the coal tar may travel both laterally (in the direction of groundwater movement) and downward within the fracture network. This may continue until the source of coal tar is depleted, the aperture of the fracture is reduced and prevents further migration, due to matrix diffusion, or a combination of variables.

Viscosity

Viscosity, which is a measurement of the internal friction present in a liquid, refers to a fluids relative resistance to flow (high viscosity = high resistance to flow). Coal tar is typically characterized as a highly viscous liquid, although water gas tars are generally much less viscous than coal gas tars (EPRI, 1993), which can often be in solid phase. The viscosity of coal tar is considerably greater than water and other DNAPLs (e.g. chlorinated solvents), and varies from one MGP site to another due to differences in coal tar chemistry. Coal tar viscosity can also vary within an MGP site owing to the different methods of gas manufacture and differential subsurface chemical weathering of the coal tar mass. In any event, coal tars with relatively high concentrations of naphthalene and MAHs typically have lower viscosity than coal tars that are rich in PAHs (EPRI, 1993).

Like most oils, the viscosity of coal tar is dependant on its temperature. As such, the viscosity of coal tar must be calculated or measured with respect to the site-specific conditions that the coal tar mass is subject to when evaluating the fate and transport of coal tar in bedrock. As such, the viscosity of a coal tar mass should generally be determined on a site-specific basis and is best to measure from a sample of coal tar collected from the site under consideration.

Because coal tars typically have a high resistance to flow relative to water, traditional methods (e.g. pumping) to recover coal tar in bedrock generally result in the preferential extraction of groundwater and minimal recovery of DNAPL.

Interfacial Tension

The ability of coal tar to migrate into a rock fracture is directly related to the coefficient of interfacial tension of the coal tar material (Kueper, et. al., 2003). Interfacial tension refers to the surface free energy, which exists as a tensile force, at the surface (interface) between two immiscible fluids, such as coal tar and water. Interfacial tension prevents immiscible fluids, including coal tar, from being infinitely soluble in water, and is expressed as force per unit length. As such, when coal tar is in the presence of water, the energy barrier produced by interfacial tension prevents the coal tar from becoming fully emulsified into the groundwater. Coal tar interfacial properties, such as interfacial tension and contact angle, has been shown to be dependent on aqueous pH (Barranco and Dawson, 2001).

The interfacial forces associated with coal tar play a critical role in the fate and transport of the coal tar mass. For example, the force (pressure) required for coal tar to enter into a fracture *(fracture entry pressure)* is generally a function of the size, or aperture, of the fracture and the interfacial tension of coal tar (Kueper, et. al., 2003). As the interfacial tension of coal tar increases, the amount of force necessary to permit the coal tar to invade the fracture increases. Because of the interfacial tension between water and coal tar, coal tar will accumulate above a fracture before it can overcome the entry pressure of the fracture and enter into the fracture. The accumulation is often referred to as a "pool". As such, the pool height is directly proportional to the interfacial tension, and inversely proportional to the difference between the density between groundwater and coal tar (Kueper, 2003).

Measurement of interfacial tension of coal tar can be performed using several methods, including the ring method, drop weight method, spinning drop method, and capillary height method (Adamson, 1960; Miller and Neogi, 1985).

Capillary Pressure

The *capillary pressure* is the difference between the fluid pressure of the coal tar and water phases, and is the absolute fluid pressure measured at the fracture interface (The Groundwater Resource Protection Group, University of Sheffield). In order for coal tar to enter into a rock fracture or the rock matrix, the capillary pressure at the fracture interface (the area where the coal tar mass is directly adjacent to the fracture) must exceed the fracture entry pressure (Pankow and Cherry, 1996). Fracture entry pressure is discussed later in this chapter.

For fractures that are groundwater saturated, the capillary pressure is the difference in fluid pressure between the wetting phase (typically the groundwater) and non-wetting phase (typically coal tar). Thus, if a rock fracture is dry, the resulting capillary pressure required for the coal tar to enter the fracture will be lower versus if the fracture contains groundwater.

DNAPL pools may form above bedrock until the capillary pressure exceeds the entry pressure of the bedrock. Similarly, a pool of coal tar is formed within the fracture network when a migrating DNAPL is prevented from making further progress through the fracture by an increase in capillary resistance; caused, for example, by narrowing of a fracture aperture (Kueper, et. al., 2003, Slough, 1999).

Wettability

Wettability refers to the affinity of an immiscible fluid (such as coal tar or other oils) to a solid surface when in the presence of another fluid or multiple fluids (e.g. water) (U.S. DOD, 1997). In practical terms, it is the degree to which the coal tar may physically contact the solid surface of a rock fracture or rock matrix that is groundwater saturated. Wettability is therefore an important condition that can severely limit, or enable, the mobility of coal tar in fractured bedrock, as well as the development and persistence of the groundwater plumes associated with the presence of coal tar in bedrock fractures. As such, there has been increased focus by the research community regarding the conditions that affect wettability with respect to DNAPL fate and transport, and remediation, in fractured bedrock.

When a liquid is "perfectly water wetting", the groundwater is distributed over the entire solid surface of the fracture or rock pore matrix, and prevents other liquids (the "non-wetting" phase) from physically contacting the solid surface. The angle between a liquid and the solid surface (e.g. the bedrock fracture) is called the contact angle. In general, the wetting phase is considered to be the liquid phase that exhibits an angle of contact to the solid surface of less than 90°. The non-wetting phase generally has a contact angle of less than 90°, as exhibited in the figure below (http://www.dnapl.group.shef.ac.uk/).



Figure 2-1

Water Wetting Condition (DNAPL has Less Affinity for the Solid Surface than Water, Contact Angle < 90°)



Figure 2-2 Coal Tar Wetting Condition (DNAPL has Greater Affinity for the Solid Surface than Water, Contact Angle > 90°)



Figure 2-3 Neutrally Wetting DNAPL Condition (Coal Tar and Water Exhibit Equal Affinity to the Solid Surface)

Figures 2-1 through 2-3 reprinted by permission of The Groundwater Protection Group.

It may be concluded from the figures that the adsorption of coal tar to the rock surface is greater when the coal tar is the wetting phase. As a result, when coal tar is the wetting phase, it may be relatively immobile, but dissolution of chemicals from the coal tar into the groundwater may result in long-term impacts to groundwater.

The contact angle is a function of the chemistry of the coal tar (relative polarity of the chemical constituents) and groundwater at a site, and is also influenced by the chemical composition of the bedrock solid material that coal tar and water may be exposed to (U.S. DOD, 1997). It is therefore likely that, at the site scale, variable degrees of wettability are present.

A bedrock fracture that is water saturated (prior to the coal tar release) is perfectly water wetting. When coal tar is introduced to the fracture system, the wetting relationship can change, resulting in either coal tar wetting conditions, water wetting conditions, or both. Depending on the degree of wetting by the coal tar within a fracture, the coal tar mass may be fully, or partially, immobilized under non-stressed aquifer conditions (e.g. typical non-pumping, equilibrium conditions) and diffusion into the rock matrix may be more significant. Wettability has been shown to be related, in part, to the pH of groundwater (Barranco and Dawson, 1999, Hugaboom and Powers, 2002).

The significance of wettability should not be underestimated when planning to investigate the suspected presence of coal tar in bedrock. For example, if we assume that the bedrock aquifer was originally perfectly water wetted (or perhaps partially water wetted) under fully saturated conditions, it may be reasonable to assume that, if coal tar has entered into the rock fracture, the aquifer system likely retains the highest degree of water wetting that is supported by the physiochemical nature of the aquifer system under non-stressed conditions. If the system is then subjected to a stress, either via drilling, pumping, dewatering, or other physical aquifer stresses commonly induced during intrusive environmental investigations, it is not clear whether the wetting conditions in rock fractures may be negatively affected, which could have a negative impact on groundwater quality and the potential recoverability of the coal tar mass.

The Geologic Framework

The geology underlying a particular site can be extremely diverse and will provide the basis for the spatial distribution of DNAPL at an MGP site. It is therefore important to review available information regarding regional and local geology in order to develop an initial understanding of the conceptual site model (framework) as it relates to the potential bedrock transport pathway. Performing this task early on will provide a site manager with information to estimate where coal tar may be located in the rock, how far and in what direction the coal tar may have migrated, and what methods may be suitable to identify and characterize the nature and extent of coal tar at the site. Section 3 discusses several planning-level techniques and methods for characterizing the nature and extent of coal tar in bedrock.

Bedrock Matrix and Porosity Considerations

Soil Versus Bedrock Porosity

The fate and transport of groundwater and coal tar through consolidated geologic media (bedrock) is fundamentally different than in unconsolidated (soil) media. In unconsolidated materials, fluid migration occurs through the pore spaces in the soil matrix (primary porosity). The pore spaces may be natural pore spaces in native soils, or pore spaces and conduits associated with anthropogenic activities (e.g. the installation of a subsurface utility). Fractures in soils are generally limited to cohesive soils such as silt and clay-rich materials that have either dried following deposition, or been deformed by slumping, loading, or tectonic activity (Fetter, 1994). In most cases, fractures in unconsolidated materials do not define or control the transport pathway in the unconsolidated zone. Rather, the geometry of the primary porosity (effective porosity) of unconsolidated materials provides the open spaces for the transport and fate characteristics of groundwater, liquids, and vapors present in the unconsolidated materials.

Overview of Coal Tar Fate and Transport in Bedrock

The porosity characteristics of consolidated materials are significantly different than those found in unconsolidated material. Similar to the porosity found in unconsolidated media, consolidated (bedrock) materials also have primary porosity, which is typically referred to as matrix porosity. Matrix porosity observed in rock formations will vary widely from one rock type to another and is lower than that of their parent materials due to diagenetic factors (e.g. compaction, cementation). The matrix porosity in rock is simply the interconnected open spaces between grains that were not completely compacted together or sealed by cementation or melting and cooling (as in metamorphic or igneous rocks).

A significant difference between the fate and transport characteristics of unconsolidated and consolidated materials is due to the *secondary* porosity found in consolidated materials. Secondary porosity refers to void spaces associated with fractures, joints, bedding plane partings, and dissolution channels. Secondary porosity will vary as a result of the post deposition conditions the bedrock was exposed to, and is usually very localized. Most all rocks have secondary porosity, and, as such, "dual-porosity" models have been developed to simulate fate and transport conditions in bedrock, as discussed in Chapter 3.

Secondary porosity is usually a very small percentage of the total (bulk) porosity in bedrock, and typically ranges from 0.001 to 0.01 in fractured rock (Kueper, et. al., 2003). However, because coal tar and other fluids prefer to travel along the pathways of least resistance (the larger openings), secondary porosity is responsible for the majority of fluid and solute transport in bedrock. Table 2-1 lists the general range of *total* porosity of several rock types, which is a cumulative expression of a rock's matrix and secondary porosity.

Type of Rock	Range of Porosity
Fractured Basalt	5 – 50%
Karst Limestone	5 – 50%
Sandstone	5 – 30%
Limestone, Dolomite	0 – 20%
Shale	0 – 10%
Fractured crystalline rocks	0 – 10%
Dense crystalline rocks	0 - 5 %
Pumice	Up to 87%

Table 2-1 Range of Total Porosity for General Bedrock Types

(Domenico and Schwartz, 1990)

* Listed range of total porosity includes primary and secondary porosity.

Primary and secondary features in bedrock can vary significantly over a very short distance both vertically and horizontally at a site, and affect the fate and transport of coal tar in much different ways. Thus, developing an understanding of both the rock matrix properties and secondary features of the associated bedrock units is fundamentally essential to properly identifying the presence or absence of coal tar, and characterizing the nature and extent of coal tar within the bedrock at a coal tar site.

Matrix Porosity

As coal tar and contaminated groundwater moves through a fractured rock aquifer or comes into contact with the bedrock matrix, it may diffuse from the fracture into the rock's pore water, or, in the case of coal tar, may physically enter into the pore space of the rock material. Once coal tar enters into the pore spaces in the bedrock matrix, the forces of diffusion and adhesion may prevent the coal tar from being physically removed from the matrix. As a result, for sites where coal tar has entered into the rock matrix, restoration to high degrees of water quality are not likely, even after coal tar has been removed from within the fractures, due to the back diffusion of coal tar constituents from the matrix into the rock fracture (Kueper, et. al., 2003).

For bedrock aquifers that have both relatively high matrix porosities and matrix diffusivities (e.g. sandstones), it can be particularly difficult to remove or purge coal tar or the associated contaminated groundwater from the rock matrix. The pore spaces in rock, which define the matrix porosity, are often considered stagnant with respect to fluid transport because most rocks have relatively low matrix porosity. Although coal tar and groundwater are unlikely to travel significant distances through the rock matrix alone at most MGP sites, coal tar and impacted groundwater diffusion out of the matrix make achieving a high standard of groundwater quality unlikely (Kueper, et. al., 2003). As such, the matrix porosity of bedrock is an important factor to consider when planning an investigation for coal tar contamination in bedrock.

Bedrock Matrix Diffusion Considerations

Matrix diffusion is the process by which solutes (NAPL and its chemical constituents in groundwater) flowing through rock fractures diffuse into the open pores of the rock matrix. The process can also occur in reverse, whereby fluids (NAPL and/or groundwater) present within the pores of the rock matrix can diffuse out of the matrix and into a rock fracture (Kueper, et. al., 2003). However, if coal tar DNAPL enters into the pore space of the rock, it is not clear whether it will remobilize out of the rock matrix as a separate phase; rather, it is likely to release its chemical constituents back into the fracture via dissolution. Whether the constituents flow into (forward diffusion), or out of (reverse diffusion), the rock matrix is determined by the concentration gradient for dissolved-phase contamination (Kueper, et. al., 2003). Because of the limited ability for fluids to readily pass into and out of the rock matrix, coal tar, if present within the rock matrix, can result in long term impacts to groundwater quality and limit the success of groundwater restoration efforts in bedrock environments.

The degree to which coal tar may enter into the rock matrix via matrix diffusion is a function of the matrix porosity, fracture aperture, and fracture density (Reynolds and Kueper, 2002). Other conditions being equal, rocks with higher matrix porosity will have higher matrix diffusion coefficients, and low fracture density and small fracture apertures generally result in increased matrix diffusion. It follows that, with increasing fracture density and aperture, coal tars will migrate further through the fracture network and to a lesser degree into the rock matrix.

Matrix diffusion is an important variable to account for when performing coal tar fate and transport analysis or modeling. Additionally, because laboratory and field-scale research has shown that matrix diffusion coefficients are significantly variable at the site scale (Zhang, et. al. 2006), accounting for a reasonable range of matrix diffusion coefficients at a site is likely to improve the results of analytical and numerical modeling the fate and transport of coal tar.

Overview of Coal Tar Fate and Transport in Bedrock

Matrix diffusion processes can retard the rate of migration of coal tar and solute migration in bedrock groundwater. For example, the retardation factor will generally increase as matrix porosity increases, and as fracture aperture and density decrease. However, the diffusive retardation of coal tar migration in bedrock will limit restoration efforts of the aquifer as a result of long-term dissolution or reverse diffusion of coal tar constituents from the bedrock matrix into the fractures.

The depth into the rock matrix that coal tar or its constituents may penetrate is theoretically a function of the amount of time the contaminant is in contact with the rock matrix, particularly for residual coal tar materials that are no longer migrating through fracture network. As a result, the importance of matrix diffusion effects at former MGP sites may be significantly greater than for more recent types of contaminant releases due to the possibility that coal tar contaminants may have been present in the bedrock environment for relatively longer periods of time, resulting in potentially deeper penetration into the rock matrix. In these cases, slow dissolution of chemicals from the coal tar may cause long term affects to groundwater quality, and successful remedial efforts to high degrees of groundwater quality are not likely.

Surface wetting conditions within the bedrock (water wetting versus coal tar wetting) are important factors influencing the rate of, and degree to which, coal tar enters into the rock matrix (Bergslein and Fountain, 1999). If the surface conditions of the rock are coal tar wetting, coal tar may diffuse freely into the rock matrix. Because the degree to which the wetting conditions may be influenced by natural and induced aquifer stresses (e.g. drilling and/or pumping) is not well understood, extreme caution should be taken when investigating bedrock for the presence of coal tar.

Matrix Diffusion "Halos"

Recent research of matrix diffusion effects in sedimentary rocks have identified significant matrix diffusion "halos" in the rock matrix along fractures (Parker, 2003). Because of the likelihood that coal tar, if present in bedrock at an MGP site, has been in the bedrock for many years prior to the initiation of site investigation activity, it is possible that a significant percentage of the coal tar mass may now be present in the rock matrix rather than in the fracture network. Parker described a core collection and analysis method that can be used to identify diffusion halos in rock as well as to use the core analysis method to characterize contaminant transport pathways. This information is important with respect to characterizing source materials at MGP sites and the associated fate and transport of possible groundwater plume.

Bedrock Matrix Entry Pressure, Capillary Pressure, and DNAPL Saturation

Sudicky, et. al. (1998) found that "the horizontal and vertical extent of the zone of DNAPL contamination within bedrock is sensitive to not only the hydraulic characteristics of the different fracture networks generated from the same set of statistical parameters, but also the DNAPL entry pressure for the rock matrix". Results of the research suggest that characterizing the migration pathways of a DNAPL in fractured porous rock can be improved through greater understanding of the matrix and fracture properties of the bedrock. The research concludes that the matrix capillary pressure versus DNAPL-saturation relationship has a significant impact of the distribution of DNAPL.

The rock matrix capillary pressure versus non-aqueous phase saturation has traditionally been an important variable in the petroleum engineering industry, and may warrant developing measurement and modeling methods in support of environmental applications. One model, developed by O'Carroll, Polityka, Bradford, and Abriola (2004), predicts drainage into and uptake into a matrix for a range of wetting conditions, and concluded that the model resulted in good predictions of capillary pressure/saturation behavior. Further, the researchers conclude that the model is easy to implement and has relatively few input parameters. It is applicable to a broad range of wetting conditions.

Bedrock Secondary Porosity and Coal Tar Migration

Secondary porosity refers to the open spaces in bedrock associated with faults, fractures, dissolution channels, and other deformational processes that cause open space within a rock mass. These secondary features, while they comprise of a small fraction of the overall porosity of the rock, will typically characterize the conduits of the transport pathway that coal tar and groundwater will migrate through. The rock matrix adds complexity to the behavior of coal tar and solute transport within the fracture network, but typically is not a migration pathway for long-distance transport. Thus, in concert with key bedrock matrix features, secondary porosity plays a critical role in determining the spatial distribution of coal tar in bedrock. For purposes of discussion, the secondary porosity features are collectively referred to as fractures in the following section.

Figure 2-1 presents a depiction of the fate and transport characteristics of a coal tar release that has migrated through the soil column and percolated into the bedrock (Kueper, et. al., 2003). The figure also depicts the difference between a typical spatial distribution of coal tar in unconsolidated materials and the spatial pattern of coal tar distribution in fractured rock. Note how the resulting groundwater plumes in bedrock can far exceed the distance that the groundwater plume extends in the soil material.

The leading edge of the groundwater plume in the shallow aquifer and the bedrock aquifer is depicted by the red line. Note the considerably greater distance that the coal tar and associated dissolved-phase groundwater plume has migrated. Additionally, consider how the matrix diffusion (5) of constituents into the aquifer could present long-term groundwater implications after the coal tar has been depleted in the fractures and the concentration gradient reverses (when groundwater concentration in fracture becomes lower than groundwater concentrations in the bedrock matrix).

Bedrock, Weathered Bedrock, and Fracture Heterogeneity

As a precursor to discussing how fractures affect the migration of coal tar in bedrock, general awareness of weathered bedrock, bedrock, and common heterogeneities is necessary because of its importance with respect to coal tar fate and transport.

In humid and semi-humid climates, where rainfall is common and a shallow groundwater zone is typically present in unconsolidated materials overlying the bedrock, there is typically a transition zone between the soils and competent bedrock that consists of weathered bedrock. A weathered bedrock interval, or sometimes saprolite, is often present as a result of the continually active

Overview of Coal Tar Fate and Transport in Bedrock

forces of chemical erosion caused primarily by the presence of shallow groundwater, and by percolation and penetration of water into the rock matrix and shallow fracture network. The transition zone can vary significantly due to the variable resistance of rock materials to chemical weathering and the degree of fractures in the shallow bedrock.

In contrast, in arid climates, where rainfall is limited, the unconsolidated zone tends to be shallow and well drained, and shallow aquifers are relatively less common. As a result, chemical erosion is typically limited and weathered bedrock zones are often negligible.

A weathered bedrock zone is typically highly fractured and variably weathered compared to the underlying competent bedrock. As a result, the weathered bedrock can have significantly higher overall porosity than both the unconsolidated soils and the underlying competent bedrock. However, groundwater flow in the weathered bedrock interval is often stagnant compared to the flow in the shallower portion of the soil aquifer.

If coal tar has migrated downward into the weathered bedrock zone, a significant amount may accumulate as a pool and remain in the weathered zone unless the underlying competent bedrock exhibits a high degree of fracture density (Kueper, et. al., 2003). The coal tar may also become intermittently mobilized by the induced pressure of the overlying groundwater, especially during precipitation events, causing the coal tar in the weathered zone to be "pushed" in the direction of slope of the weathered bedrock-competent bedrock interface. For sites located adjacent to surface water, this can result in the intermittent discharge of coal tar into the surface water.

Fracture Entry Pressure and Coal Tar Migration

In order for coal tar to enter into the bedrock from the overburden soils, coal tar that has migrated downward to the top of bedrock must first exceed the residual saturation of the soil in order to potentially migrate further into bedrock. Once the coal tar residual saturation of the soil is met, coal tar will form a "pool" (free-phase coal tar) until it can enter into the rock matrix via processes described earlier, or enter into fractures in the rock. The formation of pools at the bedrock interface depends largely on the structure of the bedrock units, and is generally more likely to occur when the bedrock units are horizontal.

In order for the coal tar to enter into a fracture, the capillary pressure of the coal tar must overcome the fracture entry pressure (Pankow and Cherry, 1996). The fracture entry pressure is directly proportional to the interfacial tension of the coal tar and inversely proportional to the aperture of the fracture (Kueper, et. al., 1993). Thus, coal tar migration in bedrock occurs preferentially in the larger-aperture fractures of the bedrock fracture system. It is therefore important to determine the geometry of the large-aperture fractures in the bedrock matrix in order to characterize the nature and extent of coal tar in fractured bedrock.

Coal tar will continue to migrate downward into bedrock fractures until either the source of coal tar invading the fracture is depleted, or the fracture aperture reduces and inhibits further coal tar penetration. A relationship is presented (Kueper, et. al., 2003, Pankow and Cherry, 1994, Mercer and Cohen, 1990) between fracture aperture and pool height that can accumulate below the water table, as defined by the following equation.
$$H = \frac{2\sigma \cos\theta}{(P_{\rm N} - P_{\rm w})ge}$$

(Kueper, et. al., 2003, Pankow and Cherry, 1994, Mercer and Cohen, 1990)

- H = pool height;
- σ = DNAPL-water interfacial tension;
- θ = contact angle;
- $P_{N} = DNAPL$ density;
- $P_w =$ groundwater density;
- g = acceleration due to gravity; and,
- e = fracture aperture.

The equation assumes that the top of the pool is subjected to zero capillary pressure. Based on the equation, the pool height of coal tar that will accumulate above a fracture prior to entry into the fracture ranges from 0.33 feet for a fracture aperture of 815.8 μ m (micrometers) to 13.12 feet for a fracture aperture of 20.4 μ m (Kueper and McWhorter, 1991).

It thus follows that coal tar does not require a significant reduction in fracture aperture with depth to inhibit the vertical migration of the coal tar, although the same reductions will inhibit the formation of coal tar pools. Because of the influence of density, coal tar DNAPLs require a much smaller aperture fracture to inhibit downward migration and pool formation than other DNAPLs such as TCE.

Coal Tar Migration through Rock Fractures

Once coal tar has entered into a rock fracture, the coal tar will migrate along rock fractures that present the least capillary resistance, resulting in coal tar migration through the fractures of greatest aperture (http://www.dnapl.group.shef.ac.uk/frac.htm). However, coal tar will also enter the smaller aperture fractures as long as the capillary pressure of the coal tar is greater than the fracture entry pressure of the smaller aperture fracture. As a result, the orientation, density, aperture, and degree of interconnectivity of the fractures will determine the spatial distribution of the coal tar within the fracture network.

Fracture orientation is largely a function of the physical stresses a bedrock unit has been subjected to throughout its geologic history. Fracture orientation is typically measured as strike (geographic direction of the fracture surface) and dip (the angle of orientation of the fracture surface). The strike and dip of largest fractures will control the direction that coal tar will migrate in, while the degree of interconnectivity of the fracture network also play a key role in determining the spatial distribution of the coal tar in bedrock. Therefore, site-specific information regarding the presence of fractures, the density of the fracture network, fracture orientation, and the interconnectivity of the fracture network should be determined as part of the site assessment process.

Coal tar migration can occur through rock fractures both vertically and laterally. Vertical migration of the coal tar will generally dominate as a result of coal tar density and gravitational forces. However, if the fracture network is primarily characterized by laterally extensive

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fractures with relatively limited presence of vertical fractures, substantial lateral migration can also occur and the limited vertical fractures will provide the interconnections that result in further downward migration, as exhibited in Figure 2-4.

The fractures present in bedrock typically are not fully interconnected, and as a result, coal tar distribution within bedrock can be extremely difficult, if not impossible, to fully characterize and remove. An important factor to consider during the evaluation of coal tar in bedrock is the historical conditions that led to the spatial patterns observed at a site. For example, at a site where coal tar penetrated bedrock and entered into fractures, there may have been a sufficient volume of coal tar to support entry into very small, "dead end" fractures (a fracture that is not connected at both ends to other fractures). Coal tar in these fractures are not likely mobile or recoverable due to the forces of adhesion and the limited surface area of the coal tar that is exposed to the larger fracture. However, as previously mentioned, the dissolution of chemicals from these discontinuous fractures containing the "residual" coal tar may make restoration of the aquifer to high standards of water quality impossible (Kueper, et. al. 2003).

Groundwater Influence on Coal Tar Transport

Studies have shown that groundwater movement in rock fractures can influence the migration path, velocity, and channeling pattern of DNAPL within a fracture network (Ji, et. al., 2003). Gravity-driven DNAPL fingering, viscous DNAPL fingering, and aperture-controlled fingering may therefore influence the spatial pattern of the coal tar present to a certain degree. The degree to which groundwater flow in the fracture network may influence the migration of coal tar may be a function of the actual groundwater velocities within the individual fractures. It would follow that establishing a preliminary understanding of the groundwater flow system in bedrock, whether conceptually, or through the use of an analytical or numerical model, would be useful as a preliminary step as part of a coal tar investigation in bedrock.

It can be assumed that the spatial distribution of coal tar-related chemicals present in bedrock groundwater can also provide useful information regarding the distribution of possible coal tar in bedrock. The dissolution of chemicals from coal tar into the groundwater will result in aqueous-phase chemical plumes, which will follow the groundwater flow path. This is one reason why an "outside-in" approach, which focuses on characterizing the aqueous-phase plumes outside of the anticipated coal tar source area prior to characterizing the "source" zone, is sometimes selected to characterize possible coal tar in bedrock. A discussion of methods and techniques that can be used to characterize coal tar in bedrock is included in Chapter 3.



Figure 2-4 Conceptual Model of Coal Tar Transport Characteristics in Unconsolidated and Bedrock Aquifers

Figure Reprinted with Permission of Environment Agency (Environment Agency, 2003)

Regional and Local Scale Geologic Patterns and the Conceptual Site Model

Understanding the nature of bedrock units, their characteristics, and the associated structural patterns at the regional scale is fundamentally important with respect to planning and executing an investigation for potential coal tar contamination in bedrock at the local or site scale. In contrast to coal tar and groundwater fate and transport in the relatively shallow unconsolidated aquifer zones, which are typically controlled by conditions at the site scale, regional bedrock structure and the resulting hyrogeologic and hydrologic framework determine the boundary conditions that control the local bedrock groundwater aquifers.

The importance of the regional bedrock structural patterns is two-fold. The first is in support of the establishment of a Conceptual Site Model (CSM) that serves as the basis to identify what data is needed, and thus guide the process of data collection and evaluation. Information regarding the regional bedrock structure and hydrologic patterns bears upon the potential local-scale geologic structure, fractures, and hydrologic features that may have developed as a result of regional geologic processes. Obtaining site-specific information therefore integrates into the broader context and evaluation of possible transport pathways, sensitive receptors, and human health and natural resource protection objectives. When the site-specific geologic framework cannot be adequately represented within the context of the regional framework, it implies that there are data gaps in the site database and/or the CSM, which infers the need to obtain additional information to complete the CSM and support the project conclusions. However, in the absence of an understanding of the regional geologic framework, site-specific information can mislead the uninformed investigator to perform unnecessary and costly additional investigation activities that yield little to no benefit to the project.

Secondly, because the prospect of identifying all of the fractures that may contain coal tar is not likely, the understanding of regional geologic patterns can facilitate the proper selection of investigation techniques and the subsequent placement of borings and/or monitoring wells used to characterize the nature and extent of coal tar. Not only does this result in the maximized value of the data collected during a bedrock investigation, but also serves to minimize the potential for remobilizing residual coal tar and increasing the connectivity of migrations pathways in bedrock.

Regional geologic and hydrologic information may be obtained from a multitude of resources such as geologic maps, water well drilling and sampling reports, oil and gas exploration reports, file reviews of subsurface investigations performed at other environmental sites. Additionally, when the availability of public information is limited, preliminary geologic and hydrogeologic maps may be generated relatively easily by performing non-intrusive bedrock reconnaissance activities such as collecting geologic measurements (strike and dip, general fracture pattern and orientation) from local and regional bedrock outcrops, analysis of spatial structures and patterns (Schultz, et. al., 2006), and lineament and fracture trace analysis. Regional and local meteorological data can be used in conjunction with surface water and bedrock information to generate regional water budgets and create preliminary hydrogeologic maps such as flow nets, both of which can aid in the eventual fate and transport analysis of site-specific conditions following completion of intrusive site investigation activities.

These are typical sources can assist in the preliminary identification of regional and local-scale structural patterns and the understanding of the geologic framework associated with an MGP site. Additional discussion regarding the methods and techniques available to characterize regional and local-scale geology with respect to an investigation for coal tar in bedrock is included in Chapter 3.

Porous, Non-Porous, and Dual Porosity Groundwater Flow

Fluid Flow through porous media is generally well understood to occur through the continuous, interconnected pore spaces of unconsolidated materials as a function of the porosity, hydraulic gradient, the hydraulic conductivity, and the cross sectional area that flow occurs through. As a result, fluid flow in porous, unconsolidated media typically follows what is known as Darcy's Law, and is referred to as "Darcian flow". The principles of Darcian flow theory in most cases cannot readily predict groundwater flow in fractured bedrock due primarily to the fact that the majority of fluid transport in fractured bedrock occurs through the network of discrete, interconnected, heterogeneous fractures that do are not geometrically uniform in the spatial context.

It is true that Darcian flow theory and modeling techniques have been successfully applied to certain large-scale bedrock groundwater modeling activities where large, regional scale geologic features sometimes behave similar to porous media. In these cases, the fracture network is modeled as an Equivalent Porous Medium (EPM) by assuming that a representative elemental volume (REV) can be represented by defined hydraulic parameters (Anderson, 1992).

Arguments can be made to apply Darcian flow models in the rare cases where the fracture system is documented to be relatively uniformly distributed in three dimensions, where the aquifer hydraulic conductivity, specific storage, and total porosity are known, and where boundary conditions are known.

Note: Boundary conditions are representations of known conditions at the physical boundary of the study area (e.g. water table elevation, no flow boundary, etc.), or in groundwater modeling, a mathematical statement specifying a constant or flux at the geographic boundary of the study area/domain.

Notwithstanding, Darcian theory rarely can be applied to simulate or even estimate groundwater and/or solute transport in fractured bedrock at the local scale since it drastically oversimplifies the flow regime and typically produces results that do not reflect observed conditions.

Fluid flow in bedrock is characterized by porous characteristics and non-porous, discrete fracture flow characteristics (Anderson, 1992). Rapid fracture flow occurs through discrete fractures and secondary features, while relatively slow diffuse flow occurs within the matrix of the fractured bedrock. The two flow domains are not mutually independent, although the general flow pattern within each of the domains is generally not affected by the flow domain of the other. The fluid flow within the block (bedrock) matrix follows principles of Darcian (diffuse) flow theory, while the fluid flow through discrete fractures generally follows fracture geometry and is independent of the flow through the rock matrix. Calculation of flow through the discrete fracture also assumes no flow in the block.

As a result, fluid and solute transport in bedrock occurs as a result of its dual porosity: the secondary porosity of the non-porous, discrete fracture domain; and the primary porosity of the porous matrix domain (Gringarten, 1982). Additionally, in rocks that are highly soluble, such as limestone, a third flow domain referred to as *conduit flow* is superimposed on the primary and secondary porosity domains. Conduit flow in limestone is referred to as karst. The geometry of the conduit system controls the transport of materials within the conduit domain, and, as might be surmised, is extremely difficult to characterize.

Solute Transport in Dual-Porosity Bedrock Domains

As previously discussed, diffusion of coal tar into the bedrock matrix can occur in rocks that have sufficient interconnected matrix porosity (generally, non-crystalline, porous rock types) to allow coal tar and groundwater penetration into the pore spaces. In such cases, chemicals will diffuse either into, or out of, the rock matrix and the fracture network based on the principles of chemical diffusion. As such, it is possible that concentrations that approach chemical solubility limits may occur in bedrock groundwater as a result of reverse diffusion (Kueper, et. al, 2003), even when pooled or residual coal tar is not present in the fracture network. This condition can be misinterpreted as indicating that coal tar is present within the fracture network, when it may be present in the rock matrix. It is therefore important to consider the possible matrix characteristics of bedrock underlying a site in the planning, implementation, and evaluation of information obtained during a coal tar investigation in bedrock.

Fluid Flow in Different Types of Geologic Media

For fractured bedrock that has little to no matrix porosity, fluid flow generally occurs within the discrete fracture network, with very limited invasion of the matrix. Metamorphic and some rocks of biochemical origin are examples of rocks that have limited matrix porosity. For other geologic materials that have considerable matrix porosity (dual porosity), fluid flow and solute transport occurs within the rock matrix and within the discrete fracture network. Lastly, in certain cases, some biochemical rocks, such as limestone and dolomite, transmit fluids through matrix porosity, fracture porosity, and dissolution channel (conduit) porosity, which some refer to as "triple porosity".

Multiphase Flow Considerations

When coal tar and water are both present in bedrock, the transport system behaves as a two phase system. Fluid flow within the two phase system is governed primarily by pressure of the phases, the degree of saturation with respect to each phase, and the relation between the permeability and the degree of saturation. The relationship between these variables is non-linear and complex.

It is likely evident that the importance of understanding the principles of fluid flow and solute transport (e.g. coal tar and dissolved chemical constituents) in fractured and non-porous fractured media is fundamental to determining how to plan and implement a bedrock investigation for coal tar, as well as how to choose an appropriate modeling technique to apply to a site.

The Role and Implication of Geologic Structure on Coal Tar Transport in Fractured Bedrock

Previous sections in this report have summarized characteristics of coal tar and bedrock materials that affect the fate and transport of coal tar in bedrock. It has been shown that the density of coal tar will cause it to migrate with respect to the secondary porosity present in fractures, faults, and dissolution conduits. In this section, we present a discussion of how the orientation of bedrock structures affect the migration and distribution of coal tar after it has mobilized in the subsurface.

The orientation of bedrock units can cause coal tar to become "trapped" and become physically impeded from further migration. Similar to how oil and gas may become trapped in a "reservoir", coal tar may also become trapped in small scale structural features that result in accumulations of coal tar within the trap. Bedrock structure refers to the orientation of the bedrock unit and the shape of the features created by their position relative to other geologic formations. A detailed discussion of bedrock structures will not be presented herein. However, a short discussion regarding types of structures and how they may affect coal tar transport is presented.

Bedrock may be formed in a layered manner, such as in sedimentary rocks and some volcanic rocks (lava), or as irregularly-shaped masses, such as with metamorphic and igneous rocks. In all cases, the formations may be deformed causing the units to be inclined, folded, or faulted. The top and bottom surfaces may be eroded, causing irregularities.

Considerations regarding the importance of common bedrock structures are discussed below.

Inclined Bedding and Folds

When bedrock has been subjected to compressional geologic stress, its position can become inclined and/or folded. The angle of the rock's inclination is referred to as the dip, whereas the imaginary line created by the intersection of the inclined plane and its original horizontal position is referred to as the strike. For a fold, the axis parallel to the fold is the strike, the limbs of the fold are measured as the dip, and if the axis of the fold is inclined, it is said to be a plunging fold, and the plunge may also be measured relative to horizontal. The strike is therefore always oriented at a right angle to the dip. Strike and dip are important concepts that must be considered in a bedrock coal tar investigation.

Coal tar that migrates vertically and comes into contact with an inclined geologic unit is likely to enter into the formation along bedding planes, and may migrate *down-dip* along the plane of the bedrock. If the strike is also inclined, the coal tar will migrate *down-dip* and *down-strike*. As previously discussed, the flow of groundwater in bedrock may influence coal tar migration *within a fracture*, but it generally will not affect coal tar migration along a structural surface such as a bedding plane. Thus, if the dip of the bedrock is in the hydraulically upgradient direction (bedrock surface deepens in the upgradient direction), or is transverse to groundwater flow, the direction of coal tar migration will be different than the direction of groundwater flow. Coal tar will continue to migrate along the inclined plane until one of the following conditions is met:

- 1. the source of coal tar is depleted or insufficient to support continued migration (capillary pressure < capillary resistance);
- 2. the opening along the bedding plane is too small and inhibits continued migration;
- 3. a bedrock fracture of sufficient aperture intercepts the coal tar and facilitates it's transfer into the fracture network or a different bedding plane;
- 4. an impenetrable unit is encountered due to a fault of other unconformity; or,
- 5. the dip of the rock upturns and forms a trough (a concave fold), potentially forming a structural trap if the rock is sufficiently non-porous and not fractured to contain the coal tar.

Coal Tar and Structural and Stratigaphic Traps

Coal tar migration can be impeded by structural and stratigraphic traps much in the same way as in oil and gas reservoirs. Folds, unconformities, subconformities, piercements (intrusions of impermeable rocks), fault seals, and combination fold/fault traps can all impede the further migration of coal tar. Figure 2-5 depicts idealized versions of structural and stratigraphic traps and how coal tar may be impeded. It follows that coal tar can become trapped in many small-scale features at a site depending on the geologic framework. As in the oil and gas industry, identifying and characterizing the geometry of these features can be a challenging endeavor.

One type of trap that is not depicted on Figure 2-5 is the fracture trap. Because coal tar DNAPL can penetrate into dead-end fractures, it can remain in the fracture until it either fully diffuses into the matrix of the surrounding rock or diffuses into the groundwater moving through the adjacent fracture. A dead end fracture is not considered a structural or stratigraphic trap, but is a common manner in which coal tar becomes trapped in the bedrock, and has similar implications to long-term groundwater quality.

Although stratigraphic and structural traps are critically important to an oil exploration project, the features may be of greater importance to environmental projects than is recognized in the environmental community. While identifying all areas where coal tar may be trapped in the bedrock at a site is not likely or practical, a combination of non-intrusive and intrusive methods may be the most practical approach to identify the presence and general geometry of possible bedrock traps containing coal tar. Techniques and methods that can be employed to characterize the bedrock framework and the presence of coal tar are discussed in Chapter 3.



(dark shaded area depicts idealized coal tar 'accumulation areas')

(figure modified from Hyne, 1984)

Figure 2-5

DNAPL Structural and Stratigraphic Traps

3 METHODS AND TECHNIQUES AVAILABLE TO INVESTIGATE AND EVALUATE COAL TAR IN BEDROCK

The evaluation of possible coal tar in bedrock may occur, or be triggered, at nearly any point during the process of investigating or remediating a site. The decision to investigate for possible coal tar in bedrock may arise as a result of indications that coal tar is present at the interface between the bedrock and the unconsolidated zone, as a result of the discovery of a coal tar seep in a bedrock outcrop or riverbed, or because of the known or suspected shallow depth to bedrock in the vicinity of a site. The decision of when to evaluate whether coal tar may be present in bedrock is dependent on the circumstances associated with an individual site, and as such, are not discussed in this summary. However, the following section presents a summary of the various techniques that are available to evaluate for the presence of coal tar before, during, or following the investigation or remediation of coal tar constituents at a site.

The following section is organized in a chronological sequence, beginning with planning-level investigation techniques and methods, non-invasive (indirect) field investigation techniques, and invasive (direct) field investigation techniques and methods. A discussion of various modeling strategies is included, followed by a short discussion regarding the general limitations of technologies, and developmental or research opportunities that may be engaged to improve the process of investigating for coal tar in bedrock.

Planning-Level Techniques for Evaluating Coal Tar in Bedrock

The planning process for evaluating whether coal tar may be present in bedrock at a site can begin as early as the site-prioritization process and during the planning stage of an initial site investigation, or as a result of confirming the presence of coal tar in the unconsolidated materials at a site. The techniques that may be selected generally depend on the specific objectives of the evaluation. Typical planning techniques and methodologies are discussed in the following subsections along with a general summary of how the information produced by these strategies may support various evaluation objectives.

Publicly-Available Records

A strategy for determining the likelihood that coal tar may be present in bedrock prior to initiating a site investigation is to review available public records. Table 3-1 lists common sources of public information that may aid in the development of a focused bedrock investigation and reduce the time, effort, and costs of performing intrusive investigation techniques. Public

Methods and Techniques Available to Investigate and Evaluate Coal Tar in Bedrock

records can provide a range of information to support activities such as a probabilistic evaluation of the potential for coal tar in bedrock, development of a conceptual site model, and details regarding local and regional bedrock fracture patterns, aquifers, and background environmental conditions.

Type/Source of Information	Information Obtained	Possible Uses
Soil Surveys (State/Federal)	Type and thickness of soil, presence/absence of known confining units, degree of saturation, depth to groundwater, relative permeability	 Develop Conceptual Site Model Probablistic evaluation for coal
		tar in bedrock
		 Initial evaluation of possible vertical and lateral coal tar fate and transport
		 Development of initial coal tar investigation locations and methods
Topographic and Geologic Maps, Aerial Photography, Satellite Images,	Type and thickness of bedrock, regional geologic structure, fracture abundance and patterns, depth, yield, chemical conditions of groundwater aquifers, presence of springs and outcrops, and surface water features.	Refine the Conceptual Site Model
Remote Sensing Data (State/Federal)		Characterize local bedrock fate and transport pathway
		 Determine applicable and appropriate investigation techniques, methods, and locations
		 Identify critical water supply units, resource protection goals
Water Well Records	Depth to bedrock, type of bedrock, depth to groundwater, type of aquifer(s), water quality, groundwater use and supply information.	 Establishment of bedrock investigation method
(Local, State, Federal)		Determine approximate depths to sampling zones
		 Identify possible influences on, and receptors of, bedrock groundwater flow
Water Quality Surveys	Aquifer chemistry, background water quality conditions, potential for groundwater use (present, future)	Develop groundwater protection goals
(Local, State, Federal)		Characterize aquifers
		Initial fate and transport analysis
		Risk Assessment
Surface Water and Precipitation Data (State, Federal)	Continuous river flow data, rainfall data	Development of hydrologic and hydrogeologic framework
		 Water budget/fate and transport support
Geological Research Reports	Detailed bedrock matrix conditions, complex groundwater flow characteristics, critical geologic controls on groundwater aquifer	 Support investigation in complex geologic environments

Table 3-1Examples of Publicly-Available Information and Possible Uses

Local and Area Bedrock Reconnaissance

A relatively simple technique that can assist in the planning or completion of a bedrock investigation is to complete a survey for local and area bedrock outcrops (where competent rock is present at the surface). Outcrops can provide important information such as the identification or confirmation of the possible depth and type of bedrock present and the structural characteristics of the bedrock, such as strike and dip of bedding planes, fractures, and folds. In cases where local outcrops are abundant, a reasonable geologic map may be prepared in a short amount of time which can provide extremely valuable insights regarding the potential direction of coal tar migration, and spatial distribution of potential coal tar and related groundwater plume if present in bedrock.

Particular caution should be used during the selection of local outcrops to be measured to ensure that surficial processes have not dislodged the outcrop from the underlying bedrock. In these cases, poor measurements collected may not accurately represent the structural characteristics of the bedrock mass and lead to misinterpretations.

Coal Tar Characterization Data

If coal tar has been identified in unconsolidated materials, analytical data regarding the chemical and physical properties of the coal tar can be obtained to guide the planning of the investigation into the bedrock. As discussed in Section 2, the chemical and physical properties of coal tar are important with respect to determining the transport and fate characteristics of the coal tar. The availability and use of this information during the planning process can remove some of the uncertainties associated with the bedrock investigation and provide a means for more informed decision making.

Lineament and Fracture Trace Analysis

Surface lineaments are often related to the dominant structural features in bedrock and highyielding groundwater fractures in bedrock aquifers. As previously discussed, the dominant fracture network typically controls the groundwater hydraulics in a fractured bedrock aquifer. Therefore, identifying lineaments can provide valuable information to guide the planning and implementation of a bedrock investigation for coal tar.

Lineaments are generally identified from aerial photographs and satellite imagery. Surface lineaments may include ridges, streams, valleys, linear tonal variations in surface soil, and anomalous vegetation patterns. A lineament will exhibit a uniform direction of orientation. These features, when identified, can be correlated with statistical trends observed in fracture measurements to assist in determining the location of bedrock test borings that may be used for geophysical tests, hydraulic tests, or installation of bedrock groundwater monitoring wells.

The location of known springs and wells can also be used in conjunction with lineament and fracture trace analysis to assist in determining the most transmissive fractures (Raymond, et. al., 2006).

Non-Invasive (Indirect) Field Investigation Techniques

Aside from performing local and area bedrock reconnaissance activities, non-invasive field investigation techniques are relatively limited. However, non-invasive surface geophysical methods are available that can be applied for bedrock coal tar investigations. Surface geophysics have been used effectively for many years in other environmental applications, as well as for oil and gas exploration. The use of these methods has been relatively limited at coal tar-related sites. Because the methods offer the same advantages to a coal tar investigation as they do for other applications, the limited use at coal tar sites may perhaps be due to institutional factors rather than the availability or potential value to a bedrock coal tar investigation.

The use of non-invasive geophysical methods is generally determined by site-specific project objectives, and typically is applied to characterize the complex stratigraphy and structural framework of the bedrock environment. In general, non-invasive geophysical methods are selected with respect to the information that is needed to fill data gaps in the conceptual site model for the bedrock pathway, and can be employed using a "tool box" approach in conjunction with other investigation techniques. The selection of a surface geophysics method is based on the advantages and disadvantages of the available methods, site-specific parameters, and other institutional factors. In any event, evaluating the use of these technologies prior to implementing an often expensive program of installing bedrock monitoring wells can provide strategic and technical value to a coal tar investigation project. Data obtained during the non-invasive work may reduce the number of bedrock wells needed to be installed during a project by providing qualitative and quantitative subsurface information used to constrain and reduce the uncertainties regarding how many wells may be needed, where to locate initial bedrock wells, what methods should be used to drill wells, and how deep a well network may need to be advanced.

There are a number of non-invasive geophysical methods that can be engaged to characterize the complex bedrock structural framework and anisotropy in the bedrock environment. Commonly used and widely available geophysical methods include ground penetrating radar (GPR) methods, electromagnetic (EM) methods, electrical methods, seismic methods, and magnetic methods. Several resources are available that offer details about the methods, and include advantages and disadvantages associated with their use and application. One resource, "Site Characterization Technologies for DNAPL Characterization" (U.S. EPA, 2004), is available directly from the internet at the following website:

• http://www.clu-in.org/download/char/542r04017.pdf

Over the past decade, advances in imaging and data processing technology have resulted in significant improvements to geophysical investigation techniques. These improvements have led to the use of the term "hydrogeophysics", and are accompanied by increased regulatory acceptance due to the expanded research and application at environmental sites (Baker, 2005). Although the majority of non-invasive geophysical methods are intended to characterize the structural and hydrogeological framework of the bedrock, recent advances in geophysical methods have introduced methods that can identify NAPL present in bedrock (Baker, 2005). Magnetic resonance (MR) imaging has been used to characterize DNAPL flow and fracture geometry in bedrock (Becker, et. al., 2003), as well as fracture aperture distribution (Dijk, et. Al., 1998), which, as discussed in Section 2, are bedrock structural features that play a critical role in the distribution, and entry of, coal tar in bedrock fractures.

Examples of notable advancements in non-invasive geophysical methods include the characterization of fracture flow anisotropy using seismic refraction tomography (Baker, 2005), the mapping of structural pathways using induced polarization methods (Hughes and Carlson, 2003), and the identification of structural hydrocarbon traps using relative amplitude (RAM) processing of seismic reflection data (Morgan and Schneider, 1981).

Example of Beneficial Use of Surface Geophysics at an MGP Site in New York

Coal tar was observed in limestone beneath glacial till at a former MGP site in upstate New York. A combination of non-invasive methods, including bedrock maps, aerial photographs, fracture trace analysis, area reconnaissance, surface seismic, down hole geophysics, and square-array resistivity were used to complete the assessment of the extent of coal tar in the limestone. The use of square-array resistivity identified linear features that coincided with strike and dip measurements at a conjugate joint sets observed in a nearby rock outcrops, confirming the presence of a lineament or a fault, and facilitating the mapping of the coal tar migration pathway along the bedrock structural feature (Zak, 2001).

Invasive (Direct) Field Investigation Techniques

Invasive field techniques generally involve the advancement of a boring into bedrock in order to perform hydrogeologic profiling, obtain groundwater samples, perform subsurface geophysics, install groundwater monitoring wells, or a combination of these activities. Prior to selecting a method to be used at a site, it is important to determine what information is necessary to be obtained and to evaluate the available methods of obtaining the information. The selection of invasive field techniques to be applied can be guided by the understanding of what data gaps need to be resolved in order to refine or complete the conceptual site model, and can be employed using a "tool box" approach.

Because of the complexity of the bedrock environment, the importance of evaluating and selecting appropriate technologies to be used at a site is critical to the success of the investigation. Unlike in coal tar investigations in unconsolidated materials, the installation of monitoring wells located in "first water" may not provide much useful or defensible information with respect to determining whether coal tar, or a groundwater plume associated with a release of coal tar, is present in the bedrock. This is largely attributable to the complex, heterogeneous fracture flow patterns and fate and transport complexity of the bedrock environment, discussed in Section 2. As such, the robustness of the planning phase of an investigation can determine the relative success or failure of a bedrock investigation.

There are numerous ways in which technologies may be combined in order to achieve the specific objectives of a bedrock investigation for coal tar, and the merits of each should be evaluated on a case-by case basis. For the purpose of this technical update, the invasive methods presented are limited to common methods that may be applied to identify and characterize coal tar in bedrock, are organized into three categories: drilling methods, detection and characterization methods, and monitoring methods. Examples of emerging technologies are included where appropriate.

General Risks Associated With Performing Intrusive Bedrock Investigations for Coal Tar

A concern with performing an intrusive investigation for coal tar in bedrock is the significant possibility that disturbing the bedrock may considerably affect the migration pathways, and distribution of coal tar in the fractured rock. This risk is generally associated with all types of rock, and should factor into any plan to perform an invasive investigation for contamination in bedrock. Drilling into, or through free or residual coal tar, or even a fracture filled with groundwater affected by coal tar contamination, can result in remobilizing the coal tar or impacted groundwater in vertical and lateral directions by creating new hydraulic connections between previously disconnected fractures and migration pathways. Certain drilling methods, such as air rotary, which forces high volumes of air into the formation to advance the borehole, may also physically exacerbate the distribution of coal tar or related groundwater plumes.

One common way to minimize the risk of cross contamination is to perform the investigation using an "outside-in" approach. This generally involves characterizing the structural and stratigraphic framework in the bedrock outside of the area of suspected coal tar impact, and subsequently performing investigation within the source area so as to avoid cross contaminating the known transport pathways. While this method has certain merits, it may not always result in lend itself to completing the vertical delineation of impacts in an efficient cost-effective manner. Some methods, such as rotasonic drilling, can install protective casing during the advancement of a borehole, which may assist in limiting the possibility for carrying coal tar impacts deeper into the subsurface or opening conduits between previously disconnected fractures. In all cases, plans to invasively investigate for coal tar in bedrock should attempt to minimize the exacerbation of environmental impacts in bedrock.

The potential influence of certain types of drilling activities on the surface wettability of bedrock in the presence of coal tar DNAPL may be an area where research is warranted in order to ensure that the environmental efforts to manage groundwater resources are not negatively impacting long-term groundwater quality.

Drilling Methods

Performing invasive investigations into bedrock generally requires the use of drilling equipment to establish a borehole. The selection of an appropriate drilling method is determined by the type of rock formation(s) present at a site and the detection or monitoring methods selected for the investigation. Once a borehole is established, specific structural and stratigraphic characterization methods, or coal tar detection or monitoring techniques, can be selected in order to obtain the information needed to satisfy the project objectives.

In general, drilling methods capable of advancing a borehole in bedrock are well known, and will not be discussed in detail this technical update. Drilling methods generally include, air rotary, mud rotary, rotasonic, and cable tool drilling methods. Variations of each method exist, each having unique advantages and disadvantages. Drilling methods are typically selected based on availability, relative ability to penetrate the bedrock, ability to maintain an open borehole, ability to minimize cross contamination during drilling, safety factors, and volume of drilling wastes incurred during drilling operations. An important factor to consider when selecting a drilling methodology is how the borehole is intended to be used. The drilling method should be selected to support the selection of a particular method to detect and characterize coal tar or characterize the hydrogeology.

Screening for Evidence of Coal Tar During Drilling in Bedrock

Rock cuttings and borehole fluids returned to the surface during drilling the borehole can be visually inspected for evidence of coal tar, screened using photoionization techniques, or screened using other methods such as use of dyes or ultra-violet light. As a borehole is advanced, PID measurements collected from a reasonably safe distance from the borehole and recorded in conjunction with the drilling depth may provide additional clues regarding whether at what depths DNAPL may be present, although this method can be complicated by coal tar or impacted materials penetrating the borehole at shallower intervals.

Borehole Logging During Drilling

Observation of drill stem rate of penetration can offer useful information regarding the presence of fractures and other structural features. While the information is qualitative, correlation of the depths where penetration rates significantly change may yield valuable insight regarding the bedrock structure in the absence of more definitive methods. Observing rock cuttings throughout the advancement of the borehole may also yield information regarding bedrock lithology. When combined with other observations, such as PID measurements and drill stem penetration rate, these observations may be critical to correlating the body of data acquired throughout the bedrock investigation program.

Coal Tar Detection and Characterization Methods

Detecting the presence of coal tar in bedrock, as well as characterizing the nature and extent of coal tar in bedrock, can be accomplished using a variety of down-hole techniques. While the installation of groundwater monitoring wells is generally well known and widely applied, this summary will also focus on the application of other tools to support the characterization of bedrock and potential coal tar and aid in the selection of aquifer zones in which to install permanent monitoring wells.

Rock Coring

Rock coring involves the use of a drill rig capable of extracting intact rock cores from a boring. Rock cores provide quantitative data regarding the relative abundance and dip angle of fractures, and the stratigraphy and type(s) of rock present at a site. Additionally, rock matrix porosity data may be obtained from rock cores, which can be used to estimate diffusion coefficients as part of a fate and transport analyses. Additionally rock cores may be examined for potential diffusion halos, as discussed in Section 2. Methods and Techniques Available to Investigate and Evaluate Coal Tar in Bedrock

Rock cores may also be used to identify the presence of coal tar, either within the rock matrix or in secondary porosity features such as fractures and along bedding planes. However, the absence of coal tar in a rock core does not provide conclusive evidence that coal tar is not present in the rock. The disturbance of the bedrock during coring and drilling may result in the evacuation of coal tar from the collected rock core, especially in the larger aperture fractures where adherence to the solid surface may be limited. For small scale features, such as very small bedding plane partings, coal tar may not immediately be recognized during the inspection process. Bringing the cores to approximate room temperature (70 $^{\circ}$ F) can facilitate the process of visually inspecting rock cores.

Oriented cores offer the additional advantage of providing geospatially oriented structural characteristics of strike and dip, which are very useful in determining the potential direction of possible coal tar migration and accumulation in bedrock. In the absence of well known bedrock orientation near a site, oriented rock cores can be an effective technology to identify coal tar and characterize the structural framework of the bedrock. However, the absence of coal tar in rock cores may not provide conclusive evidence that coal tar is not present in bedrock, and as such, rock cores are most useful in establishing the physical and structural characteristics of the bedrock.

Rock coring is often used as an initial activity to refine the site conceptual model, and to provide information that may guide subsequent drilling programs and characterization activities.

Borehole Geophysics

There are a number of borehole geophysical methods that can be employed to investigate possible coal tar contamination in bedrock. Similar to the non-invasive surface geophysical methods discussed previously in this report, the use of invasive geophysical methods is generally determined by site-specific project objectives, with methods selected with respect to the information that is needed to fill data gaps in the conceptual site model for the bedrock pathway using a "tool box" approach. The selection of borehole geophysical methods is highly site-specific and based on the respective advantages and disadvantages of the available methods.

The use of borehole geophysics can similarly provide strategic and technical value to a coal tar investigation project. Data obtained may assist in selecting groundwater monitoring zones and reduce the number of bedrock wells needed to be installed during a project by reducing the uncertainties regarding well siting and increase the amount of information provided from boreholes drilled into the rock.

Geophysical methods that may identify and characterize coal tar in bedrock are relatively limited. However, advancements in partitioning tracer test (PITT) technology suggest that coal tar may be able to be mapped three dimensionally using tracer data (Pope, 1998). PITT have typically been conducted to estimate the volume of coal tar, and not as an identification technique. In general, the use of PITT has been relatively limited due to the costs of implementation.

Geophysical techniques, such as natural gamma, single point resistance, spontaneous potential, caliper, fluid temperature, fluid resistivity, borehole flow meter, acoustic televiewer, and optical televiewer may also be used to characterize hydraulically-active fractures and determine the spacing and orientation of the fractures (Bridge, et. al., 2001). These methods are often used to determine the appropriate zones to collect groundwater samples or install permanent monitoring systems. Certain methods, such as combining the acoustic and optical borehole imaging tools, provide the specific location and orientation of structural bedrock features (Johnson, 2002). Developments in imaging technology have significantly increased the resolution of the optical imaging techniques, which provide an alternative to collecting oriented rock cores. Crosswell tomography, a method that emits signals from a source in one borehole to a receiver in other boreholes, can be applied in 2-dimensional or 3-dimensional arrays, can be used to characterize the structural characteristics of fractures and other bedrock features (U.S. EPA, 2004).

As previously mentioned, specific information regarding geophysical techniques, their application, advantages, and disadvantages, can be obtained from the "Site Characterization Technologies for DNAPL Characterization" (U.S. EPA, 2004), which is available directly from the internet at the following website:

• http://www.clu-in.org/download/char/542r04017.pdf

Example of Beneficial Use of Down Hole Geophysics to Support Closure at an MGP Site

Site-specific selection of geophysical methods was conducted at an MGP site in Pennsylvania to support the refinement of the site conceptual model, characterize bedrock impacts due to coal tar, and inform the decision making process regarding the vertical and horizontal distribution of associated groundwater plumes and monitoring network. The site was located in an urban area near surface water bodies and local supply wells. A combination of down hole geophysical methods were used to support the refinement of the conceptual site model, select appropriate intervals for monitoring well installation, and complete the fate and transport analysis. The geophysical methods provided appropriate data to support the reduction in the number of bedrock wells required to be installed in the dense, urban area, and reduced the time and cost to complete the characterization of coal tar impacts in the bedrock.

Packer Testing

Packer testing involves the use of inflatable assemblies lowered into a boring to isolate selected intervals in an open borehole. Once the interval is isolated, groundwater tests can be performed. Groundwater tests facilitated by packer testing include groundwater sampling (often coupled with onsite or rapid analysis), and hydraulic characterization (pump tests and measurement of hydraulic pressure). Packer assemblies include multipurpose straddle packers, straddle packers, and single packer assemblies. Packer testing can be useful in determining the vertical extent of groundwater impacts, groundwater flow gradients, selection of intervals to be included for groundwater monitoring, as well as correlating fracture connectivity with other site wells. Use of the technique can reduce the number of monitoring wells required to complete a bedrock groundwater evaluation. A disadvantage of packer testing is the general need to establish an open borehole for testing, which could result in temporary cross-contamination between aquifer zones. Packer testing is not a method used to identify the presence of DNAPL.

Methods and Techniques Available to Investigate and Evaluate Coal Tar in Bedrock

The United States Geological Survey (USGS) developed a multi-function Bedrock Aquifer Transportable Testing Tool (BAT³), which is similar to the multi-function packer system, but includes the ability to conduct single hole tracer tests by injecting and later withdrawing a tracer solution (Shapiro, 2001). Pressure transducers above, within, and below the packer assembly measure hydraulic responses to pumping the selected interval. As in conventional packer assemblies, the tool is lowered into an open borehole to desired intervals selected for testing.

Bedrock Monitoring Well Placement and Construction

The selection of the location and number of monitoring wells necessary to be installed is generally based upon the objectives of the investigation and the efficacy of the information obtained during planning activities. As previously mentioned, an "outside-in" approach is often used as a means to characterize stratigraphy, structural characteristics of the rock, and to define and characterize the aquifers that are relevant to the coal tar investigation. This allows the majority of the monitoring wells installed at a site to be used solely for monitoring and environmental protection purposes, while invasive activities in the suspected source area can be limited so as to avoid negative environmental consequences. Initial wells outside of the source area may be placed strategically to intercept bedrock groundwater flowing along defined bedrock structural features in the direction of identified receptors, such as a potable supply well or a spring. Investigation wells within the suspected area of coal tar contamination are typically placed at areas where coal tar was observed at the bedrock interface or near the suspected primary coal tar source areas.

In the absence of qualitative or quantitative bedrock structural information, monitoring wells can be installed to evaluate multiple aquifers. Nested well pairs or multi-zone groundwater monitoring wells can be constructed in a single borehole to monitor multiple water-bearing zones.

Bedrock Groundwater Concentration as a Coal Tar Indicator

As described by Kueper, et. al. (2004), observed groundwater concentrations can be back calculated to estimate whether a coal tar source is likely to be present at or upgradient of a monitoring well. If chemical concentrations of the coal tar source are known, the chemical concentration can be expected to be roughly 1% of the effective mole fraction of the particular compound. Other factors such as borehole dilution (caused by multiple fractures intersecting the monitoring interval) should be accounted for when evaluating groundwater data against the calculated solubility limit of a respective compound.

Modelling Strategies

Groundwater models are used to predict how groundwater system may behave given a set of defined criteria. The use of a model to predict the behavior of a chemical plume in fractured rock associated with coal tar can be a difficult, time-consuming task. However, when the questions that models are asked to answer are well defined, selecting an appropriate model and completing a modeling exercise can be relatively straightforward.

The development of a modeling strategy begins with the development of the conceptual site model. As the CSM is refined, groundwater modeling objectives are identified, groundwater model parameters become better understood, and uncertainties and data gaps regarding the bedrock groundwater pathway are identified.

Relatively straight-forward questions such as "Is the plume expanding?" or "Is the plume contracting?" can sometimes be answered using a plume stability analyses approach, which generally are based on statistical methods to analytically demonstrate the behavioral of chemicals a groundwater plume. However, when a model is needed to more complex groundwater issues, such as the possible discharge of chemicals in bedrock groundwater to a nearby stream, diffuse-flow models often cannot simulate the complex chemical fate and transport in bedrock groundwater. The complex diffusive properties, fracture heterogeneity, and multi-phase flow characteristics at a fractured bedrock site may require a more complex discrete fracture model.

Models applied to complex fractured bedrock environments need to account for the bedrock matrix domain (the flow into and out of the bedrock matrix), and fracture domain (flow within the discrete fractures and secondary porosity features) in three dimensions, and simulate the interaction between the bedrock matrix and fracture system. Numerical models such as CompFlow have been applied to depict multi-phase advective, dispersive, and diffusive flux of NAPL in fracture domain (Slough, et. al., 1997). Discrete fracture network models (DFNMs) can incorporate the three-dimensional nature of the fracture system and also incorporate the transport of the fluid phase through the fractures; however, the vast data needs and the range of values for specific model parameters make their use limited (Weatherall and Lerner, 2004).

As discussed in Section 2, equivalent porous media (EPM) models may be able to simulate groundwater and solute behavior in bedrock fractures if a representative elemental volume (REV) of the fracture system can be represented by defined hydraulic parameters (Anderson, 1992). The EPM approach may be applicable in cases where the fracture system and rock matrix is documented to be relatively uniformly distributed in three dimensions, where the aquifer hydraulic conductivity, specific storage, and total porosity are known, and where boundary conditions are known.

4 DEVELOPING THE DECISION MAKING FRAMEWORK FOR A COAL TAR INVESTIGATION IN BEDROCK

Developing a Management Approach

Site owners are faced with making a number of decisions regarding how to manage former MGP sites. The decision making process regarding the management of a site or group of sites may be highly complex within an organization, or may be a relatively simple formula. In either case, a successful management strategy may involve the development of objectives which are in turn supported by information that can be used as the basis for making informed decisions. Because of the variety of technical and non-technical factors that may affect how a site is addressed, the objectives, method for establishing objectives, or process of managing and implement an investigation for coal tar and it's constituents in bedrock are best developed at the organizational level.

Developing a decision making approach can be extremely useful as it will serve to guide the management of all technical and non-technical factors that may arise. For investigations in bedrock, the decision making framework may address any number of elements, such as:

- the likelihood a bedrock investigation may occur
- when and how to begin planning
- what will be, or how to determine, the proper objectives
- what methods may be used to meet those objectives
- what, and when, key stakeholders may be involved.

The elements mentioned above are presented as an example of certain factors that may assist a party in developing a decision tool that can meet the specific objectives of the organization. These types of questions may be developed and addressed for a single site or portfolio of sites without conducting any onsite activities. An organization can determine what types of decisions it can anticipate during the process, which may be related to environmental factors, regulatory requirements, community concerns, technology availability, and business constraints, and the specific management objectives associated with the decisions. Establishment of clear objectives and the management framework often predicates the success of the technical objectives.

Developing a Technical Decision Making Framework

A bedrock investigation in coal tar can be extremely complex as a result of the chemical and physical complexity of coal tar, the complex nature of bedrock environments, and the difficulty and limitations associated with investigating deep into the subsurface bedrock. Establishment of the project technical objectives early on in the process is important with respect making decisions throughout the process of implementing a bedrock investigation. By establishing the technical project objectives, a determination can be made with respect to what information is needed, what methods are available to obtain it, and how information will be used to support the project objectives.

Establishing Objectives

The establishment of project technical objectives for a bedrock investigation is an important first step to developing technical approach. Project objectives are typically guided by natural resource protection goals and requirements, human health and ecological protection goals, and risk management goals. Identifying the appropriate factors that may influence the establishment of, and satisfaction of the technical goals is an important initial step to developing a decision making framework. These factors may include the relative flexibility of the regulatory objectives, proximity of a site to groundwater users or other sensitive groundwater receptors, or other specific risk management objectives.

It has been relatively accepted in the professional community that, once coal tar has entered into bedrock, the restoration of groundwater near the source area is generally not achievable to a high standard.

The Relationship Between the Decision Framework, the Conceptual Site Model, and the Tool Box Approach

Once technical objectives can be anticipated or are established, a framework can be established regarding how technical decision will be made throughout the planning and implementation of the bedrock investigation. The complexity of the framework may reflect the complexity of the technical and non-technical factors associated with a site. The complexity of the bedrock investigation can be estimated early in the process by developing a preliminary conceptual site model (CSM).

The decision framework can be further informed by the development of the preliminary (CSM). As part of the CSM, an owner may establish a preliminary understanding of the bedrock environment, how fluids may travel laterally and vertically within the bedrock, the mechanisms that may affect the transport of fluids present in bedrock (e.g. infiltration, pumping of wells), and where fluids may discharge (e.g. river, lake, regional groundwater basin). Once these types of information have been obtained, an owner can begin to identify the likelihood that coal tar may be present in bedrock, where to begin investigating, and how complex an investigation may be. Additionally, the CSM will establish what information may be needed to fill gaps in the CSM, when such information may be necessary, and provide preliminary guidance regarding the technical methods that may be necessary to obtain the information.

A "tool box" type of approach can be used to identify the optimal methods and sequencing of activities used to fill data gaps in the CSM. Similarly, the CSM can be used as a tool to guide not only the data that is needed, but the selection of the technical methods used. For example, if a bedrock monitoring well network is installed in the initial groundwater zone encountered in a bedrock aquifer, its use may be limited because of the lack of information used to characterize the bedrock structural framework that controls bedrock flow. Additionally, the defensibility of the dataset may also be limited due to the inability to draw meaningful technical conclusions from the hydraulic head and chemistry data alone. As an alternative, the use of non-invasive and invasive techniques (described in Section 3) available to characterize the groundwater flow pathway in bedrock can remove uncertainties in the bedrock transport pathway and provide an owner with greater decision certainty and control throughout the execution of the project. Doing so in advance can reduce the total cost associated with installing and monitoring bedrock monitoring wells and the resources needed to complete the bedrock investigation.

Selection and Evaluation of Methods

A key component of the technical decision making framework is the identification of appropriate technical methods that will be used to address site-specific needs. For example, if the site conceptual model has identified that the bedrock structural pathway is highly heterogeneous, it may be inappropriate to use a common groundwater flow model such as ModFlow (which assumes diffuse flow aquifer characteristics) to evaluate the fate and transport characteristics. Additionally, if bedrock orientation is identified as a data gap in the coal tar migration pathway, and the method selected to fill the gap is the collection of bedrock cores, although the cores may be useful in providing lithologic an fracture data, they will not determine the direction of strike and dip of the bedrock fractures and bedding planes unless the cores were collected using oriented coring equipment, which is more costly. It would be an unfortunate circumstance to consider this after completing a bedrock coring activity. However, if strike and dip data is available from other sources, the cost of performing oriented cores may be avoided.

These are just a few examples of how the method used to characterize bedrock must be part of the decision making framework to ensure the information obtained can fulfill the data gaps in a CSM and meet project objectives.

Decision Support Tools

Technical decision support tools can be established to address the needs of a site or portfolio of sites. An integrated approach to developing an effective decision support tools is to design the tools to reflect the management techniques used by a respective party of company. Decision support tools can include the guidance documents, relational databases, generic work plans and methods, and other organizational tools that can be referenced to assist in making decisions.

There are a number of available resources in the public domain that can be used to assist a company in developing appropriate decision support tools desired.

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