Abstract

Kunberger, Tanya Marie K.. Temperature Effect on Desorption Kinetics of Benzene on Various Soils. (Under the direction of Mohammed Gabr.)

Since the advent of diesel fuel use, insufficient storage and inadequate transport and disposal practices have resulted in widespread contamination of the subsurface environment. Beginning in the 1970's, the United States EPA has established a number of regulations controlling current and future storage, transport, and disposal efforts and address the need to remediate existing contaminated sites. However, regulations provide only the desired goal, not a roadmap of how to accomplish remediation. It falls then, to individuals in research and industry, to devise techniques effective in reducing / eliminating contamination levels at sites of concern.

Existing remediation techniques of pump and treat and air sparing / soil vapor extraction are effective, but often take many years to accomplish remediation to regulatory levels. Thermal treatments such as steam stripping and electrical heating of soils, are much less time consuming, but much more costly endeavors. Low temperature thermal desorption (at temperatures less than 80 °C) holds promise by incorporating the benefits of higher temperatures, such as the increase in vapor pressure and the decrease in viscosity, without the extreme cost usually associated with thermal treatments.

In order to test this hypothesis, a research testing program focused on batch testing in the laboratory setting was developed to assess the viability of increased temperatures on the desorption efficiency of benzene on various soils. Testing consisted of three soils, a poorly graded Ottawa sand, kaolinite, and a natural silty sand soil from the Lockbourne Air Force

Base experimental testing site. The contaminant of concern is benzene, a carcinogenic and mutagenic compound that is one of the four major components of BTEX, a constituent of most diesel fuels. Benzene was chosen because of its presence at the LAFB testing site at contamination levels 164 times groundwater regulation limit of 5 µg/L. Laboratory testing was conducted at initial benzene solution concentrations of 10, 100 and 1000 mg/L. Four temperatures; 20, 40, 60, and 80 °C, were used in the batch testing program.

Results from testing support the theory that increased temperatures result in higher desorption efficiency. For lower concentrations of 10 and 100 ppm, temperatures as low as 40 °C correlated to increases in desorption levels from 40 % (at 20 °C) to over 80 % for the kaolinite and natural soil. Sand also experienced a doubling in desorption efficiency (from roughly 30 % to roughly 70%) at the 60 °C temperature and 10 and 100 ppm concentrations. The 1000 ppm testing concentration resulted in more modest, but still increasing removal efficiencies at increased temperatures.

Remediation at moderately increased temperatures appears to be a promising technique, but further research needs to be performed on soils that have experienced long term exposure to contamination to assess whether or not increased desorption efficiency trends are maintained.

TEMPERATURE EFFECT ON DESORPTION KINETICS OF BENZENE ON VARIOUS
SOILS

by

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This work is dedicated to my parents,
for reasons too numerous to mention.

Biography

Born in 1975, Tanya Marie King Kunberger grew up in the mountains of North Carolina with her parents, David and Mary Ann King, and her younger brother Kevin. After graduating as valedictorian from her high school, Tanya moved to Atlanta, Georgia to pursue her studies at Georgia Institute of Technology. She “got out” (graduated) cum laude in 1999 with a Bachelor of Civil Engineering degree and a certificate in Geochemistry, as well as having successfully completed the co-operative education program. Tanya then began her graduate education at North Carolina State University. In 2001 she married Jeff Kunberger and they currently live in the Raleigh area.

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Chapter 1 Introduction

1.1 Background

From as early as the ancient Persian Empire in 3000 B.C., man has been using some form of diesel oil to create light or fuel machinery. In 1859, wells were drilled in Pennsylvania in order to better recover this rediscovered and more efficient raw material. (ASME, 1948) Today, diesel oil is used to fuel vehicles and create electricity, and the demand is higher than ever. Unfortunately, the lack of government regulations on storage and disposal during the early stages of development has resulted in contamination at levels far exceeding present day standards.

One of the main components of diesel fuel is a combination of benzene, toluene, ethylbenzene and xylene, more commonly called BTEX. BTEX is a light non-aqueous phase liquid (LNAPL) which means that it has a density less than that of water and does not readily dissolve in water. The four BTEX components are carcinogenic and mutagenic at concentrations in the $\mu\text{g/L}$ (ppb) level, but are commonly found at many contaminated sites at the mg/L (ppm) level.

Remediation of diesel fuel is complicated not only because of its hydrophobic nature, but also because of the numerous types of contaminants in its composition. The lack of affinity for water causes fuel components to attach, or sorb, readily to almost any type of soil. The different types of contaminants each have their own characteristics, which cause each of their affiliations with the soil to be unique to a greater or lesser extent. When the heterogeneity of the soil is added into the equation, the complication of remediation is compounded by an order of magnitude.

Numerous research studies (e.g. Adams & Reddy, Cho et. al., Gabr et. al., Johnston et. al., Kirtland et. al., and Rael et. al.) have been conducted to assess the qualitative and quantitative aspects associated with the removal of diesel fuel from various types of soil and groundwater. In recent years, researchers have become fascinated with the possibilities that thermal remediation offers over traditional pump and treat systems.

Commonly, thermal desorption has been applied as an ex-situ treatment option. Equipment employed is typically rotary dryers or thermal screw units with screw conveyors. Soil is heated and exposed to carrier gas to transport organic compounds volatilized from soil and water. Less common are the in situ thermal techniques of steam stripping and Six Phase Soil Heating. Steam stripping involves the injection of steam into the contaminated zones. The steam not only establishes a pressure gradient to push contaminants to an extraction point, but also increases the vapor pressure which results in an increase in solubility and a decrease in viscosity. Six Phase Soil Heating passes standard AC electrical currents through the soil and is used in conjunction with vapor extraction wells. The increase in temperature due to the electrical current increases the volatilization of some compounds and thus the removal rate of vapor extraction.

Work in this thesis is focused on investigating an in situ version of thermal treatment through introducing heated water to the contaminated subsurface profile. In this case, low temperature thermal desorption ($T < 80^{\circ}\text{C}$) is employed by the injection of hot water through prefabricated vertical wells. The work here is focused on estimating the desorption capacity with increasing temperature and the benefit of implementing such an approach for different types of soils.

1.2 Objective

The objective of this research is focused on two main categories within the context of evaluating desorption capacities, temperature and concentration. The first concern is related to the temperature effect associated with desorption of benzene from various soils. Although subsurface temperatures remain fairly constant throughout the year, introducing flushing solutions at elevated temperatures could result in an increase in removal rates corresponding with a decrease in overall removal times. Figure 1.1 illustrates the balance of cost and time as they relate to increasing temperatures. The curves represent general trends, but are effective in demonstrating the existence of an ideal temperature which maximizes removal efficiency, while minimizing remediation time and cost.

Figure 1.1 General trends of cost and time with increasing temperature

The second concern is that of the concentration effect as it relates to desorption removal rates. Although increased temperatures may prove beneficial at lower concentrations, at higher levels, this increased temperature may not prove to be economically viable, or visa versa. An experimental program was established to integrate and test both temperature and concentration in order to effectively address both categories of the research objective.

Specifically, the objectives of this research are as follows:

1. To determine the effect of varying temperatures from 20 – 80 °C on desorption efficiency of benzene from various types of soil.
2. To compare the response of different soil types, including sand, kaolinite, and a natural sandy silt to desorption rates as temperature is increased.
3. To establish a relationship between desorption rate and magnitude versus initial compound concentration.

1.3 Research and Investigation

Observation of field operation led to the contemplation of a more effective means to increase contamination removal rates while still maintaining a cost effective system. Previous studies have focused on extreme temperature variations ($> 100\text{ }^{\circ}\text{C}$) that are effective only at significantly increased operating costs. Although the results are effective from a research standpoint, they are not yet regarded as a primary alternative from a practical point of view. This is due to the difficulty of maintaining extreme high temperatures in field applications while safely and effectively manipulating the remediation system and the cost associated with this process. To this end, it was important to try and balance the benefits of

increased temperature on removal rates with the more cost effectiveness and easier handling of lower temperature treatments.

Due to the importance of regulating temperature in order to establish an accurate temperature – desorption rate relationship, this research is performed in a controlled laboratory setting. The first objective is to establish a temperature range that illustrates benefits of elevated temperatures while still not requiring costly generators for higher temperature production. A range of 20 to 80 °C is instituted, with testing performed at 20, 40, 60, and 80°C intervals. This range is identified as the Low Level Desorption Temperatures (LLDT).

The importance of considering concentration levels as the second objective is addressed with a concentration range of 10 to 1000 ppm, and testing occurring at 10, 100, and 1000 ppm. Testing is performed at all four testing temperatures for each of the three concentrations.

In addition, testing consists of determining sorption and desorption partition coefficients for each of three soils; a poorly graded sand, natural soil from the field testing site, and kaolinite, a 1:1 clay mineral. These soils were chosen because they possess different sorption / desorption capacities based on their physio-chemical properties. All testing was performed using deionized water to eliminate the introduction of possible influential variables, such as dissolved cations, present in tap water. Solution concentrations of benzene were determined using a Tekmar Purge and Trap for solution concentration in combination with a Varian Gas Chromatograph for analysis.

1.4 Scope of Work

A literature review of the nature of NAPL contamination and the history of the contamination problem as well as an overview on remediation technologies, focused on thermal technologies, is presented in Chapter Two. Chapter Three discusses the materials and methods utilized, including site history and soil properties, testing equipment and methods, and the batch testing program employed. Research results are presented and discussed in Chapters Four and Five, with the former focusing on sorption testing and the latter on desorption testing. Chapter Six summarizes the results and offers conclusions, while recommendations for future research are postulated in Chapter Seven.

Chapter 2 Literature Review

2.1 History of Problem

Although the use of non-aqueous phase liquids has been traced back as early as 3000 B.C., regulations associated with production, storage, and distribution date back only as far as the 1970's. For this reason, it is not difficult to understand the presence of an enormous magnitude of contamination caused by many years of uncontrolled and unregulated activities. What is difficult, however, is the development of effective remediation procedures to restore contaminated sites back to pre-spill conditions and the implementation of regulations to reduce and eliminate future contamination. Significant progress has been made both in the area of remediation and regulation, but much more needs to be accomplished in order to reverse the magnitude of the environmental damage.

2.1.1 History of Diesel Fuel

Ancient history traces the use of diesel fuel back to the Persian Empire, but it was not until more recent times that production and consumption reached astronomic levels. The mid-1800's saw the emergence of diesel as the new and improved fuel of choice, due to the relative ease of recovery and higher comparative results (ASME, 1947). The development of the diesel engine in 1892 in Germany by Rudolph Diesel and later in the United States by Adolphus Busch, perpetrated the demand for diesel fuel. The conclusion of World War I saw the knowledge gained by soldiers of diesel engine operation adapted to the new world of peace by incorporating aspects of the diesel engine in commercial trucks. Present day is a witness to diesel fuel use in trains, planes and other machinery, not to mention the pharmaceutical, plastic and synthetic fiber industries.

Diesel fuel is an immensely complex polymeric mixture composed mainly of numerous hydrocarbons. These compounds can be divided into four main types: paraffins, olefins, naphthenes, and aromatics (ASME, 1947). Paraffins are the most prevalent hydrocarbons and are also known as normal or straight-chain alkanes. These consist of straight chains of carbons each forming four single covalent bonds with either other carbons or hydrogens. Olefins, or alkenes, are also straight chains of carbons, but are considered unsaturated because some carbon atoms share double bonds instead of only single bonds. Thus, the ratio of the number of hydrogens to the number of carbons is reduced from 3:1 (in alkanes) to 2:1 for alkenes. Naphthenes are also referred to as cycloalkanes or cyclic alkanes. These are composed of closed loops of carbon and also have a hydrogen to carbon ratio of 2:1 while still maintaining carbon-carbon single bonds. The final type of compound is the aromatics. These are carbon rings with alternating single and double bonds. They can exist as complicated as a number of rings joined together with or without various side groups, a single ring with various side groups, or simply a single ring. This most basic single ring aromatic hydrocarbon is benzene.

2.1.2 History of Benzene

In 1825, the compound we now know as benzene was first isolated by Michael Faraday. Discovering this new compound upon its separation from other compounds in the oily film residue from lighting gas, Faraday proposed the name “carbureted hydrogen” because of the equal number of carbons and hydrogens. Nine years and several iterations later, the C_6H_6 compound became known as benzene as is the simplest of the aromatic

hydrocarbons. Figure 2.1 presents the benzene structure of a ring of six carbon atoms alternating single and double bonds with a single hydrogen attached to each carbon.

Figure 2.1 Atomic Structure of Benzene

Existing in the environment due to both natural and man-made causes, benzene is a clear, colorless liquid with a sweet odor. It is highly volatile and has a water solubility of 1800 mg/L. Ranking in the top 20 chemicals produced in the United States by production volume, the main sources today are industrial processes. Benzene is used as a basis for plastic, rubber, dye, detergent, drug and synthetic fabric production.

Short term exposure to benzene can result in nervous system disorders, immune system depression, anemia, nausea and headaches; while long term exposure can lead to a disruption in blood production, cancer formation, and a disruption of healthy chromosome formation. The Agency for Toxic Substances and Disease Registry states that smoking or exposure to tobacco smoke accounts for almost half of the nationwide exposure to benzene. Another 20% is attributed to industrial emissions and auto exhaust. Ingestion, either by food or drink, as well as dermal adsorption are also possible exposure routes.

The United States EPA has set a maximum contaminant level (MCL) of 0.005 mg/L, or 5 ppb, for drinking water standards. The MCLG (MCL goal) is zero due to the known carcinogenic and mutagenic properties of the compound.

2.1.3 History of Regulations

The year 1970 ushered in the beginning of regulations with the Clean Air Act, a Federal law allowing the EPA authority in regulating area, stationary and mobile emissions. Amendments followed in 1977 and 1990 which established increasingly stringent standards for emissions reductions and addressed issues such as acid rain, stratospheric ozone depletion, and ground-level ozone that were not previously covered. The Safe Drinking Water Act (SDWA) of 1974 protects drinking water sources both above and underground by requiring compliance with primary, or health-related, standards. The EPA also encourages states in this act to comply with secondary standards, which are nuisance, rather than health, related. In tandem with the SDWA, the Clean Water Act, a 1977 amendment to the 1972 Federal Water Pollution Control Act, established standards for industry effluent and surface water contamination. The 1987 revision funded sewage treatment plants and focused further on reducing toxic pollutants.

The 1976 Resource Conservation and Recovery Act, or RCRA, “gave the EPA the authority to control hazardous waste from the ‘cradle-to-grave’ [and] also set forth a framework for the management of non-hazardous wastes” (EPA Website). Amendments in 1984 (called Hazardous and Solid Waste Amendments) and 1986 addressed phasing out land disposal of solid waste and underground storage tank issues respectively.

In contrast to RCRA, which focuses only on active and future sites, the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) focused on those sites that have been closed or abandoned. The law imposes a tax on the chemical and petroleum industries in order to fund clean-up for sites where the owners can not be determined. Both short-term and long-term responses are addressed in CERCLA; short-term covering sites where prompt response is necessary to prevent a life threatening release and long-term which involves placing the site on the National Priorities List (NPL) as a serious, but not currently life threatening contaminated location. CERCLA is commonly referred to as Superfund, and thus, sites on the NPL are considered Superfund sites. The year 1986 saw the establishment of the Superfund Amendments and Reauthorization Act, termed SARA, which was the amendment to CERCLA. SARA re-evaluated the existing standards and encouraged state, local, and individual involvement in site clean-ups. The importance of permanent solutions and accuracy in human health risk evaluation was also addressed in this amendment.

All of this legislation has gone a long way in improving the overall quality of life in the United States. CERCLA and SARA are effectively addressing the need to fix past problems, and RCRA is insuring that these problems do not happen again, however the legislation only provides a framework for what needs to be accomplished, and does not take any definitive action on how to accomplish these objectives. It is necessary therefore, for individuals in research and industry to discover remediation methods best suited to carry out legislative objectives.

2.2 Non-Aqueous Phase Liquids

Non-Aqueous Phase Liquids (NAPLs) are so named for their immiscibility in water. They can be divided into two main categories, light and dense, and exist in four phases: free, dissolved, vapor, and residual. (Bedient et. al., 1999) Each category and phase combination presents a unique challenge in the remediation process, and the presence of multiple combinations further exacerbates the issue.

2.2.1 Two Categories of NAPL

NAPLs are commonly classified into two main categories: light, or L, NAPLs and dense (D) NAPLs. These classifications are based on the density of the liquids. Those that are less dense than water (density = 1.00 g/cm^3 at 4°C) are LNAPLs, while those with a density greater than that of water are DNAPLs. Tables 2.1 and 2.2 list some of the more problematic light and dense NAPLs respectively, along with their densities and classifications.

Table 2.1 Common Problematic LNAPLs (Bedient et. al., 1999)

LNAPL Name	Density (g/cm^3)	Classification
Benzene	0.8737	Aromatic
Decane	0.7301	Aliphatic Alkane
Ethyl Benzene	0.8670	Aromatic
Naphthalene	0.9752	Aromatic
Octane	0.7025	Aliphatic Alkane
Toluene	0.8623	Aromatic
Xylenes	0.8611 – 0.8802	Aromatic

Table 2.2 Common Problematic DNAPLs (Bedient et. al., 1999)

DNAPL Name	Density (g/cm ³)	Classification
Chlorobenzene	1.1063	Halogenated Volatile
Cresols	1.0140 – 1.0380	Non-Halogenated Semi-Vol
Dichlorobenzenes	1.2417 – 1.3003	Halogenated Semi-Volatile
Phenol	1.0533	Non-Halogenated Semi-Vol
Tetrachloromethane	1.5842	Halogenated Volatile
Trichloromethane	1.4985	Halogenated Volatile
Trichloroethylene	1.4679	Halogenated Volatile

Although this classification differentiation may appear as a simplistic and arbitrary separation, the behavior of the two different types is drastically different, and methods and effectiveness of remediation is based on this difference. The main difference in behavior is that LNAPLs will float on top of the water table, contaminating the unsaturated area and the capillary fringe and fluctuating with the rise and fall of the water table itself. Contrasting this behavior, DNAPLs will sink below the water table and continue to migrate downward until they encounter a low permeability layer which impedes migration. This lower permeability layer is not guaranteed to stop contaminant movement however, as the DNAPL will either flow laterally until it encounters higher permeability layers, as in the case of a clay lens within a sand layer, or pool until the thickness of the product exerts a great enough pressure to enter the lower permeability layer, as would happen at a sand-clay interface or at bedrock depth.

2.2.2 Four Phases of NAPL

In addition to the two types of NAPLs, four phases of the contaminant also exists. These four phases are: free, vapor, dissolved, and residual and are illustrated in Figure 2.2.

Figure 2.2 Four NAPL Phases (Fetter, 1993)

Free phase is that portion of the NAPL that is still in the original immiscible form. The vapor phase is the portion of the NAPL that has volatilized into the air, while the dissolved phase is the portion that has solubilized in water. The portion of NAPL that remains held between particles is the residual phase.

In the same way that the two types of NAPL present different challenges for remediation efforts, the four phases also offer varying degrees of difficulty in contaminant removal. The dissolved and vapor phases are the easiest to treat in situ, but without an effective way to address the free and residual phases, clean-up of the former two is an almost constant battle. Equilibria exist between the four phases, and removal of any results in a redistribution of contamination. This constant redistribution is one of the main sources of extended contamination. Groundwater migrates through a contaminated area and becomes a carrier of dissolved phase contamination. This water then proceeds through an

uncontaminated soil, where some of the dissolved phase equilibrates to the other three phases. This trend continues and results in widespread contamination, even from a relatively small spill.

Because of the difficulty in removing contamination in the free and residual phase, it is necessary to convert the contaminant from these phases to the dissolved or vapor phases. Remediation effectiveness is based on the ability to maximize the conversion to the latter phases, while minimizing time, cost and detrimental effects of challenging the equilibrium balance.

2.3 Sorption and Desorption

Understanding the processes of sorption and desorption is critical for an overall understanding of how NAPLs behave in the subsurface environment. When discussing sorption, three terms related to the partitioning are important to understand and differentiate. A sorbent is the solid surface to which the material, known as a sorbate, adheres. Material that has the potential to become sorbate, but is still in solution, is termed the sorptive. Knowledge gained from the study of sorption mechanisms can help develop insight to the desorption mechanisms, which are not currently clearly understood.

2.3.1 Sorption Processes

Sorption, or the “general term that is used when the retention mechanism at a surface is unknown,” (Sparks, 1995) has been divided into six main mechanisms. These mechanisms are surface precipitation, polymerization, cation exchange, chemisorption, absorption, and adsorption. Surface precipitation occurs when the amount of cations or anions on the surface increases to such a level as to form a new 3-D solid phase. Polymerization is defined as

“the formation of small multinuclear inorganic species such as dimers or trimers” (Sparks, 1995). The process by which cations become attracted by electrostatic forces to clay mineral negative sites is cation exchange, and includes ions in the diffuse double layer (DDL). “Chemisorption occurs when the solute is incorporated on a sediment, soil, or rock surface by chemical reaction” (Fetter, 1993). Absorption is defined as the process by which “a solute diffuse[s] into the particle and [becomes bound] to interior surfaces” (Fetter, 1993). The chemical process that results in “an accumulation of a substance at a solid-water interface, usually into a 2-dimensional structure” (Sposito, 1989) is adsorption. Because NAPL is the focus contaminant, the first three types of sorption are highly unlikely, and thus will not be discussed to any greater extent. The last three types are all possible sorption mechanisms for NAPL contamination, but differentiation can be accomplished only through study of the molecular level. The importance in the remediation effort is the removal itself, to a greater extent than the process by which it occurs, and as such, future references to sorption will include the latter three mechanisms.

One of the largest factors influencing the tendency of a contaminant to sorb is its octanol-water partitioning coefficient. This compound property, also referred to as the K_{ow} , can be evaluated by the octanol-water partition test. This test is conducted by placing equal volumes of octanol (as a liquid substitute for organic soil) and water in a test tube, introducing the contaminant, and allowing the system to obtain equilibrium. Once equilibrium is reached, the amount of contaminant in each phase is measured, and the coefficient is calculated using the following equation:

$$K_{ow} = [A]_{octanol} / [A]_{water} \quad \text{Eqn. 2.1}$$

where: K_{ow} = octanol-water partitioning coefficient
 $[A]_{octanol}$ = concentration of contaminant in octanol phase (mg/L)
 $[A]_{water}$ = concentration of contaminant in water phase (mg/L)

Numbers less than one indicate a higher concentration in the water phase than in the octanol phase and thus a preference for water over organic matter. Numbers greater than one indicate a higher concentration in the octanol phase than in the water phase and thus a preference for organic matter over water. K_{ow} values have been tested “as high as 1×10^6 , indicating that common organic contaminants are highly attracted to a hydrophobic phase and will associate strongly with the natural organic fraction of soils or aquifer materials” (Bedient et. al., 1999). Benzene has a K_{ow} value equal to 130, demonstrating the low water and high organic affinity of this contaminant.

2.3.2 Desorption Processes

Even more important to remediation than sorption mechanisms, desorption processes dictate the rate of removal at many sites. Despite this, very little is actually understood about the reactions and processes that occur during desorption. Some contaminated sites experience very little desorption from soils, resulting in low dissolved and volatile concentrations, but a constant persistence of contamination that is virtually impossible to remove. On other sites, the opposite occurs, with desorption occurring at a rate so fast as to reach maximum solubility in the dissolved phase and result in widespread groundwater contamination. Both extremes, as well as the more temperate cases, further complicate an already complex problem.

Another difficulty in the prediction of desorption levels is related to the property of hysteresis. Hysteresis is the irreversible phenomenon that results when a process is run from two different directions and nonsingular results are obtained. In this case, “the adsorption and desorption isotherms corresponding to the forward and backward reactions would not coincide” (Sparks, 1995) implying that it is very difficult to desorb all the sorbed contaminant.

2.3.3 Isotherms

A plot that shows the concentration of sorptive versus the amount of sorbate on the sorbent at constant temperature is known as a sorption isotherm. There are three empirical, macroscopic models that are commonly used to describe sorption; the linear equation, the Freundlich equation, and the Langmuir equation. Although all are valid models, it is important to realize “that adsorption isotherms are purely descriptions of macroscopic data and do not definitively prove a reaction mechanism” (Sparks, 1995).

2.3.3.1 Linear Equation

The linear equation models the most direct relationship between sorptive concentration and mass of sorbate on the sorbent. The isotherm is described by the following equation:

$$Q = K_d C \quad \text{Eqn. 2.2}$$

where:

Q = mass of sorbate on the mass of sorbent (mg/kg)

K_d = distribution coefficient (L/kg)

C = concentration of sorptive (mg/L)

Values for Q and C can be obtained from laboratory testing and thus K_d can be determined as the slope of the plot of C versus Q. Linear sorption isotherms are ideal from a calculations perspective, but two main limitations exist with this type of model. The first is that no maximum level exists for the amount of contaminant that can be sorbed on the solid. From a practical point of view, this concept is obviously incorrect. The second limitation is that a small data set, when taken alone, can often be misinterpreted as a linear isotherm, but when combined with a larger data set is actually a non-linear function. This makes extrapolation from limited data sets a questionable endeavor.

2.3.3.2 Freundlich Equation

The second empirical model is based on the non-linear equation:

$$Q = K_d C^n \quad \text{Eqn. 2.3}$$

where:

- Q = mass of sorbate on the mass of sorbent (mg/kg)
- K_d = distribution coefficient (L/kg)
- C = concentration of sorptive (mg/L)
- n = correction factor (unit less)

As with the linear isotherm, values for Q and C can be obtained from experimental data and plotted on a C versus Q graph. When plotted as log C versus log Q, “the result will be linear with a slope of n and an intercept of log K_d ” (Fetter, 1993). It is important to realize that if n is 1, the equation reverts to the linear equation.

As with the linear equation, the Freundlich equation does not set a limit on a maximum sorption value, and extrapolation outside of the experimental data is not

recommended. However, the non-linearity of the Freundlich model often results in a better fit to tested results than the linear equation.

2.3.3.3 Langmuir Equation

The main difference between the Langmuir equation and previous models is the limit placed on the sorption capabilities of the sorbent. Therefore, the equation does what the others do not, and establishes a maximum sorption level to correspond with the sorption isotherm. The equation that accomplishes this is as follows:

$$Q = (C\alpha\beta) / (1 + \alpha C) \quad \text{Eqn. 2.4}$$

where:

Q = mass of sorbate on the mass of sorbent (mg/kg)

C = concentration of sorptive (mg/L)

α = adsorption constant related to binding energy (L/mg)

β = maximum amount of sorptive that can become sorbate (mg/kg)

The main disadvantage to the Langmuir model is the assumption of the homogeneity of the sorbent. Since most soils are heterogeneous this assumption is not valid and thus the equation “should only be used for purely qualitative and descriptive purposes” (Sparks, 1995).

2.4 Remediation Efforts

The technologies for remediating contaminated sites are as varied as the site contaminations themselves. Before a remediation method can be chosen however, it is necessary to consider several properties of the contaminated site which will affect remediation. Once these properties are known, an educated decision can be made on the type of technology best suited for remediation measures.

2.4.1 Site Properties

Of the innumerable site properties that can be analyzed, two of the most basic but important are the contaminant and soil profiles. Other properties, such as site history and weather conditions at the site are important, but to a lesser degree.

2.4.1.1 Contaminant Profile

The contaminant profile consists first and foremost of the type of contamination. Sites with DNAPL contamination require a different approach to those contaminated with an LNAPL. Certain technologies that effectively clean LNAPL contamination could have little or no effect on a DNAPL spill. In tandem with the type of contamination, the extent of contamination, both in space and time, is the other profile factor. The extent to which contamination has migrated on a site plays a primary role in the clean up method. A small area of shallow contamination can be handled much differently from a large area or contamination that has migrated fairly deep in the soil profile. Time also plays a factor in that older spills not only have had a longer time to migrate, but they have also had a longer time to sorb to the soil and may be either more tightly bound or have infiltrated deeper into the soil particles. This infiltration makes the desorption process infinitely more difficult.

2.4.1.2 Soil Profile

The soil profile consists of the types and location of soils, the presence and location of water, and any unusual site characteristics that may affect remediation efforts. The type of soil is important not only because it dictates the amount of contaminant sorption, but also because it controls void ratio and permeability of the soil. Sand tends to have a much lower tendency to sorb contaminant, as well as having higher void ratios and permeability values

than other soils. Clays, on the other end of the spectrum, tend to have higher sorption capacities, as well as lower void ratios and permeability values orders of magnitude less than that of sands. The presence of organic matter in a soil also influences that amount of sorption, as contaminants have a high affinity for and readily adsorb to organic matter. The location of the soils is a factor because a site with many alternating layers of soils requires an approach unlike that of a more uniform site profile. In addition, alternating layers results in a higher variation of permeability with depth, a challenging issue to overcome in many treatment technologies.

Depth to the water table can dictate the depth to which an LNAPL will migrate and also controls the depth to saturated soil in a profile. Saturation affects the effectiveness of many remediation measures, some favorably, and other negatively. Some measures even require a lowering of the water table in order to proceed with the remediation chosen.

Features such as shallow bedrock with numerous fractures, artesian aquifers and wetland conditions are examples of unique site characteristics that can complicate remediation efforts. Fractures in bedrock provide excellent flow paths for migrating NAPL, but the hard bedrock is immune to many clean up technologies. Artesian aquifers make it virtually impossible to drill wells for determining the extent of contamination as well as for remediation, and wetlands introduce a host of difficulties from permitting to staging to the clean up itself.

2.4.2 Treatment Technologies

A number of treatment technologies, with varying degrees of effectiveness, exist from the remediation of various contaminants. This section will focus on the more promising

technologies available that have been shown to effectively remediate LNAPL contamination. These technologies consist of conventional pump and treat, enhanced pump and treat, air sparging / soil vapor extraction, and thermal treatments.

2.4.2.1 Conventional Pump and Treat

Conventional Pump and Treat is defined as the process of pumping water to the surface for treatment or hydraulic containment of contaminated groundwater (Fetter, 1993).

A schematic diagram of pump and treat remediation is shown in Figure 2.3.

Figure 2.3 Schematic Diagram of Conventional Pump and Treat Remediation (www.frtr.gov/matrix2/section1/toc.html, 2001)

Although the number of extraction wells can vary, as well as the treatment employed at the surface, the general components of pump and treat are presented in the preceding figure. The advantages of this type of technology are that it has few limitations associated with soil profile and NAPL phases present. There are also benefits associated with the possibility of

adaptive pumping. Adaptive pumping is changing the amount of time pumps are running or the pumping rate to maximize contaminant removal while minimizing pumping times and rates. This can be accomplished in multiple pump systems by adjusting which pumps are running at certain times or in a single pump system by adjusting the pumping regime of the single pump.

Disadvantages of the pump and treat system are extremely long remediation times, problems with sufficient drawdown, and problems with tailing and rebounding. Times connected with site clean up to regulation levels can be on the order of 50 to 100 years. The lack of sufficient drawdown results in the lack of a significant hydraulic gradient and thus the lack of flow to the extraction wells. Tailing is when levels of contaminant concentration in the extracted water drop from high levels to levels so low that almost no contamination is being removed. Rebounding is when low concentration levels in the subsurface are measured at the end of a pumping stage, but after the pumps are turned off, subsurface concentrations return to previous high levels of contamination. Both rebounding and tailing can be addressed, but not totally overcome with the use of adaptive pumping.

2.4.2.2 Enhanced Pump and Treat

Enhanced Pump and Treat is similar in operation to conventional pump and treat, but introduces additional technologies designed to improve remediation. The most well-known of these is surfactant flushing, or the process of utilizing surfactants to increase contaminant mobility and thereby enhance recovery. Surfactants are surface-active agents that reduce the hydrophobic nature of many contaminants, resulting in their higher concentrations in extracted groundwater. As with conventional pump and treat, it is effective in most soil

profiles and on all phases of NAPL, but traditionally has shorter remediation times than the conventional technology. Unfortunately it also has the disadvantages similar to those of conventional pump and treat. An additional disadvantage is that there is the possibility of the surfactant chemicals adversely affecting the subsurface.

2.4.2.3 Air Sparging / Soil Vapor Extraction

The processes of air sparging and soil vapor extraction (SVE) combine the injection of air into the saturated zone to volatilize contaminants and the removal of contaminants in vapor form to the surface for treatment. Figure 2.4 illustrates the general schematic diagram of an air sparging / soil vapor extraction system.

Figure 2.4 Schematic Diagram of Air Sparging / Soil Vapor Extraction Remediation System (www.epa.gov, 2001)

There are few soil profile limitations associated with this type of remediation. Another advantage is that the addition of oxygen can enhance in situ bioremediation. Disadvantages are the difficulties in flushing low permeability zones and extracting multi-component mixtures. This technology is also only effective on volatile or semi-volatile compounds,

limiting sites at which it can be employed. Despite this, according to the EPA, SVE is the most frequently used innovative treatment technology at Superfund sites (www.epa.gov, 2001).

2.4.2.4 Thermal Treatments

Thermal treatments are relatively new techniques compared to those previously mentioned. Three of the most highly researched are those of steam stripping, electrical heating of soils, and hydrous pyrolysis/oxidation. Each utilizes a fairly simple premise for improved remediation, but approaches it in a different manner.

Steam stripping is the process of injecting steam into the subsurface to volatilize contaminants. The layout of injection and extraction wells varies from site to site, but most sites surround the contamination with injection wells and place the extraction wells in the center. This layout is illustrated in a simple two-dimensional design in Figure 2.5.

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Figure 2.5 Schematic Layout of Steam Stripping Remediation
(www.frtr.gov/matrix2/section1/toc.html, 2001)

As with previously mentioned technologies, steam stripping is effective on all phases of NAPL and exhibits few soil profile limitations. The main advantage is that it usually takes less than two pore volumes of flushing for remediation, resulting in less contaminated groundwater removed from the subsurface and a shorter remediation time. Difficulty in volatilizing from low permeability zones and maintaining sufficient temperatures for steam to remain in the vapor phase, as well as the applicability only to volatile and semi-volatile compounds, are disadvantages of this type of remediation technology.

Electrical heating of soil uses electrical energy to heat the subsurface. Low frequency AC currents, as well as radio frequency currents are delivered through electrodes placed in the subsurface. The electrical currents cause an increase in temperatures, which increases the vapor pressure of volatile and semi-volatile compounds and improves removal rates.

Methods that utilize the lower frequency have the major disadvantage that:

the water in the pore spaces of the soil absorbs essentially all the applied energy in the soil and, therefore, limits the heating process. Thus ... the boiling point of water is the highest temperature that can be achieved ... [and] may not be adequate to effectively recover the contaminants (Davis, 1997).

This disadvantage has been overcome with the utilization of radio frequency (RF) currents, which the soil itself is able to adsorb, allowing for higher temperatures and increased volatility to occur. Davis (1997) states that this type of remediation is effective in sands and may also prove to be more beneficial in lower permeability soils than other methods.

Limitations of use confine RF technology to the unsaturated zone, a disadvantage that can be overcome currently only by dewatering.

Developed by Lawrence Livermore National Laboratory scientists, Hydrous Pyrolysis/Oxidation (HPO) is a process that works in connection with Dynamic Underground Stripping (DUS). DUS operates in the same manner as that of steam stripping, but also employs the injection of oxygen simultaneously with steam. The steam increases contaminant mobility and volatilization, while the oxygen stimulates biodegradation. The increase in temperature has also been found to facilitate microbial growth in thermophile communities, previously unobserved, but effective combatants in NAPL degradation (Davis², 1997). HPO is the conversion of contaminants to benign species such as carbon dioxide, chloride ions, and water. This is accomplished after DUS has concluded and the steam begins to condense. This condensation mixes with oxygen and groundwater and, in the presence of heat, the contaminants “rapidly oxidize into carbon dioxide, chloride, and water” (DOE, 2000). Like other thermal treatments, DUS and HPO work only on volatile and semi-volatile compounds and can cause complications from the introduction of sustained high temperatures in the subsurface.

2.5 Previous Benzene Contamination Studies

A number of studies have already been conducted on the remediation of benzene from contaminated soils. This section will briefly present five studies, each of which is based on a different existing contaminated site. Two of the studies involve leaky underground storage tanks (USTs) at gas stations. Another two studies are petroleum spills at industrial sites, and the final site is a United States Coast Guard Support Center.

2.5.1 Gas Station in South Carolina

In 1993, Kirtland, Aelion, and Widdowson began a three and a half year study on the long term effects of air sparging and soil vapor extraction on the remediation of gasoline contamination from a leaky UST. The site under consideration was an abandoned gas station in Columbia, South Carolina. Clay and silt dominated the upper portion of the site, while below 7.0 m “the clay and silt content decreased allowing much greater permeability [with] gravel layers intercalated with coarse to medium sands” (Kirtland et. al., 2001).

Groundwater was located an average of 7.0 meters below ground surface, but fluctuated annually more than a meter. Soil and groundwater were tested for BTEX, methyl tertiary butyl ether (MTBE) and total petroleum hydrocarbons (TPH) and initial concentrations are presented in Table 2.3.

Table 2.3 Initial Concentrations of Soil and Groundwater Contaminants (Kirtland et. al., 2001)

Contaminant (location)	Concentration
BTEX (groundwater)	0.03 – 358.66 mg/L
BTEX (soil)	Not detected – 793 mg/kg
MTBE (groundwater)	0.05 – 155.31 mg/L
MTBE (soil)	Not detected – 24 mg/kg
TPH (groundwater)	<1 – 958 mg/L
TPH (soil)	Not detected – 7400 mg/kg

A comparison was performed between Soil Vapor Extraction (SVE) alone and a combination of SVE and Air Sparging (AS) both in a continuous run and pulsed operation. Results show “there was not a statistical difference between SVE and AS/SVE petroleum extraction rates, suggesting that the majority of contamination was removed from the vadose

zone via SVE” (Kirtland et. al., 2001). Total physical contaminant removal was estimated at 5300 g of BTEX and 19,000 kg of TPH during the entire testing period, although BTEX levels in the groundwater were not significantly reduced.

2.5.2 Gas Station in West Virginia

A former gas station in Weston, West Virginia was the site used in the 1999 paper by Gabr, Sabodish, Williamson and Bowders. Six UST at the site caused soil and groundwater BTEX contamination. The soil profile was characterized as a low plasticity silty clay (CL) overlaying a sandstone bed which was 3 to 20 m below ground surface. The groundwater table was located approximately 1.5 m below ground surface and the “total BTEX concentration as measured from the onsite groundwater wells was 0.77 mg/L” (Gabr et. al., 1999).

Remediation involved the utilization of five prefabricated vertical drains (PVDs) attached to a vacuum system and installed perpendicular to the direction of groundwater flow. The system operated for two days with an extraction time of 360 minutes the first day and 540 minutes the second day. “Results from the grab samples of the extracted groundwater indicated a mobilization of the BTEX toward the PVDs and the feasibility of extracting the compounds” (Gabr et. al., 1999). Table 2.4 lists maximum concentrations of each of the four BTEX compounds during the time of operation.

Table 2.4 Maximum BTEX Concentrations Removed (Gabr et. al., 1999)

BTEX compound	Concentration (mg/L)
Benzene	~ 0.4
Toluene	0.025
Ethylbenzene	0.19
Xylene	0.27

2.5.3 Oil Refinery Industry in Canada

Storage tank and piping leaks, in addition to hydrocarbon spills, occurring from 1960 to 1990 provides the basis for contamination at the subject site of Chen, Huang, and Chakma. Located in western Canada, the oil refinery industry site contains around 23,000 m³ of contaminated soil and has a depth to groundwater of between 1.1 to 1.5 meters.

The subject of this research was not the remediation of the soil, but rather the testing of “an integrated risk assessment approach...for environmental risk assessment of petroleum contaminated sites” (Chen et. al., 1998). The model is the Hydrocarbon Spill Screening Model (HSSM) and Fuzzy Relation Analysis (FRA), and was utilized to assess the detrimental effects of BTEX and TPH compounds. Chen et. al. conclude that the “results are useful for risk analysis of LNAPL spill and/or leakage as well as their impacts on soil, groundwater, and potential receptors.”

2.5.4 Industrial Complex in Australia

Johnston, Rayner, Patterson and Davis consider gasoline spills at an industrial site in Kwinana, Australia. Near Perth in Western Australia, the site is only 900 meters from the ocean and has been contaminated by gasoline and dissolved hydrocarbon compounds. The site is predominately medium to fine grade sand to a depth of 15 meters, with an unusually hard 0.1 m thick limestone layer at the 1.5 m depth. Below 15 meters is clay layered over

limestone. The water table fluctuates between depths of 2.7 to 3.4 m below ground surface and was at a depth of 3.1 meters during the testing period. BTEX compounds were the contamination under investigation, and Table 2.5 summarizes initial concentrations in the groundwater at a depth of 4.5 meters.

Table 2.5 Initial Groundwater BTEX Concentrations (Johnston et. al., 1998)

BTEX compound	Concentration (mg/L)
Benzene	~ 15.0
Toluene	2.5 – 4.0
Ethylbenzene	2.0 – 3.0
Xylene	2.0 – 3.0

Air Sparging was the remediation method of choice, with a single injection well in the center of a 4-m square with extraction wells at each of the four corners. The testing period was continuous for a seven day period, except for three 4 hour breaks on days 2, 3, and 5. Results from the test indicate that “the rate of removal of dissolved organics from groundwater was very rapid [and] most were removed within 3 days of the start of sparging” (Johnston et. al., 1998). Total masses of BTEX extracted in the first 5 days of operation are listed in Table 2.6.

Table 2.6 Mass of BTEX Extracted in Soil Gas (Johnston et. al., 1998)

BTEX compound	Total Mass in Soil Gas (g)
Benzene	135
Toluene	16
Ethylbenzene	48
Xylene	0

2.5.5 US Coast Guard Site in North Carolina

In 1992, an eighteen month study was undertaken to remediate the United States Coast Guard Support Center site in Elizabeth City, North Carolina. Degradation of the underground pipelines that carried jet fuel, JP-4, on the site had released approximately 3600 kg of the fuel to an area 50 by 100 meters in size. The site profile was characterized as mainly sand with a 1.5 meter thick overlying silty clay. The water table was at a depth of roughly 2 m and fluctuated 0.6 m annually.

A combination of remediation efforts, including air injection, soil vacuum extraction and enhanced biodegradation were employed with the goal of reducing “the concentration of total petroleum hydrocarbons (TPH) to concentrations less than 100 mg/kg of soil” (Cho et. al., 1997). Upon completion of the 18-month testing period, 2000 kg of TPH was removed from the site, 1700 kg of which was removed by the SVE method. Although the remediation goal was not met, a significant amount of contamination was removed from the site. Table 2.7 summarizes concentrations prior to and post testing in several monitoring wells on site.

Table 2.7 Initial and Final Groundwater TPH and BTEX Concentrations (Cho et. al., 1997)

	Well	Initial Concentrations (µg/L)		Final Concentrations (µg/L)	
		TPH	BTEX	TPH	BTEX
Outside NAPL Boundary	70A	3016	1037	50.3	46.3
	70S	7	<1	10.4	<1
	70Y	200	<1	18.4	<1
Inside NAPL Boundary	70D	10990	7460	1395	9000
	70Q	7240	1730	1861	479
	70V	3960	3120	8.4	1230

“Locations where the initial average TPH concentration was less than 100 mg/kg were considered to be outside of the NAPL boundary, and locations ... greater than 100 mg/kg were considered to be within the boundary of the NAPL oil lens” (Cho et. al., 1997). For the most part, concentrations after remediation were lower than those initially measured.

Chapter 3 Materials and Methods

3.1 Test Soil

Three soils were used in the testing program, two of which were ideal homogeneous soil materials while the third was a natural soil from the testing site. The two homogeneous soil materials were a sand and kaolinite, while the third natural soil was a silty sand from a glacial till deposit.

3.1.1 Sand

The sand used in testing was a poorly graded fine white Ottawa sand with a grain size distribution as shown in Figure 3.1. The average particle diameter is 0.15 mm and the specific gravity is 2.64 g/cm³.

Figure 3.1 Grain Size Distribution Curve for Sand Used in Testing

From the grain size distribution graph it is possible to determine the coefficient of uniformity (Cu) which is defined as the ratio of the diameters of the portion 60% finer to the portion 10% finer. For this sand the diameters are .15mm and .08mm, resulting in a $Cu = 1.875$, which is fairly uniform because a smaller number indicates greater uniformity. (Holtz & Kovacs, 1981) Typical sands are composed mainly of quartz and have an average specific gravity of 2.65 g/cm^3 . Because of the fairly spherical shape of the grains (See Figure 3.2) and chemical composition, sand usually exhibits a relatively low surface activity, or tendency to react with contaminants. However, it is possible that the highly hydrophobic nature of the contaminant will overcome the low activity and result in sorption, although fairly weak in nature.

Figure 3.2 Microscopic Photograph of Sand Grains (Das, 1998)

3.1.2 Clay

Kaolinite was the clay used in this research testing. A 1:1 clay mineral, kaolinite is composed of a silica tetrahedral layer bonded with an aluminum octahedral layer. The specific gravity of kaolinite is 2.65 g/cm^3 , which is on the low end of the range of values for most clay minerals. The test kaolinite has a liquid limit of 56% and a plastic limit of 31%,

which results in a plasticity index of 25% and a USCS classification of a high plasticity clay (CH). Seventy-five percent of the particles are less than 0.002 mm in diameter from the grain size distribution curve. Very little interlayer space is present due to the hydrogen bonding between layers, and thus kaolinite has almost no shrink-swell potential and a relatively low specific surface area (SSA) compared to many other clay minerals. This low SSA in combination with the lack of isomorphic substitution results in a low cation exchange capacity (CEC) of between 2-15 cmol/kg. (Sparks, 1995) In addition, kaolinite has an activity of 0.33, low when considering some clays have activities as high as 7. Therefore kaolinite can be considered to be much less active sorbent than some other clays such as smectite.

3.1.3 Soil

The natural soil used in experiments was a silty sand from the experimental testing site in Columbus, Ohio. The site was formerly Lockbourne Air Force Base (LAFB) and is now a part of the Rickenbacker Port Authority. Approximately 12 miles south of Columbus, the site is located in the flat uplands between Walnut and Big Walnut Creek drainage basins. The March of 1992 Site Investigation Report by Martin Marietta characterizes the local geology as that of a preglacial shale and limestone bedrock valley of the Devonian age at a depth of 190 to 219 feet below ground level. Filling this valley is a Pleistocene glacial drift overlain mainly by a ground moraine surficial till. A boring log of the site from ground surface to a depth of 34 feet is shown in Figure 3.3. The soil profile exhibits a layering of silty sand (SM) with a low plasticity clay (CL) or a combination (SC-SM) from about 12 to 23 feet below ground surface.

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SHEET 1 OF 2

DEPTH (FT.)	SAMP. NO. LENGTH TYPE	BLOW COUNTS RECOV. (%)	FIELD PID (ppm)	STRATA DEPTH (FT.)	STRATA IDENTIFICATION	REC
0.0		0.0	4			
	TB02-01	1.5	6	-		
		1.5	4	1.5	-FILL- Brown, claye. SAND with gravel, some asphalt fragments, dry to moist, loose (SP)	97%
	TB02-02	3.0	3	0	-POSSIBLE FILL- Brown to gray, clayey SILT, trace sand and gravel, dry to moist, stiff to very stiff (ML)	53%
	TB02-03	4.5	4	0	← began EnCore sampling at: 4.5'	100%
5.0	TB02-04	6.0	4	0		100%
		6.0	6		sand and gravel content increasing with depth	100%
	TB02-05	7.5	7	0		100%
		7.5	9		↓	100%
	TB02-06	9.0	7	0		100%
		9.0	12			100%
10.0	TB02-07	10.5	7	0		100%
		10.5	12			100%
	-	10.5	5	-	← varying degree of odor detected from '2' to '24'	0%
		12.0	9			
		12.0	10	12.3		
	TB02-08	12.0	10	>1000 (max)	Gray, claye, silty SAND with gravel, moist, medium dense (SC-SV)	100%
		13.5	12			
		13.5	13			
	TB02-09	13.5	8	8	Brown to gray, sandy, lean CLAY, trace gravel, some iron stains, moist, very stiff (CL)	100%
		15.0	10			
	TB02-10	15.0	6	0		100%
		16.5	6			
		16.5	10	16.3		
		16.5	11		← becomes wet at: 15.5'	
	TB02-11	18.0	13	>1000 (max)	Gray, silty SAND, some iron stains, moist; to wet, medium dense (SV)	100%
		18.0	7			
		18.0	3	18.3		
	TB02-12	19.5	3	>1000 (max)	Gray, silty clayey SAND with gravel, wet, medium dense (SC-SW)	97%
		19.5	8	19.5		
20.0	-	19.5	5			

GENERAL REMARKS: Note: Field PID readings may have been affected by sample moisture

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BORING NO. TB-02
SHEET 2 OF 2

[illegible]

GENERAL REMARKS: T502 was constructed into a monitoring well upon drilling, some ing some other

38

Contamination, caused by leaks in the Underground Storage Tank (UST) and failure of the underground piping system holding Jet Petroleum 4 (JP-4), is found at this 12 to 23 foot depth and the water table is at roughly 19 feet below ground surface. The lack of any significant hydraulic gradient has prevented migration of contamination from the site over the past 50 years. Field sampling and subsequent testing has shown the contamination to be confined mainly to the SM layers. Figure 3.4 graphs the grain size distribution curve for the SM soil used in batch testing.

Figure 3.4 Grain Size Distribution Curve for SM Natural Soil Used in Testing

The soil is from a depth of 16.5 to 18 feet below ground surface and has a specific gravity of 2.72 g/cm³ and an activity of 0.73. The organic carbon content is 4.67%. Only the portion of the soil passing the number 10 (2 mm) sieve was used in testing in order to eliminate gravel-

sized particles from interfering in testing results. From Figure 3.4, it is possible to see that this separation resulted in only 5% of the soil distribution not being used.

3.2 Test Contaminant

The contaminant, used in the testing program for a number of reasons, was benzene. First, it was desirable to consider a single compound, rather than the more complicated JP-4 contaminant. This eliminates compound interactions, which can complicate results, as well as allows for a more individualized testing program focused on benzene alone. Benzene was chosen as the single compound because concentrations at the LAFB site were over 150 times greater than the EPA groundwater regulations (MCL = 5 ppb). Several properties of benzene also make it desirable as the testing contaminant. Benzene's boiling point of 80.1 °C is just outside the testing temperatures and thus does not affect the majority of testing results. None of the concentrations (10, 100, or 1000 mg/L) used in testing are greater than the solubility of benzene in water, which is 1800 mg/L. Finally, the vapor pressure of benzene increases dramatically as the temperature increases due to the increase in the available kinetic energy. Figure 3.5 graphs the change in vapor pressure for benzene with the change in temperature.

Figure 3.5 Vapor Pressure of Benzene as a Function of Temperature (www.s-ohe.com, 2001)

Although not shown in Figure 3.5, the vapor pressure of benzene at 10 °C is 47.8 mm Hg. (Davis, 1997) This is over an order of magnitude less than the vapor pressure at 80 °C, which from the graph is 750 mm Hg. A difference in vapor pressure this large can greatly facilitate the removal of benzene and other volatile compounds from a contaminated site by the conversion of free and residual phase NAPL to vapor phase NAPL.

3.3 Benzene Solution Preparation

Testing procedures required various known concentration of benzene in solution. In order to accomplish this, calculations were performed to determine the mass of benzene required in the known volume of water to obtain these concentrations. A specific mass of benzene was then added to methanol, shaken and allowed to equilibrate. A measure of this

solution was added to the deionized water to obtain the desired benzene concentration. The methanol step in the process is necessary to allow dissolution of benzene in water, and the measure of solution added to the DI water was less than .5% of the total solution volume to prevent complications from excessive methanol presence. In all stages of solution preparation, benzene or benzene solution was injected using airtight syringes with the tip submerged to reduce volatilization.

3.4 Testing Equipment

Testing was performed in 150 mL Wheaton glass bottles with Teflon closure screw tops. The Innova 4230 refrigerated incubator shaker by New Brunswick Scientific was employed at a rate of 275 rpm for shaking of samples. After shaking, samples were placed in Nalgene brand Teflon centrifuge tubes and separated into soil and liquid components utilizing the International Equipment Company (IEC) Centra MP49 refrigerated centrifuge, as shown in Figure 3.6, which operated for 10 minutes at a rate of 12,000 rpm and a constant temperature of 20 °C.

Figure 3.6 Interior View of IEC Centra MP49 Refrigerated Centrifuge with Samples

A.C.S. certified benzene and purge and trap grade methanol in their purest forms were used in solution preparation. The Tekmar 3000 Purge and Trap Concentrator and Varian Star 3400 Gas Chromatograph (GC) with a photo-ionization detector (PID) on intensity level 9 were employed in tandem to analyze liquid solution samples. GC carrier gas was UHP Helium and UHP Hydrogen was the reaction gas. Data was transferred from the GC to a connected computer using the Varian Star data collection software program which provided graphs as well as data file reports in separate files for each analysis run.

3.5 Batch Testing

Batch testing was considered the best method of testing for a number of reasons. First, the temperature could be better regulated in the refrigerated incubator shaking table utilized in both the sorption and desorption phases of the testing process. Second, the amount of volatilization was reduced by having a closed system during testing, something difficult to achieve in column testing. And finally, batch testing allowed for the most uniform testing conditions for all three soils.

3.5.1 Sample Preparation

150 mL Wheaton glass bottles were cleaned, dried and filled with 125 mL deionized water. Fifteen glass beads were added to each bottle to facilitate agitation of the soil and ensure mixing. Next, 12.5 grams of oven-dried testing soil was added to each bottle, followed by the measured concentration of contaminant solution injected from an airtight syringe below the water surface in order to reduce volatilization. Teflon closure lids were employed in order to prevent adsorption to the caps and cross contamination of samples.

Samples were then placed in the New Brunswick incubator shaker for the initiation of sorption testing, as shown in Figure 3.7.

Figure 3.7 Batch Testing in the New Brunswick Incubator Shaker

3.5.2 Soil Solution Ratio

Prior to the commencement of batch testing, it was necessary to establish a soil solution ratio (SSR) that would be the most ideal for this testing program. SSR is defined as the ratio of the number of parts of soil (grams) to the number of parts of water (grams) in a suspension. To promote uniformity, it was desirable to use the same SSR for all three soil types. However, because of the differences in the soils, a delicate balance needed to be achieved in order to maximize results from all soil tests. To this end, ratios of 1:2, 1:4, 1:5,

1:10, 1:20, 1:25, 1:100 and 1:200 were initially tested. These ratios correspond with soil masses of 62.5, 31.25, 25, 12.5, 6.25, 5, 1.25, and 0.625 grams, in 125 grams of water, respectively. The three lowest ratios (1:2, 1:4, and 1:5) exhibited complications with the kaolinite. The solutions contained such a high amount of soil that adequate mixing was not possible and transfer from sorption to desorption was almost impossible. On the opposite end of the spectrum, the amount of sand in the ratios of 1:20 and higher was not sufficient to result in sorption of even 5 % of the contaminant in a 24 hour period. The remaining SSR of 1:10 (12.5 grams of soil) was sufficient for sand and kaolinite, allowing the sand to sorb roughly 20 % of the contaminant, while also allowing thorough mixing of the kaolinite samples. The soil was not an issue in the determination of a SSR because the amount of sand prevented any mixing issues from arising, while the presence of silt and clay, as well as organic matter, also resulted in sufficient sorption at any ratio.

3.5.3 Sorption / Desorption Testing

The next major testing parameter under consideration was that of sorption and desorption testing times. Testing times of 12, 24 and 36 hours were initially used to determine equilibrium times for all soil types and concentrations. Results from the 12 hours tests were comparatively lower than the 24 hour test results. This indicates that equilibrium has not been reached because the soil still has the capacity to sorb more contaminant. The 36 hour test resulted in erroneous numbers that can be attributed either to the re-dissolution or possible biodegradation of contaminant. The 24 hour testing time was sufficient to allow for levels of sorption that could be accurately measured with GC analysis, as well as providing sufficient contamination for initial desorption concentration levels in testing. The desorption

time resulted in higher volatilization for the higher temperature runs, but still provided results within the range of GC analysis. Shorter times resulted in concentrations less than 20 ppb and too low to be accurately calculated by GC analysis.

Sorption testing occurred immediately after batch preparation and ran for a 24 hour period. For each concentration and temperature, five bottles were in each batch. This consisted of one bottle for each soil type, one bottle repeating a soil as quality control, and one bottle with contaminated solution and no soil to account for volatilization. Upon completion of the testing period, soil and solution were separated using the IEC centrifuge. A 5 mL portion of the solution was stored with zero headspace in PTFE lined septa closure glass bottles for GC analysis, while the remaining solution was discarded. The soil was removed from the centrifuge tubes by means of a piston as shown in Figure 3.8. This soil was then placed back in the Wheaton bottles and 125 mL of deionized water was added to begin desorption testing.

Figure 3.8 Contaminated Soil Before and After Removal from Centrifuge Tubes

Batch desorption testing was performed on soil that had previously undergone sorption testing. This was due to the fact that it was necessary to have soil contaminated with

known concentrations of benzene in order to accurately measure the desorption rates. The soil plugs ejected from the centrifuge tubes were quickly dispersed into suspension by a combination of shaking and the presence of the glass beads, and quickly established a relatively homogeneous suspension suited for desorption testing. Due to the fact that it was impossible to completely dry or completely remove the soil from the centrifuge tubes, the SSR for desorption was not quite 1:10. However, calculations determined that this ratio was never greater than 1:12, or a loss of less than 16% soil by volume. An adjustment to the amount of water used in desorption experiments could have corrected for this SSR variation, however this would have resulted in non-uniform headspace and thus a fluctuation in volatilization, which would have been extremely difficult, if not impossible, to measure.

3.6 Gas Chromatograph Analysis

The first step in GC analysis was to establish a calibration curve for benzene in solution. This was accomplished by mixing known concentrations of benzene with methanol and injecting them into 5 mL of distilled water in a lure lock syringe. This contaminated water was then injected into the Tekmar purge and trap 20 mL liquid glass sampler and then directly transferred to the Varian GC. The calibration curve for benzene, as shown in Figure 3.9, was created from 11 points between 100 and 10000 ppb and has an R^2 value of 0.994.

Figure 3.9 Benzene Calibration Curve for Gas Chromatograph Analysis

The program for the purge and trap requires a 35°C ambient trap temperature in order to begin and utilizes a Tenax Silica Gel Charcoal trap. The purge time is 11 minutes, followed by 3 minutes of dry purge time. Next the trap heats up to a temperature of 250 °C for a 4 minute desorption and then raises the temperature another 10 °C in order to bake for 10 minutes. An automatic transfer in the program injects the concentrated sample into the GC at the beginning of the desorption run.

The gas chromatograph program is specifically designed for the analysis of benzene. Since compounds elute at different times and temperatures, it is necessary to formulate a program that is specific for compounds of concern. The program for benzene begins at 35 °C and ramps up the temperature at a rate of 4 °C per minute to 100 °C. The total run time in

the GC is 16.25 minutes, and benzene eludes at approximately 4.6 minutes or a temperature of 53.4 °C.

The Varian software program presents results as peaks eluting at times specific to three places after the decimal point and an area count determined as the area under the curve. This area count is then correlated to a concentration utilizing a previously developed calibration curve. Typical examples of a Varian graph and report are presented in Figures 3.10 and 3.11 respectively.

Figure 3.10 Typical Varian Results Graph

```

Title      :
Run File   : C:\RESEARCH\TANYA\MODULE16\LOCK215.RUN
Method File : C:\RESEARCH\TANYA\RESEARCH\LOCKTEST.MTH
Sample ID  : 20/20/100 V

Injection Date: 23-AUG-1 12:01 PM    Calculation Date: 23-AUG-1 12:17 PM

Operator   : tmk                      Detector Type: ADCB (10 Volts)
Workstation:                          Bus Address  : 16
Instrument  : 1                      Sample Rate   : 10.00 Hz
Channel    : B = PID                 Run Time    : 16.252 min

***** Star Chromatography Workstation ***** Version 4.51 *****

Run Mode      : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

Peak No.   Peak Name   Result      Ret. Time   Time Offset   Area   Sep. 1/2   Status
          ( )          (min)      (min)      (counts)      Code (sec)   Codes
-----
1          100.0000    4.645      0.000      27686      BB   4.9
-----
Totals:    100.0000          0.000      27686

Total Unidentified Counts :      27686 counts

Detected Peaks: 1          Rejected Peaks: 0          Identified Peaks: 0

Multiplier: 1          Divisor: 1

Baseline Offset: 1 microVolts

Noise (used): 100 microVolts - monitored before this run

Manual injection

Revision Log:

23-AUG-1 12:17 PM: Calculated results from channel B using method:
'C:\RESEARCH\TANYA\RESEARCH\LOCKTEST.MTH'

*****

```

Figure 3.11 Typical Varian Results Report

3.7 Quality Assurance / Quality Control

Precautions were taken during all stages of testing to ensure the highest quality of test results. Each temperature and concentration combination was conducted as a separate batch test so as to eliminate the possibility of cross contamination of different concentrations. Each batch test also consisted of a fourth soil solution as a repeat of one of the three soil types, and a solution only bottle to account for volatilization in addition to the three soil type solutions.

Benzene solutions were prepared new for each batch test to eliminate volatilization and / or degradation from test to test, with initial concentration testing occurring for each solution prepared. Adsorption and centrifuge tests were conducted at 20 °C to regulate ambient conditions. Between batch testing and GC analysis, samples were stored with zero headspace in 5 mL glass bottles with PTFE lined septa and screw top closures. In accordance with the EPA SW-846 manual, samples were stored in a 4 °C refrigerator and analyzed within 14 days of collection.

Prior to daily runs, deionized water alone was run through the purge and trap and GC analysis to verify that no analytes remained in either machine. All glassware, including injection syringes and the Tekmar 20 mL liquid sampler, were rinsed twice with solvent and once with deionized water between every test. Batch testing bottles and Nalgene centrifuge tubes were cleaned with hot water and chemical glassware soap between each testing sequence.

Chapter 4 Sorption Testing

4.1 Testing Justification

Although sorption testing itself was not an objective of this research program, it was necessary to obtain contaminated soil samples with known sorbate concentrations in order to accurately perform desorption testing. For this reason, sorption testing was conducted on all three soil types immediately prior to desorption testing. Results from testing were graphed as equilibrium solution concentration versus amount sorbed and then sorption isotherm equations, as presented in chapter 2, applied to determine the best fit model.

4.2 Benzene Sorption on Sand

Sorption values for the testing program sand were expected to be relatively low due to the absence of organic matter and the low specific surface area (SSA) of the grains. The fine texture however provided a higher SSA than a coarser grain sand and thus at least marginal sorption capabilities. Figure 4.1 shows the sorption results of the testing sand.

Figure 4.1 Sorption Isotherm for Benzene on Sand

The Freundlich equation isotherm resulted in the best fit with an $R^2 = 0.874$. The distribution coefficient of 0.0081 L/g indicates that the majority of the contamination remained in the aqueous phase and was only slightly sorbed to the solid phase. An exponent of 0.7093, as compared to 1 for the linear model, was obtained as the slope from a linear regression plot of Log C versus Log Q.

4.3 Benzene Sorption on Kaolinite

Despite the tendency for high sorption capacities of clay minerals, kaolinite actually exhibited a fairly low sorption of benzene. The low activity and cation exchange capacity (CEC) values for kaolinite, as compared to other clay minerals, as well as the lack of hydrophobicity, are the main contributing factors to this limited sorption capacity. The testing kaolinite sorption results are graphed in Figure 4.2.

Figure 4.2 Sorption Isotherm for Benzene on Kaolinite

Again, the Freundlich isotherm was the best fit model for the testing data with an $R^2 = 0.949$. The slope of the linear regression of the Log C versus Log Q graph resulted in an n value of 0.9636. The distribution coefficient for this soil was 0.0021 L/g, showing a low degree of sorption for the soil. However, the kaolinite showed considerable increase in sorption capability as compared to the sand, especially at higher solution concentrations.

4.4 Benzene Sorption on Natural Soil Material

Unlike the two previous ideal homogeneous soils tested, expectations for the natural testing soil material were more difficult to predict. The high percentage of sand, especially coarser grains, would support the belief of low sorption levels. In contrast, the presence of even a small amount of high activity clay could easily counteract that assumption and endorse higher sorption capabilities. The presence of an organic content of 4.67% also significantly contributes to a higher sorption capability. The distribution coefficient of a soil can be defined by the following equation:

$$K_d = K_{oc}f_{oc} \quad \text{Eqn. 4.1}$$

where:

K_d = distribution coefficient

K_{oc} = organic carbon partitioning coefficient

f_{oc} = fraction of organic carbon

Fetter (1993) presents equations from twelve various researchers that develop a relationship between the organic carbon partitioning coefficient (K_{oc}) and the octanol water partitioning coefficient (K_{ow}). From these twelve studies, Fetter presents a range of 1.34 – 2.54 for the organic carbon partitioning coefficient of benzene. The mean was 1.86, with a standard deviation of 0.35 and a coefficient variation of 0.19. Utilizing the mean value of 1.86 as well

as the organic carbon content of 4.67%, a theoretical distribution coefficient of 0.087 L/g was calculated for the soil. Figure 4.3 shows the isotherm for benzene on the soil material along with experimental results of the distribution coefficient.

Figure 4.3 Sorption Isotherm for Benzene on Soil Material

As with the previous two samples, the best fit model is the Freundlich equation possessing an $R^2 = 0.934$. A value of 0.016 L/g was obtained for the distribution coefficient and supports the theory of a small amount of organic matter having a large influence on sorption. The theoretical value of 0.087 L/g as a distribution coefficient is the correct order of magnitude, although higher in value than the experimental distribution coefficient value of 0.016 L/g. The slope of the Log C versus Log Q graph, or correction factor n, equals 0.7666.

4.5 Soil Sorption Comparison

A graph comparing the sorption capabilities of the three testing materials is presented in Figure 4.4.

Figure 4.4 Sorption Isotherms for Benzene on Sand, Kaolinite, and Soil

As expected, the testing sand possesses the lowest sorption levels of any of the soils. Results also illustrate the limiting nature of low CEC and low hydrophobicity values for clay minerals, with kaolinite sorption only slightly higher than that of the fine grain testing sand. The natural soil exhibited the highest sorption of the three soils, a fact attributed to the presence of organic matter in the heterogeneous mixture.

All three materials followed increasing trends, with higher equilibrium solution concentrations resulting in higher ratios of mass of sorbate to mass of sorbent. A maximum

sorbate level can not be determined from this graph, although trends would suggest that the natural soil material would hold the highest sorption capacity, while the sand would possess the lowest. Table 4.1 lists the three material types, along with their isotherm equations and R^2 values.

Table 4.1 Testing Materials with Isotherm Equations and R^2 Values

Material Type	Isotherm Equation	R^2 Value
Sand	$y = 0.0081x^{0.7093}$	0.874
Kaolinite	$y = 0.0021x^{0.9636}$	0.949
Natural Soil	$y = 0.016x^{0.7666}$	0.934

Comparing the three distribution coefficients, the most obvious variation is the order of magnitude difference between the homogeneous sand and kaolinite and the more heterogeneous natural soil material. An example of this variation is presented in Table 4.2, which lists masses of benzene sorbed per gram of soil on each of the three soil matrices at 100 and 500 ppm solution concentrations.

Table 4.2 Comparison of Sorbed Benzene Mass at Different Solution Concentrations

Material Type	Mass of Benzene Sorbed (mg/g)	
	100 ppm	500 ppm
Sand	0.212	0.665
Kaolinite	0.178	0.837
Natural Soil	0.546	1.876

The amount of benzene sorbed on solid on the natural soil is more than double that of the kaolinite or sand at both the dissolved concentrations of 100 and 500 mg/L, and illustrates the vastly different sorption nature of the soils.

Chapter 5 Desorption Testing

5.1 Testing Outline

Once sorption testing was complete, it was possible to commence desorption testing and analysis. These tests were focused on accomplishing the objectives of determining the temperature effect on desorption capabilities of three soils, and establishing a relationship between desorption magnitude and initial compound concentration. The same batch testing analysis is used for both temperature and concentration, but it is necessary to present results in a different manner for each objective. To that end, desorption testing results for individual soils will be split into two main sections, temperature and concentration, and furthermore into minor sections devoted to each soil. Comparisons among the soils for temperature and concentration effects will be the final section of the chapter.

5.2 Temperature Testing

Temperature testing was conducted at 20° intervals from 20 °C to 80 °C. Results are presented for each soil comparing three different concentrations; 10, 100 and 1000 ppm. These concentrations represent the initial solution concentrations prior to sorption and are used to qualitatively label the different concentration levels. Isotherms are graphed as a plot of temperature versus mass desorbed over mass initially sorbed ($C_0 - C/C_0$), where C_0 is mass initially sorbed and C is mass sorbed remaining.

For all soils, desorption levels are expected to increase with an increase in temperature. This can be attributed to an increase in the vapor pressure and decrease in viscosity. From sorption testing, it was determined that higher initial sorptive concentrations resulted in higher sorbate concentrations. This process results in a greater mass of

contaminant initially sorbed to the soils in higher concentration testing. However, the graphs for temperature comparison plot desorption as a ratio of mass removed over mass originally sorbed, so it is not certain that this ratio will increase when compared to other concentration ratios at the same temperature.

5.2.1 Benzene Desorption on Sand

Figure 5.1 graphs the desorption isotherm for the testing sand at 10, 100 and 1000 ppm.

Figure 5.1 Desorption Isotherm for Benzene on Sand

Desorption levels for the sand are expected to be relatively high for all temperatures. This is due to a number of reasons. First, sorbed contaminant concentrations on the testing sand were initially the lowest of the three soils and thus less contamination exists to be

removed. Second, contaminant that is sorbed is held rather weakly to the soil because of the absence of strong binding mechanisms such as organic matter and charged surface sites. Finally, desorption testing was conducted immediately upon the conclusion of sorption testing, allowing little, if any, time for contamination to migrate deep into the soil particles where desorption becomes very difficult

Results conform to the expectation of increased desorption with an increase in temperature. Looking at the 10 and 100 ppm concentrations, less than a third of the contaminant initially sorbed is desorbed during testing at 20 °C, while almost half is desorbed at 40 °C and nearly three-quarters at and above 60 °C. The 1000 ppm concentration exhibits higher removal at lower temperatures, but this is still an increase from roughly 60% to close to 90% as the temperature increases from 20 °C to 60 °C.

5.2.2 Benzene Desorption on Kaolinite

Similarly, an increase in temperature is projected to result in increased desorption efficiency for kaolinite testing. Desorption isotherm results for kaolinite are graphed in Figure 5.2.

Although initial sorbed mass is still fairly low for kaolinite tests, as well as the time between sorption and desorption almost non-existent, the higher bonding strength of the soil and contaminant could result in desorption levels that are only moderately high, especially at lower temperatures.

Figure 5.2 Desorption Isotherm for Benzene on Kaolinite

As with the sand, results coincide with expectations of increased desorption levels with increasing temperature. Desorption levels for 10 and 100 ppm jump from 40% removal at 20 °C to almost 80% at 40 °C and above. The amount of desorption for the 1000 ppm does not vary significantly with temperature, less than 20%, but does experience an increasing trend, from 80% at 20 °C to 97% at 80 °C, as temperature increases.

5.2.3 Benzene Desorption on Natural Soil Material

The natural testing soil varies from the previous two soils in that the initial mass of contaminant on the soil mass is significantly higher. The time between sorption and desorption is similar to the other tests however, as well as the prediction of a direct relationship between temperature and desorption levels. The natural soil desorption isotherm is graphed in Figure 5.3.

Figure 5.3 Desorption Isotherm for Benzene on Natural Soil Material

At 20 °C, desorption levels are at 40% for 10 and 100 ppm and roughly 55% for 1000 ppm. The results follow the trends of increasing temperature corresponding with increasing desorption. Levels rise to over 70, 80 and 90% removal for 10, 100 and 1000 ppm respectively at 40 °C. At 60 °C, almost 100% removal is achieved for 100 and 1000 ppm.

Since the soil is heterogeneous, it is not known what particles to which the contaminant is attached. If contamination happens to be sorbed mainly to the sand grains, it is likely that desorption results will be fairly high. Conversely, if contamination is bound to clay particles, particularly those with high activities and CECs, desorption levels will be much lower. An understanding of sorption behavior tends towards the latter assessment; consequently results are expected to be moderate at lower temperatures. The lack of time

between sorption and desorption can reduce this influence though, because sorbed strengths increase with time.

5.3 Concentration Testing

The objective associated with concentration was to develop a relationship between desorption and initial solution concentration. This was performed in order to assess the ability to desorb considerable contamination levels at various temperatures. Unlike earlier graphs, these desorption isotherms graph mass desorbed versus mass sorbed for each of the four temperatures; 20, 40, 60, and 80 degrees Celsius. Results are presented for all four temperatures, for each soil, and then compared among the soils for each individual temperature. Within the individual soil graphs, one temperature contains a duplicate testing isotherm. For sand this occurs at 20 and 60 °C, natural soil at 40 °C, and kaolinite at 80 °C.

For all three soils, mass desorbed is expected to increase as the mass sorbed increases. Possible limitations associated with batch testing would be the maximum solubility of benzene in water, but this was addressed in testing by the inclusion of sufficient water to allow the total mass sorbed to become desorbed well before the solubility limit is reached.

5.3.1 Benzene Desorption on Sand

Since no solubility limitations exist on the desorption levels under consideration, it is expected that the mass desorbed will increase with an increase in the mass sorbed. Figure 5.4 graphs the results of testing for the sand at the four different testing temperatures.

Figure 5.4 Graph of Mass Desorbed Versus Mass Sorbed for Test Sand

Duplicate tests were performed at the 20 °C and 60 °C temperatures and are presented as separate data sets. The majority of the points fall in the low mass sorbed area due to the sorption nature of the sand. The few extreme points are associated with the 1000 ppm initial solution concentration which resulted in higher sorption levels. Even at these sorption levels, desorption removed much of the mass present on the soil. Table 5.1 lists the best fit linear regression equation and R^2 values for each of the different temperatures. In the equations, y is equal to the mass desorbed, while x is equal to the mass sorbed. Duplicate temperatures are listed first by data set and then as a single data set.

Table 5.1 Linear Regression Equations and R^2 Values for Sand Desorption

Temperature	Linear Regression Equation	R^2 Value
20 °C (data set 1)	$y = 0.6055x$	.9706
20 °C (data set 2)	$y = 0.3057x$	.9993
20 °C (combined data set)	$y = 0.5744x$	.9787
40 °C	$y = 0.6759x$	.9957
60 °C (data set 1)	$y = 0.8941x$	.9999
60 °C (data set 2)	$y = 0.7202x$	.9999
60 °C (combined data set)	$y = 0.7462x$	.9894
80 °C	$y = 0.8245x$	.9966

In an ideal situation of 100% removal, the slope of the lines would be 1, so the greater the slope, the greater the removal efficiency. Duplicate data set equations do not overlap precisely, but combined data sets result in linear equations with R^2 values of almost 0.98 and 0.99.

5.3.2 Benzene Desorption on Kaolinite

As with sand testing, no solubility limitations exist that could cause complications during kaolinite desorption. This fact, combined with equilibrium desorption testing times is expected to result the amount of mass desorbed to increase with an increase in the amount of mass sorbed. The results for the testing kaolinite at different temperatures are graphed in Figure 5.5.

Figure 5.5 Graph of Mass Desorbed Versus Mass Sorbed for Test Kaolinite

Eighty degrees Celsius is the duplicate temperature data set for kaolinite testing. Again, the majority of data points fall on the low end of mass of sorbed contaminant. Points on the higher levels of sorbed mass are related to tests where initial solution concentration was 1000 ppm. Best fit linear regression equations are listed with R^2 values in Table 5.2. The y variable is mass desorbed, while the x is mass sorbed for the equations listed. For the duplicate 80 °C temperature, values are listed first for the two data sets separately, and then for a single combined data set.

Table 5.2 Linear Regression Equations and R^2 Values for Kaolinite Desorption

Temperature	Linear Regression Equation	R^2 Value
20 °C	$y = 0.8032x$	.9920
40 °C	$y = 0.7901x$	.9627
60 °C	$y = 0.8897x$	1.000
80 °C (data set 1)	$y = 0.9613x$	.9991
80 °C (data set 2)	$y = 0.8915x$	.9999
80 °C (combined data set)	$y = 0.9178x$	.9973

The increase in the slopes of the linear regression lines corresponding to the increase in temperature (noting the dip from 20 °C to 40 °C is very slight) indicates the greater removal efficiency of the higher temperatures. The duplicate graphs in kaolinite testing are the closest of any testing, and possess an R^2 value for the combined data set of over .99.

5.3.3 Benzene Desorption on Natural Soil Material

Although more difficult to predict due to the heterogeneity of the material, the increasing trend of mass desorbed corresponding to an increase of mass sorbed is expected to hold true for the natural soil as well. Figure 5.6 presents the results at four different temperatures with a duplicate at the 40 °C temperature.

Figure 5.6 Graph of Mass Desorbed Versus Mass Sorbed for Natural Test Soil

In contrast to the low sorption levels present for the most part in the sand and kaolinite testing, sorption levels for the natural soil are much higher, even at the lower initial solution concentrations of 10 and 100 ppm. The 1000 ppm initial solution concentration points still exhibit significantly higher sorbed masses, but the data appears to be less clustered than other soil data. Table 5.3 presents the best fit linear regression equations along with the related R^2 values for the natural testing soil.

Table 5.3 Linear Regression Equations and R^2 Values for Natural Soil Desorption

Temperature	Linear Regression Equation	R^2 Value
20 °C	$y = 0.5442x$	.9836
40 °C (data set 1)	$y = 0.9631x$	.9980
40 °C (data set 2)	$y = 0.7111x$	1.000
40 °C (combined data set)	$y = 0.8097x$	.9577
60 °C	$y = 0.9965x$	1.000
80 °C	$y = 0.7751x$	.9995

Comparing duplicate data sets reveals some differences in the two data sets. The combined data set possesses an R^2 value of almost .96, but this is the lowest of all combined data sets. This lower value is believed to be caused by the heterogeneous nature of the soil. From test to test it is impossible to exactly match soil types in the natural soil, as opposed to a homogeneous soil. Results variations can be attributed to slight differences in the ratio of sand and silt to clay particles from test to test. All data points are valid for the soil tested, they just do not fall into a linear pattern as well as data from a more homogeneous soil.

5.4 Temperature and Concentration Comparison of Soil Types

In order to prevent confusion from an excess of data on a single graph, the comparison among the three types of soils will be presented in three separate graphs, each corresponding to an initial solution concentration. Figure 5.7 graphs the 10 ppm initial concentration, Figure 5.8 graphs the initial concentration of 100 ppm, and the 1000 ppm initial concentration is graphed in Figure 5.9.

Figure 5.7 10 ppm Desorption Isotherm Comparing Testing Materials

Figure 5.8 100 ppm Desorption Isotherm Comparing Testing Materials

Figure 5.9 1000 ppm Desorption Isotherm Comparing Testing Materials

As with the previous graphs of individual soils, increasing desorption with increasing temperature is evident. A few of the 80 °C points (e.g. kaolinite 10 ppm and natural soil 1000 ppm) show evidence of decreasing trends. It is believed that this is not a trend but rather discrepancy associated with the boiling of benzene. The New Brunswick Incubator Shaker temperature is accurate to ± 0.3 °C. Benzene has a boiling temperature of 80.1 °C. When tests are run in the shaker at the 80 °C temperature, it is possible that the temperature exceeds the boiling point of benzene, and thus complicates results. In order to test this hypothesis, tests were run for the two previously mentioned points at 75 °C to circumvent the

possibility of benzene boiling. Results are plotted on the previous figure and support the discrepancy belief.

Looking at Figure 5.7, data suggests that at lower concentrations, a change in temperature from 20 to 40 degrees Celsius results in almost a doubling of the desorption percentage from 40% to over 70% for the kaolinite and natural soil. Sand experiences a more constant increase from 20 to 60 °C, before leveling off.

Data from Figure 5.8 supports the drastic jump in desorption levels from 20 to 40 degrees Celsius for the kaolinite and natural soil, with a doubling from 40% to 80%. Above 40 °C, the kaolinite desorption levels off, while the natural soil increases slightly between 40 and 60 °C and flattens out above 60 °C. The trend for sand is also similar to the 10 ppm in an increasing linear fashion between 20 and 60 degrees Celsius and leveling off after that point.

Sand continues a linear trend in Figure 5.9, although not quite as smooth a line as in the lower concentrations. Kaolinite also appears to be more linear in nature at this higher concentration, with no significant jumps occurring between two adjacent temperatures. Desorption of natural soil shows a marked increase between 20 and 40 degrees Celsius, but above 40 °C flattens out considerably.

Considering the three graphs in tandem, the effect of temperature is greater at the lower concentrations and much less influence on higher concentrations for all three soils. Even an increase to only 40 °C results in significant desorption removal efficiency increases for kaolinite and natural soil at the lower 10 and 100 ppm concentrations.

For all testing, desorption results were not corrected for the mass of benzene in entrained solution. Calculations for testing determined that this mass was less than 6% of the total mass desorbed. Thus, desorption level results are slightly, less than six percent, higher than actual desorption levels. Since this is a factor in all testing, any comparisons or trends are still valid.

Figure 5.10 presents four similar graphs of mass sorbed versus mass desorbed for each of the four testing temperatures (a) 20 °C, (b) 40 °C, (c) 60 °C, and (d) 80 °C.

Figure 5.10 Mass Sorbed Versus Mass Desorbed at (a) 20 °C (b) 40 °C (c) 60 °C (d) 80 °C

For all four graphs, duplicate testing data was combined into a single data series, doubling the number of points in the sand series at 20 and 60 degrees Celsius, in the natural soil series at 40 °C, and in the kaolinite series at 80 °C. Comparing the slope of the lines in all four graphs reveals that as the temperature increases, the slopes of the lines increase. An increase in slope relates to an increase desorbed mass relative to sorbed mass, or an increase in the removal efficiency. This trend holds true in all temperature increases for the kaolinite and sand and in all but one for the natural soil. The natural soil experiences a decrease in slope from 60 to 80 degrees Celsius which could be attributed to complications with boiling at the 80 °C temperature.

5.5 Site Application

It is important to realize that laboratory results have real value if applied to real world situations. For this reason, it is necessary to evaluate the potential impact this research program can have on the remediation of existing contaminated sites. It is also necessary to assess the costs and benefits of this type of remediation compared to other existing measures currently in use. Even if a technique is effective, if the costs outweigh benefits, or if other mechanisms are able to accomplish the same results with lower costs and higher benefits, the technique is effectively useless.

First a comparison can be performed against those treatments that do not utilize thermal remediation. Obviously, the cost of heating water is higher than using water at ambient temperature. So the question focuses on the increased effectiveness of the heated water versus that of ambient temperature water.

Results from the research testing suggest that even moderate heating (i.e. to 40 °C) can double the efficiency of desorption removal in some cases. Much of the cost associated with pump and treat remediation is connected with the length of time the system must operate in order to achieve contaminant regulation levels. If the efficiency of the system is doubled the time can be cut in half, so a site that formerly took 20 years to remediate now takes only 10. An additional benefit is the reduction in the number of pore volumes it takes for remediation. Each pore volume of water extracted must be properly disposed of, often at high cost. The reduction of pore volumes required for remediation directly relates to a reduction in cost for disposal of extracted water, a cost reduction that can offset the cost increase associated with heating the injected water.

The opposite comparison would be considering current high temperature thermal treatments versus the lower temperature thermal desorption (LTTD) tested in this program. Current techniques such as steam stripping and electrical heating of soil have proven extremely effective at remediation. Unfortunately, they are also cost prohibitive and require complicated field set up at this time. Although LTTD is not as effective as some of the higher temperature techniques, cost related to implementation is much more likely to fall into an acceptable range from the viewpoint of those individuals responsible for shouldering the financial responsibility of remediation.

Very few laboratory tests results and field scale results directly correspond. However, trends found in the laboratory are often representative of field scale trends. Laboratory tests have proven that higher temperatures result in higher desorption efficiency. These results are related to the increase in vapor pressure and increase in volatilization

caused by the increase in temperature. Temperature increases also result in a decrease in the viscosity of a NAPL, allowing for increased movement and faster removal. All of these factors combined indicate unquestionable benefits related to the use of increased temperatures in remediation techniques.

Chapter 6 Summary and Conclusions

6.1 Summary

Throughout history, diesel fuel has been a major source of energy for people in all nations of the world. Although the benefits of fuel energy are widely known, the disadvantages associated with subsurface contamination have only recently been addressed. The United States EPA has established regulations controlling the transport, storage and disposal of possible contaminants, as well as establishing provisions for the remediation of sites previously affected by contamination. The issue now is the development of techniques that can effectively remediate subsurface contamination in a timely and cost effective manner.

Numerous remediation techniques including pump and treat, air sparging / soil vapor extraction, and surfactant flushing have been employed for contaminant clean-up. Recently, promising steps have been made in the utilizing thermal technologies as enhanced remediation measures. Increased temperature offers benefits including increased vapor pressure and volatilization and decreased viscosity. Previous studies have focused on thermal measures such as steam stripping and electrical heating, both of which offer increased removal efficiency, but only at significantly increased cost and complicated logistics regarding equipment configurations and set up. The possibility exists that increased efficiency can be accomplished at the more moderate temperatures of less than 80 °C, while not significantly increasing cost or complicating the remediation operation. Studies of this nature focus on low temperature thermal desorption (LTTD) which provides the benefits of

increased vapor pressure and decreased viscosity without the cost associated with higher temperature measures.

To this end, a research program focused on batch testing in the laboratory setting was developed to assess the viability of increased temperatures on the desorption efficiency of benzene on various soils. Benzene was chosen as the contaminant of choice because of its presence at the field site of Lockbourne Air Force Base (LAFB) at groundwater contamination levels over 150 times the EPA regulation limit. Laboratory testing was conducted at initial solution contaminant concentrations of 10, 100, and 1000 ppm and temperatures of 20, 40, 60, and 80 degrees Celsius. Soils used in the testing program included a poorly graded fine texture sand, kaolinite, and a natural soil silty sand from the LAFB field site. Soil samples first underwent sorption testing at 20 °C, before being subjected to desorption testing at the previously listed temperatures. Results obtained were then compared among all three soil types at four temperatures and three different initial solution concentrations.

6.2 Conclusions

From the research testing program, the following conclusions can be drawn:

1. At 10, 100 and 1000 ppm initial solution concentration, an increase in benzene concentration results in an increase in sorbed contaminant mass on all three testing soils.
2. The natural soil material experienced the highest levels of contaminant sorbed mass, followed by the kaolinite. Sand experienced the lowest levels of sorbed contaminant

- mass. These trends are consistent with expected sorption levels due to physical and chemical properties of the soils.
3. For contaminant concentrations tested, an increase in sorbed mass resulted in an increase in desorbed mass, indicating a constant or increasing desorption efficiency with increasing contamination concentration.
 4. An increase in temperature results in an increase in desorption efficiency for all three soils tested.
 5. For initial solution concentrations of 10 and 100 ppm, desorption efficiency for the kaolinite and natural soil material increase dramatically from 20 to 40 °C, doubling from 40% to almost 80% , and level off to close to 90% at higher temperatures. The desorption efficiency for sand is more linear in nature from 20 to 60 °C, running from 30% up to 75%, and then levels off.
 6. For an initial solution concentration of 1000 ppm, desorption efficiency for sand and kaolinite possess linear trends from 20 to 60 °C, increasing from roughly 60 % to 90% for sand and 80 % to 90% for kaolinite before leveling off. The natural soil material still experiences a drastic increase, 55% to 95%, from 20 to 40 °C, and then flattens out considerably above that temperature. The leveling off of removal above 40 °C for the natural soil material can be attributed to the hysteresis, or non-uniformity, effect and the inability to removal 100% of contamination.
 7. Overall, temperature appears to have a greater influence on desorption efficiency at lower contamination levels, than at higher contamination levels.

8. The optimum temperature determined from this testing program for a balance of decreased time without a significant increase in cost is 40 °C.

Chapter 7 Recommendations for Future Research

Based on the research performed, the following recommendations are made for future research:

1. Performance flow testing needs to be performed on the same soils with the same concentrations and temperatures as an additional laboratory support of the batch testing performed in this research program.
2. Testing of additional soil types, such as a high activity clay (e.g. montmorillonite) and various natural soils, needs to be performed in either a batch or flow test program to further confirm increased desorption efficiency with increased temperature trends.
3. Complications associated with the effect of aging (i.e. remediation of sites with long term contamination) needs to be addressed to determine if increased desorption efficiency with increased temperature trends exist with an increase in the age of contamination.
4. Field scale application of low temperature thermal desorption (LLTD) needs to be performed to assess the applicability to larger scale applications.

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