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ABSTRACT

AN ANALYSIS OF FIELD DATA FOR EVIDENCE OF ANAEROBIC DEGRADATION OF PAH AND BTEX PLUMES AT MANUFACTURED GAS PLANT SITES

by
Georgene Mortimer

Field data (including geology, hydrogeology, soil chemistry, groundwater chemistry, and aquifer characteristics) were analyzed at eight MGP sites located in the New Jersey Coastal Plain. These data were used to calculate biodegradation rate constants, which were then compared with laboratory microcosm data and published values. Isopleths were drawn from the field data to indicate the dominant biodegradation mechanisms at each of the sites, and stoichiometric calculations were used to determine the total capacity of the electron acceptors present to degrade the plume contaminants. In examining these data, the protocol described by the Air Force Center for Environmental Excellence (AFCEE) was used.

The results of this study showed that at most of the sites, first-order decay constants calculated from field data were generally greater than values reported for the same contaminants at fuel sites. Furthermore, the total capacity of electron acceptors at five of the sites could account for only about a third of the contaminant mass, although at the other three sites there appeared to be sufficient electron acceptors for complete plume attenuation. For most sites, at the plume periphery, aerobic degradation played a major role. However, within the plume, the dominant mechanisms were nitrate, iron, and sulphate reduction.

These findings were corroborated in the microcosm studies conducted for two of the sites, which indicated the importance of sulfate reduction in groundwater collected within the plume. The rate constant calculated for benzene from one of the microcosms was about the same order of magnitude as the constant calculated from field data. However, the rate constant calculated for naphthalene in the other microcosm from a different site was up to two orders of magnitude greater than the field data indicated.

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Georgene Mortimer

**A Dissertation
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Doctor of Philosophy in Environmental Science**

**Department of Chemical Engineering, Chemistry, and Environmental
Science**

May 2002

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APPROVAL PAGE

**AN ANALYSIS OF FIELD DATA FOR EVIDENCE OF ANAEROBIC
DEGRADATION OF PAH AND BTEX PLUMES AT MANUFACTURED GAS
PLANT SITE**

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To Loren, Michael and Nicole

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CHAPTER 1

INTRODUCTION

1.1 General

During the 1800s and early 1900s the solution for most industrial waste disposal problems was to locate an industry such that nearby waterways were large enough to allow dilution of wastes without creating nuisances (True, 1923). As the size and numbers of both industry and population increased, using dilution as a disposal solution became increasingly difficult to implement. Industries thus turned to an increasing reliance on land for disposal of wastes. This period of time coincided with the MGP era.

There are more than 1,500 towns and cities in the United States with decommissioned MGP plants, which were employed in the United States between the early 1800s and the mid 1900s to produce gas from coal and oil (Rajan et al., 1997). MGPs used coal, coke, and oils as raw materials, and generated by-products such as tar, sludge, oils and other chemicals (ERT, 1984). When possible, the MGP industry attempted to recover and sell these by-products. However, tar disposal also occurred, especially in situations where tars emulsified by water were difficult to refine or sell. These tars were often dumped into the ground. In addition to disposal practices, contamination often occurred during various gas-cleaning operations and process train leaks from the complicated network of tanks and pipes. Consequently, large amounts of oily, tarry wastes exist in the subsurface in the form of light or dense non-aqueous phase liquids (LNAPLs or DNAPLs, respectively). Associated with these NAPLs are the following major classes of chemicals:

- polynuclear aromatic hydrocarbons (PAHs): major components of tars;
- volatile organic compounds (VOCs), including benzene, toluene, ethyl benzene and xylenes (BTEX);
- inorganics (ammonia, sulfur and iron compounds, and cyanide); and
- trace metals (e.g. aluminum, antimony, arsenic, barium cadmium, iron, lead, manganese, nickel and zinc). (GRI, 1987).

When these constituents are in the form of DNAPL, they sink below the water table into deeper less oxygenated parts of the aquifer, where they act as a continual source to groundwater contamination. The more soluble components of the NAPL, primarily BTEX and naphthalene, continue to dissolve into the aquifer. The lack of oxygen, coupled with the long time factor (in some cases, over a century) the NAPL has been in place, creates conditions for plumes to migrate significantly before they dissipate.

Practitioners in the field face many challenges when attempting to remediate these sites. The current trend is to separate the problem into two components: source material (NAPL contamination in the form of free and/or residual product) and groundwater contamination. In areas of the country where the water table is high, where there is no confining layer in the unsaturated zone, and the site is not located adjacent to a major body of water, groundwater contamination can be significant.

Groundwater treatment options for large groundwater plumes can be expensive. Options that are commercially available and proven to be feasible for the treatment of one of the MGP plumes in this study are priced below:

<u>Groundwater Treatment Method</u>	<u>Estimated Cost*</u>
Pump and Treat	\$3,200,000
Chemical Oxidation	\$4,500,000
Biosparging	\$1,700,000
Intrinsic Bioremediation	\$375,000

(* Costs provided by site owner)

From a cost perspective, the most desirable option would be intrinsic bioremediation (natural attenuation). However, several factors must be considered prior to selecting this remedial alternative. One of the most important factors is the ability to demonstrate that contaminants are being destroyed through microbial metabolism, as opposed to dilution processes such as advection and adsorption alone.

Another important factor is insuring that there is no risk associated with the long time frames typically associated with intrinsic bioremediation. In order to assess risk over time predictive models can be used. If sufficient levels of oxygen in the groundwater plume are not available, slower anaerobic pathways will dominate the intrinsic bioremediation processes. The accuracy of plume modeling is dependent on two factors: site specific hydraulic information and the kinetics of the dominant microbial mechanisms. However, anaerobic degradation kinetics are difficult to obtain at real sites, leading)) to inaccurate predictions of plume migration.

In the case of the site costed above, the next less costly option is biosparging. However, significant issues associated with this option may be present. Adding oxygen to the subsurface environment that is rich in dissolved iron could cause iron oxide precipitation resulting in well or aquifer plugging. In addition, aerobic respiration sustains large microbial population densities, exacerbating well plugging. A more

feasible option may be to amend the aquifer to enhance anaerobic degradation. However, due to a lack of understanding of the mechanisms, no commercial remedies for doing so are currently available.

Two major areas where state-of-the-art information falls short are: (1) an adequate understanding of the dominant anaerobic mechanisms in the field (i.e. nitrate, sulfate, and/or iron reducing pathways); and (2) the availability of reliable anaerobic rate constants in the field. The availability of this information would improve the potential use of intrinsic bioremediation at anaerobic field sites.

1.2 Objectives

The objectives of this dissertation were to:

- calculate biodegradation rate constants for MGP constituents from field data at eight former MGP sites
- compare the rate constants obtained in the field with those obtained from laboratory microcosms, and literature values
- determine the dominant anaerobic mechanisms at those field sites
- calculate the assimilative capacity of the electron acceptors at those sites

The results will allow an estimation of the efficacy of intrinsic bioremediation at the MGP sites, and establish a methodology for site evaluation.

A combination of laboratory and field studies was used to accomplish these objectives. Laboratory microcosm studies examined the ability of indigenous organisms, at two MGP sites in southern New Jersey, to degrade benzene, toluene and naphthalene under anaerobic conditions. Degradation rate constants were calculated from these

microcosm data and were compared with rate constants calculated from field data collected at several sites. Although field data were collected in conjunction with remedial investigations (RIs), this dissertation involves the analysis of more extensive data, with considerably greater chemical and mathematical analysis, than is common in RIs (which are essentially feasibility studies).

Using BIOSCREEN, a plume migration model developed by the Air Force Center for Environmental Excellence (AFCEE) Technology Transfer Division at Brooks Air Force Base, two kinetic models were compared for each site to determine which model best predicts the rate of biodegradation. The two models are classic first-order decay, and instantaneous reaction limited by electron acceptor availability (i.e. transport limited). This information is essential in determining which type of numerical model is best suited for use at MGP sites. For example numerical models such as BIOPLUME II, Bio Trans[®] and Bio 1D[®] allow for the simulation of aerobic and anaerobic degradation using first-order rate constant, while models such as BIOSCREEN and BIOPLUME III allow simulation of both first-order biodegradation and instantaneous reaction between electron acceptors and dissolved contaminants (i.e. where the extent of plume travel is entirely a function of transport processes). Khan and Husain, (2002) used BIOSCREEN to model xylene concentrations at a gasoline spill site. Their results showed that the instantaneous model was a better predictor of field data.

Another significant question this study attempted to answer is if dissolved MGP contaminant plumes inherently contain sufficient electron acceptors to support anaerobic degradation. MGP plants used coal or coke, which typically contain significant amounts of iron and sulfate. Consequently, it would be important to determine if sulfate reducing

and/or iron reducing pathways are playing a role in the biodegradation of BTEX and naphthalene. As a result, the stoichiometric capacity (also referred to as the “assimilative capacity”) of each electron acceptor at each field site was also determined as an indication of anaerobic potential. By calculating the assimilative capacity (based on the concentration of electron acceptor and the stoichiometric ratio of electron acceptor to contaminants), a determination was made regarding the potential for anaerobic degradation at each of the MGP sites.

The eight MGP sites provide an ideal source of data for this analysis for two reasons: 1) because the groundwater plumes are well defined and very well studied; and 2) the contaminants have been in the ground for almost a century, and therefore contaminant behavior over a large time-scale can be studied. The practical application is that information gained at these well-studied sites can be used to infer fate and transport at MGP sites where (more typically) less data is collected.

1.3 Literature Search

Freeze and Cherry (1979) pointed out that oxidation of organic matter can occur in the subsurface in the absence of oxygen by bacterial utilization of alternate electron acceptors such as nitrate, manganese, ferric ion, sulfate, and other constituents. They listed redox reactions toward increasingly reduced ground water conditions (Table 1.1):

Table 1.1 Summary of Oxidation-Reduction Reactions

(After Freeze and Cherry, 1979, Table 3.11)

Process	Reaction
Denitrification ¹	$5\text{CH}_2\text{O} + 4\text{NO}_3^- \rightarrow 2\text{N}_2 + 5\text{HCO}_3^- + \text{H}^+ + 2\text{H}_2\text{O}$
Manganese (IV) reduction	$\text{CH}_2\text{O} + 2\text{MnO}_2(\text{s}) + 3\text{H}^+ \rightarrow 2\text{Mn}^{2+} + \text{HCO}_3^- + 2\text{H}_2\text{O}$
Iron (III) reduction	$\text{CH}_2\text{O} + 4\text{Fe}(\text{OH})_3 + 7\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{HCO}_3^- + 10\text{H}_2\text{O}$
Sulfate reduction ²	$2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{HS}^- + 2\text{HCO}_3^- + \text{H}^+$
Methane fermentation	$2\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{HCO}_3^- + \text{H}^+$

Notes: 1) CH_2O (formaldehyde) is representative of organic matter2) H_2S exists as a dissolved species in water: $\text{HS}^- + \text{H}^+ \rightarrow \text{H}_2\text{S}$ H_2S is the dominant species at $\text{pH} < 7$

Longmire (1986) reports a case history of a gasoline spill near Albuquerque, New Mexico that documents increased levels of dissolved iron, manganese, bicarbonate, reduced sulfate and a slight reduction of pH in an aquifer as the result of biodegradation of the gasoline. Ehrlich, et al. (1982), Wilson, et al. (1986) and Chiang, et al. (1986) provide other early examples of anaerobic biodegradation as important mechanisms that limit transport of organic pollutants. Ehrlich, et al. (1982) provides a case history of biodegradation of phenols in ground water by anaerobic bacteria at a coal tar facility in St. Louis Park, Minnesota. Their study included sampling of soil cores, which confirmed the presence of methane generating bacteria cultured from soil samples. Their study also demonstrated that phenol concentration decreased much more rapidly than the concentration of conservative tracers such as sodium. Wilson, et al. (1986) cites similar results for degradation of alkyl benzenes from a gasoline spill in Traverse City, Michigan. Chiang, et al. (1986) studied rates of benzene, toluene and xylene biodegradation in an aquifer contaminated by a refinery flare pit in Michigan. They performed experiments in the laboratory with aquifer soils containing indigenous

populations of aerobic and anaerobic microbes. They found that the biodegradation reactions could be described as a first-order rate process; however, the aerobic benzene degradation rate constant determined in the laboratory was about an order of magnitude higher than that obtained from field data.

Benzene degradation in the absence of oxygen was noted as early as 1980, with the formation of small amounts of $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ from [^{14}C] benzene in methanogenic enrichments derived from petroleum-contaminated salt marsh and estuarine sediments (Ward et al., 1980). More recent studies indicate that under the right conditions, benzene can be oxidized to CO_2 in the absence of oxygen with either sulfate or Fe (III) serving as the electron acceptor. Edwards and Grbic-Galic (1992) demonstrated 90% mineralization of ^{14}C -labeled benzene to CO_2 by aquifer-derived microorganisms, in microcosms containing gasoline-contaminated subsurface sediments and an anaerobic mineral medium supplemented with 20mM sulfate.

In a study by Lovley et al. (1994), highly reduced sediments incubated under strictly anaerobic conditions metabolized benzene within 55 days. When ^{14}C -labeled benzene was added to the benzene-adapted sediments, 92% of the added radioactivity was recovered as $^{14}\text{CO}_2$. Molybdate, an inhibitor of sulfate reduction, inhibited benzene uptake and production of $^{14}\text{CO}_2$ from ^{14}C -labeled benzene. The stoichiometry of benzene uptake and sulfate reduction was consistent with the hypothesis that sulfate was the principal electron acceptor for benzene oxidation.

The 1998 Mihelcic and Luthy study also indicated that PAHs persist under sulfate reducing or methanogenic conditions. However, as reported by Coates et al., (1996), sulfate reduction was necessary for PAH degradation in heavily contaminated sediments

from San Diego Bay. Further investigations by Coates et al., 1997 indicated that naphthalene oxidation in the San Diego Bay soil was sulfate-dependent. Incubating the sediments with additional naphthalene for one month resulted in a significant increase in the degradation of ^{14}C naphthalene. In sediments from a less heavily contaminated site, where PAHs were not readily degraded, naphthalene degradation could be stimulated through inoculation with active PAH-degrading sediments from the more heavily contaminated sites. Molybdate, a specific inhibitor of sulfate-reduction, inhibited degradation. Zhang and Young (1997) conducted a similar study with soil from the Arthur Kill in New York/New Jersey Harbor. Complete loss of naphthalene was observed after 150 days of incubation. Also in this study, intermediates of PAH degradation under sulfate-reducing conditions were reported for the first time.

Evidence of benzene mineralization under Fe (III)-reducing conditions was also observed (Lovely et al. 1995). Fe (III) chelated to compounds such as EDTA, humic acids, and phosphates stimulated benzene oxidation coupled to Fe (III) reduction in anaerobic sediments from a petroleum-contaminated aquifer. The stoichiometry of benzene metabolism and Fe (III) reduction indicated that Fe (III) was the sole electron acceptor for benzene oxidation in these sediments. Anderson et al. (1998) provide data consistent with in-situ (unamended with chelating agents) anaerobic oxidation of benzene to carbon dioxide in a Fe (III)-reducing zone of a petroleum-contaminated aquifer. Kazumi et al. (1996) also report benzene loss under Fe (III)-reducing conditions in Potomac River sediments in the absence of added Fe (III) chelators.

Evidence for the microbial degradation of benzene under denitrifying conditions is less persuasive. Kazumi et al. (1996) found that benzene persists under denitrifying

conditions. However recently, Burland and Edwards (1999) report that benzene oxidation to carbon dioxide was linked to nitrate reduction in enrichment cultures developed from soil and groundwater microcosms. They reported that benzene biodegradation occurred concurrently with nitrate reduction at a constant ratio of 10 moles of nitrate consumed per mole of benzene degraded. However, this is not consistent with the theoretical stoichiometry as shown:



Similar to benzene, unsubstituted PAH compounds such as naphthalene were thought to be refractory in anaerobic soil-water systems until recently. In 1988, Mihelcic and Luthy were the first to demonstrate that naphthalene and acenaphthene were degraded under denitrifying conditions. In another study that year, they demonstrated that under those conditions, naphthalene was degraded from an initial aqueous-phase concentration of 7 mg/liter to nondetectable levels in 45 days. Al-Bashir et al. (1990) conducted a similar study that demonstrated naphthalene degradation under denitrifying conditions. They showed that 90% of naphthalene, at an initial concentration close to the aqueous phase saturation level (30 mg/L), mineralized within 50 days with an adaptation period.

The studies discussed above have all been laboratory studies. Several field studies documenting the roles of electron acceptors in aerobic and anaerobic biodegradation (intrinsic bioremediation) of petroleum hydrocarbons have been demonstrated in the literature. In 1989, Chiang et al. demonstrated natural attenuation of BTX in the field under aerobic conditions. The natural attenuation rate was calculated to be 0.95% per day and spatial relationships between dissolved oxygen and BTX were strongly correlated by statistical analysis and solute transport modeling. In addition, laboratory

microcosm biodegradation experiments were performed to determine possible threshold limits for aromatic hydrocarbon oxidation under varying levels of dissolved oxygen.

Several field studies describing intrinsic biodegradation at MGP sites have been presented at symposia such as the Battelle sponsored "*In Situ and On-Site Bioremediation*" and the IGT sponsored "*Environmental Biotechnologies and Site Remediation Technologies Symposium*". These studies go little beyond describing the fact that the contaminants present no risk to human health or the environment, and therefore monitored natural attenuation can be selected as a remedial option. However, these studies do not describe the mechanisms responsible for the biodegradation (if any) occurring at these sites.

Ginn et al. (1994) point to several lines of evidence regarding the natural attenuation of PAHs at an MGP site in New York. The study shows that PAH concentrations within an aquifer plume were observed to decrease with time subsequent to source removal. There was also an inverse correlation between contaminant concentrations and dissolved oxygen concentrations. Laboratory studies conducted with MGP contaminated soils indicate that indigenous microorganisms in the soil were capable of degrading naphthalene and phenanthrene. In addition, a biochemical metabolite of phenanthrene degradation (1-hydroxy-2-naphthoic acid) was tentatively characterized at the site. This study qualitatively demonstrated aerobic degradation of a naphthalene plume.

Durant et al. (1995) studied the naphthalene degradation from MGP aquifer microcosms under aerobic and nitrate reducing conditions. This study reported that

oxygen amended conditions resulted in the greatest rate of biodegradation. However, some MGP site sediments prefer mixed NO_3^-/O_2 conditions.

Davis et al. (1994) conducted microcosm studies with sulfate reducers and methanogens, which indicated benzene could be degraded in a period of a few weeks (after acclimation). When compared to the time required to replenish electron acceptors in a plume, it appears appropriate to simulate anaerobic biodegradation of dissolved hydrocarbons as an instantaneous (transport-limited) reaction. This has also been suggested by Newell et al. (1995).

Colberg et al. (1994) provides preliminary evidence of anaerobic microbial activity in the subsurface of a former MGP site in Baltimore, Maryland. Gas chromatographic analysis of the headspace of sampling wells installed at the site suggested that anaerobic biotransformation might be a significant process. Chemical analysis of groundwater indicated high levels of sulfate (300 to 7,800 mg/L) and iron (0.5 to 3,000 mg/L) at the site; and both hydrogen sulfide and methane were routinely detected in the soil vapor. This suggested that sulfidogenesis and methanogenesis were occurring. Analysis of laboratory microcosms from shallow subsurface soils at the site (0.15m to 1.5 m below the surface) suggested that anaerobic condition might be readily establish in situ. This is the first published study suggesting anaerobic mechanisms at an MGP site.

The literature search also uncovered a number of other studies that consistently indicated field degradation rates an order of magnitude lower than those of laboratory microcosms. Chiang et al. (1986) noted order of magnitude lower degradation rates in the field at a Cody, Wyoming refinery wastewater disposal site compared with laboratory

test rates. Also, as summarized in Rifai et al. (1995), three different approaches were applied at the Rocky Point, North Carolina site to estimate intrinsic bioremediation rates: (1) comparing contaminant concentrations in monitoring wells versus travel time from the source; (2) monitoring laboratory microcosms under anaerobic conditions; and (3) monitoring in situ test chambers, (which are areas in the field isolated by inserting hollow tubes into the ground) to determine loss over time. The results are summarized in Table 1.2. There appears to be a progression of the rate constants as a function of scale, with laboratory (microcosm) degradation rates an order of magnitude greater than rates calculated from field data.

Table 1.2 Comparison of Intrinsic Bioremediation First-Order Rate Constants (days⁻¹) from Field Monitoring, Laboratory Microcosms, and In-situ Test Chambers (Rifai et al., 1995)

Compound	Field Data	In-Situ Test Chamber	Microcosm
Benzene	0.0002	0.004	0.024
Toluene	0.0021	0.012	0.045
Ethylbenzene	0.0015	Not Sampled	0.002
O-xylene	0.0021	Not Sampled	0.056
M, p-xylene	0.0013	0.014	0.020

1.4 Technical Protocol

Over the past several years, many technical protocols have been developed for data collection and analysis in order to support intrinsic bioremediation for the restoration of contaminated groundwater. The model used in this study was developed by the Air Force Center for Environmental Excellence (AFCEE), and is described in their publication: *Technical Protocol for Implementing the Intrinsic Remediation with Long-Term Monitoring Option for Natural Attenuation of Dissolved-Phase Fuel Contamination in*

Ground Water. This protocol is based on work performed at 40 fuel-contaminated sites across the United States, and provides a methodology to scientifically support and document intrinsic biodegradation in the field. A detailed discussion of this protocol can be found in Chapter 2. In a recent publication (2001) by the National Research Council on *Natural Attenuation for Groundwater Remediation*, which reviewed 14 protocols for evaluating natural attenuation, the following was said about the AFCEE protocol: “From a technical standpoint, this is among the most thorough and scientifically sound of the available protocols”.

CHAPTER 2

BACKGROUND

2.1 Biological Processes Controlling Biodegradation

Biological degradation is the most important process controlling the natural attenuation (NA) of organic contaminants of concern (COC) in groundwater flow systems (Wiedemeier et al., 1995). Native microflora in groundwater systems utilize organic carbon as a carbon and energy source to be viable, grow, and multiply. This energy source may be obtained through the biological degradation of naturally occurring soil organic matter (SOM) or many organic COCs. More specifically, the energy is obtained through the transfer of electrons from electron donors (*e.g.*, SOM, COCs) to terminal electron acceptors (TEAs), such as dissolved oxygen (DO), nitrate, iron, and sulfate.

Microorganisms will utilize TEAs with higher reduction potentials before using those with lower values. Wiedemeier et al. (1995) listed reduction potentials for the primary TEAs associated with COC biodegradation:

- DO, +200 mV to +1,350 millivolts (mV);
- nitrate, +665 mV to -200 mV;
- iron (III), +100 mV to -900 mV;
- sulfate, -200 mV to -1,300 mV; and
- carbon dioxide, -500 mV to -1,300 mV.

Once the TEA with the highest reduction potential is depleted, micro flora use the TEA with the next lowest reduction potential (assuming its availability). This continues in stepwise fashion, from DO, to nitrate, to iron, to sulfate, to CO₂.

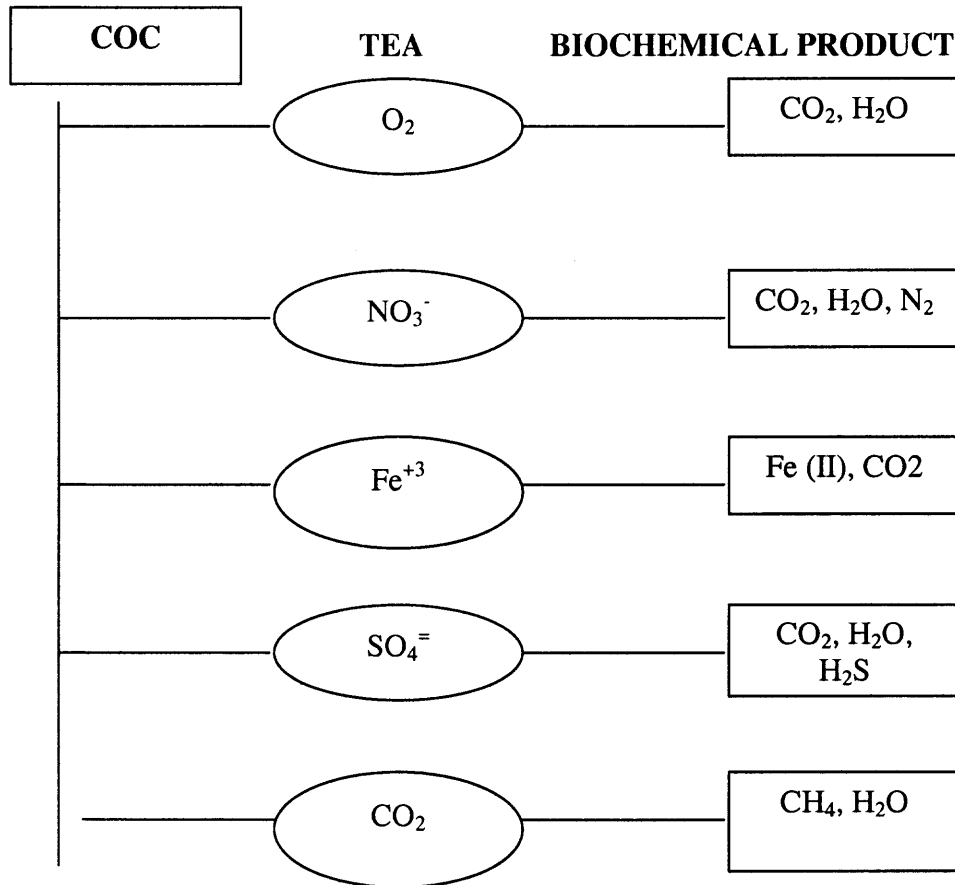


Figure 1.1 TEA Ladder, from higher reduction potential s to lower.

Data obtained for each TEA may be used to assess the relative importance of COC biological degradation processes, as follows:

Aerobic Respiration – Dissolved oxygen is the most thermodynamically favored electron acceptor used in the biodegradation of hydrocarbons. During aerobic biodegradation, dissolved oxygen concentrations decrease. Each 1.0 mg/L of dissolved oxygen consumed by microbes will mineralize approximately 0.32 mg/L of BTEX (the stoichiometry is discussed later in this report). Depressed DO concentrations for COC plume groundwater monitoring locations, relative to background locations, suggest that

aerobic respiration by native micro flora is attenuating COCs. The biochemical products of this transformation are ultimately carbon dioxide and water.

Nitrate Reduction – After dissolved oxygen has been depleted in the plume, nitrate may be used as an electron acceptor by anaerobic biodegradation via denitrification. Anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L. Each 1.0 mg/L of ionic nitrate consumed by microbes results in the mineralization of approximately 0.21 mg/L of BTEX. Depressed nitrate concentrations for COC plume groundwater monitoring locations, relative to background locations, suggest that nitrate reduction by native micro flora is attenuating COCs. The biochemical products of this transformation are ultimately nitrogen gas, carbon dioxide, and water.

Iron Reduction – Once DO and nitrate have been depleted in the COC plume, ferrous iron (Fe^{2+}) concentrations increase as native micro flora use ferric iron (Fe^{3+}) as their TEA. Elevated Fe^{2+} for COC plume groundwater monitoring locations, relative to background locations, suggest that iron reduction by native micro flora is attenuating COCs. The mineralization of 1 mg/L of BTEX results in the production of approximately 21.7 mg/L of iron (II) during iron (III) reduction. The biochemical products of this transformation are ultimately Fe^{2+} and carbon dioxide.

Sulfate Reduction – Once DO, nitrate, and Fe^{3+} have been depleted in the COC plume, sulfate concentrations decrease as native micro flora use sulfate as their TEA. Each 1.0 mg/L of sulfate consumed by microbes results in the mineralization of approximately 0.21 mg/L of BTEX. Depressed sulfate concentrations for COC plume groundwater monitoring locations, relative to background locations, suggest that sulfate

reduction by native micro flora is attenuating COCs. The biochemical products of this transformation are ultimately hydrogen sulfide, carbon dioxide, and water.

Methanogenesis – Once DO, nitrate, ferric iron, and sulfate have been depleted in the COC plume, methane concentrations increase as native micro flora ferment COCs. Elevated methane concentrations for COC plume groundwater monitoring locations, relative to background locations, suggest that methanogenesis by native micro flora is attenuating COCs. The mineralization of 1 mg/L of BTEX results in the production of approximately 0.78 mg/L of methane during methanogenesis.

As biological degradation of COCs occurs throughout the contaminant plume, TEAs become depleted in the stepwise order shown. Given an equivalent stoichiometric ratio of TEA to COC mass, conducive subsurface conditions for micro flora, and sufficient time, the COC plume may be entirely mineralized.

2.2 AFCEE Protocol

Over the past several years, many technical protocols have been developed for data collection and analysis in order to support intrinsic remediation for the restoration of contaminated groundwater. One of these protocols, developed by the Air Force Center for Environmental Excellence (AFCEE) was used as a model to evaluate data collected at the southern New Jersey MGP sites examined in this study. The development of this protocol was based on work performed at 40 fuel-contaminated sites across the United States. It provides a means to scientifically support and document intrinsic biodegradation through aerobic and anaerobic processes in the field. The protocol is described in the widely accepted document: *Technical Protocol for Implementing the*

Intrinsic Remediation with Long-Term Monitoring Option for Natural Attenuation of Dissolved-Phase Fuel Contamination in Ground Water (AFCEE Protocol).

The primary objective of any intrinsic remediation investigation is to show that natural processes of contaminant degradation will reduce contaminant concentrations in groundwater to below regulatory standards before reaching a potential receptor. To support implementation of intrinsic remediation, one must scientifically demonstrate that degradation of site contaminants are occurring at rates sufficient to be protective of human health and the environment. Three lines of evidence can be used to support intrinsic remediation including:

- (1) documented loss of contaminants at the field scale
- (2) use of chemical analysis in mass-balance calculations for potential biodegradation
- (3) laboratory microcosm studies using aquifer samples collected from the site.

The first line of evidence involves using historical trends in contaminant concentration in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in the total mass of contaminants is occurring at the sites. The second line of evidence involves the use of chemical analysis and mass balance calculations to show that decreases in contaminant concentrations can be correlated to changes in electron acceptor concentrations. This evidence can be used to show that electron acceptor concentrations in groundwater are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models can be used to aid mass balance calculations and to collate information on degradation. The third line of

evidence, direct microbiological evidence, can be used to show that indigenous biota are capable of degrading site contaminants.

In order to get to the point where one can examine the various lines of evidence, extensive site characterization and data reduction is necessary, as described in the following sections. The data from the MGP sites were collected and reduced according to the AFCEE Protocol. These site characterizations were performed during the Remedial Investigation/Feasibility (RI/FS) Studies under the direction of the New Jersey Department of Environmental Protection.

2.2.1 Site Characterization

The level of site characterization necessary to adequately evaluate a site for intrinsic remediation requires extensive knowledge of soil and groundwater, including the following:

- extent and type of soil and groundwater contamination
- location and extent of contaminant source areas
- aquifer geochemical parameters
- site-specific hydrogeology, including
 - aquifer hydraulic conductivity
 - locations and types of surface water bodies
 - areas of local groundwater recharge and discharge
 - preferential flow paths
- regional geology/ site stratigraphy
- grain size distribution of soil
- identification of potential exposure pathways and receptors.

Soil

In order to adequately define the subsurface hydrogeologic system and to determine the amount and three-dimensional distribution of mobile and residual NAPL that can act as a continuing source of groundwater contamination, extensive soil characterization must be completed. Soil sampling must be conducted with the objective of determining the subsurface distribution of hydrostratigraphic units and the distribution of mobile and residual NAPL. These soils samples should be analyzed for several parameters:

Hydrocarbons - Knowledge of the location, distribution, concentration, and mass of hydrocarbons (especially BTEX and PAHs), sorbed to soils or present as NAPL, is essential to determine contaminant partitioning into groundwater. This information is particularly important in defining the extent of the contaminant source area. In addition, the baseline total organic carbon (TOC) content of the aquifer matrix is important in sorption and solute-retardation calculations. TOC samples are collected from a background location in the zone(s) where contaminant transport is expected to occur.

Groundwater

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of intrinsic remediation, groundwater samples must be collected and analyzed. Biodegradation of hydrocarbons brings about measurable changes in the chemistry of groundwater in the affected area. By measuring these changes, one can document and quantitatively evaluate the importance of intrinsic remediation at a site. Groundwater samples are analyzed for hydrocarbons, dissolved oxygen, nitrate, iron (II), sulfate, and methane in order to determine the three-dimensional distribution of contaminants and groundwater geochemical parameters.

Alkalinity - In general, areas contaminated by hydrocarbons exhibit total alkalinity that is higher than what is seen in background areas. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction, and less pronounced during methanogenesis (Morel and Hering, 1993). Additionally, Willey et al. (1975) show that short-chain aliphatic acid ions produced during biodegradation of fuel hydrocarbons can contribute to alkalinity in groundwater. Each 1.0 mg/L of alkalinity produced by microbes results from the mineralization of approximately 0.13 mg/L of total BTEX. The production of alkalinity can be used to cross-check calculations of expressed assimilative capacity based on concentrations of electron acceptors.

Oxidation/Reduction Potential - Redox reactions in groundwater contaminated with petroleum hydrocarbons are usually biologically mediated, and therefore, the redox potential of a groundwater system depends upon and influences rates of biodegradation. The redox potential of groundwater generally ranges from -400 millivolts (mV) to 800 mV. Redox potential can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. At least one redox measurement from a well located upgradient from the plume must be taken as a background reference.

pH, Temperature and Conductivity - Microbes capable of degrading petroleum hydrocarbon compounds generally prefer a pH between 6 and 8. Groundwater temperature directly affects the solubility of oxygen and other geochemical species, as well as the metabolic activity of bacteria. Although measured in the field, groundwater temperatures tend to remain fairly constant.

Conductivity measurements are used to insure that groundwater samples collected at a site are representative of the water comprising the saturated zone in which the dissolved contamination is present. If the conductivity of samples taken from different sampling points are radically different, the waters may be from different hydrogeologic zones.

Aquifer Parameter Estimation

Hydraulic Conductivity - Hydraulic conductivity is a measure of an aquifer's ability to transmit water, and is perhaps the most important aquifer parameter governing fluid flow in the subsurface. The velocity of groundwater and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential paths for contaminant migration. Estimates of hydraulic conductivity are used to determine residence time for contaminants and to determine the seepage velocity of groundwater. Aquifer pumping tests and slug tests are commonly used to measure hydraulic conductivity.

Hydraulic Gradient - The hydraulic gradient is the change in hydraulic head over a given distance in the direction of groundwater flow. To accurately determine the hydraulic gradient, it is necessary to measure groundwater levels in all monitoring wells with piezometers. Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific groundwater elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in groundwater flow direction can have a profound influence on contaminant transport.

2.2.2 Data Reduction

Site characterization data are used to quantify groundwater flow, sorption, dilution, and biodegradation, employing geologic logs, hydrogeologic sections, potentiometric surface/water table maps, contaminant contour (isopleth) maps, and electron acceptor and metabolic byproduct isopleth maps.

Geologic logs of all subsurface materials encountered during the soil boring phase of the field work were constructed. Descriptions of the aquifer matrix include relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations such as visible NAPL or hydrocarbon odor. The depth of lithologic contacts and/or significant textural changes are recorded to the nearest 0.1 foot.

A minimum of two hydrogeologic sections are required: one parallel to the direction of groundwater flow and one perpendicular to the direction of groundwater flow. Hydraulic head data, including potentiometric surface and/or water table elevation data, are plotted on the hydrogeologic cross section. These sections are useful in locating potential preferential contaminant migration paths and in simulating contaminant transport using fate and transport models.

A potentiometric surface or water table map showing a two-dimensional graphical representation of equipotential lines is prepared, using water level measurements (in wells screened in the same relative position within the same hydrogeologic unit) and surveyor data. Because groundwater flows from areas of high hydraulic head to areas of

low hydraulic head, such maps are used to estimate the probable direction of plume migration and to calculate hydraulic gradients.

Contaminant contour maps were prepared for each compound of concern for each discrete sampling event, as well as for electron acceptors consumed and metabolic byproducts produced [iron (II) and methane] during biodegradation. During aerobic biodegradation, dissolved oxygen concentrations decrease to levels below background concentrations. Similarly, during anaerobic degradation, the concentrations of nitrate and sulfate will be seen to decrease to levels below background. Additionally, the metabolic byproducts methane and iron will be seen to increase above background levels. The electron acceptor and metabolic byproduct contour maps allow interpretation of data on the distribution of the electron acceptors and the relative transport and degradation rates of contaminants in the surface. Thus, these contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors.

2.2.3 Examining The Three Lines of Evidence

As seen above, a substantial amount of data are collected at each site and put into a usable form before the potential for intrinsic remediation can be evaluated. According to the AFCEE protocol, the three lines of evidence, which can be used to support intrinsic bioremediation in the field include:

- documented loss of contaminants at the field scale
- use of chemical analysis in mass-balance calculations
- laboratory microcosm studies using aquifer samples collected from the site.

(1) **The first line of evidence** involves collecting and analyzing data from monitoring wells and noting decreasing trends in contaminant concentrations over time. The change in solute concentration in the groundwater over time often can be described using a first-order rate constant. In order to ensure that observed decreases in contaminant concentrations in the field can be attributed to biodegradation, measured concentrations of the degradable constituents must be corrected for the effects of advection, dispersion, dilution from recharge, and sorption. Two methods for determining first order biodegradation rates at the field scale are used. The first method involves the use of a conservative tracer to compute a decay rate. The second method was derived by Buscheck and Alcantar (1995) for steady-state plumes. The conservative tracer method is based on the fact that typically at fuel sites trimethylbenzene (TMB) is present and has sorptive and volatilization properties similar to those of BTEX, but is recalcitrant under aerobic and anaerobic conditions. This results in the following equation from (Wiedemeier et al., 1995):

$$C_{B,\text{corr}} = C_B [TMB_A / TMB_B]$$

Where $C_{B,\text{corr}}$ = corrected concentration of compound of interest

C_B = measured concentration of compound of interest

TMB_A = measured concentration of TMB at point A

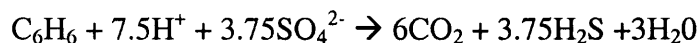
TMB_B = measured concentration of TMB at point B

The other method described by Buscheck and Alcantar (1995) involves regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) and relating the result to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption and biodegradation. For a steady-state plume, the first-order decay rate is given by:

$$k = v [d(\ln S)/dx] \{ (D_x/v)d(\ln S)/dx - 1 \}$$

where: k = first-order biological decay rate (s^{-1})
 v = groundwater velocity in the x direction (cm/s)
 D_x = axial dispersivity (cm^2/s)
 $d(\ln S)/dx$ = slope of line formed by making a log-linear plot of contaminant concentration versus distance downgradient along flow path (cm^{-1})

(2) **The second line of evidence** involves the use of chemical analysis in mass balance calculations to show that a decrease in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic byproduct concentrations. Based on stoichiometric relationships between electron acceptors and contaminants, mass balance calculations can be completed for each of the electron acceptors. The results of the mass balance calculations give an indication of the intrinsic capacity of the groundwater to degrade the contaminants. For example, if analysis of the contour maps shows that the spatial relationship between benzene and sulfate concentrations in the plume indicates the use of sulfate as an electron acceptor for the degradation of benzene, the mass balance can be calculated from the following equation (neglecting biomass production):



Therefore, 3.75 moles of sulfate are required to metabolize 1 mole of benzene. On a mass basis, the ratio of benzene to sulfate is 0.22. Thus,

$$\text{Benzene}_{\text{Bio},s} = 0.22 (S_B - S_M)$$

Where: $\text{Benzene}_{\text{Bio},s}$ = reduction in benzene concentration via sulfate reduction
 S_B = background sulfate concentration (mg/L)
 S_M = measured sulfate concentration in plume (mg/L)

This evidence can be used to show that electron acceptor concentrations are sufficient to degrade dissolved-phase contaminants. Borden and Bedient (1986) indicated

that microbially mediated reactions between dissolved oxygen and BTEX are limited by the amount of electron acceptor available, and can be considered instantaneous relative to normal groundwater flow velocities. The time required for the biomass to degrade the dissolved hydrocarbon is on the order of days or weeks, whereas the overall time to flush a plume with fresh groundwater is on the order of years to tens of years.

(3) **The third line of evidence**, the microcosm study, involves studying site aquifer material under controlled conditions in the laboratory to show that indigenous biota are capable of degrading site contaminants, and (perhaps) to confirm rates of contaminant degradation measured at the field scale.

2.2.4 Similarities and Differences Between Fuel Sites and MGP Sites

Although the AFCEE Protocol was developed to evaluate intrinsic remediation at fuel hydrocarbon sites, it is appropriate to use the protocol to evaluate intrinsic remediation at MGP sites because of the similarities in the nature of the contaminants. For example, fuels and MGP residuals are hydrocarbons, which are released into the subsurface from oily-phase liquids. Fuels tend to be less dense than water and form LNAPLs while MGP residuals form both LNAPLs and DNAPLs. Regardless of their density, most of the contaminant mass at MGP sites and fuel-contaminated sites is associated with these NAPLs and they act as a continual source to groundwater. Both MGP and fuel hydrocarbon sites contain large amounts of BTEX and naphthalene (to a lesser extent at fuel sites) which dissolve into the groundwater to form contaminant plumes.

However, MGP mixtures are more complex and contain more naphthalene and larger ring PAHs, while fuels tend not to have a high percentage of PAHs and do contain

more aliphatics. Therefore, the differences in the composition of the hydrocarbon mixture may affect the biodegradation of the specific compounds. First-order degradation rate constants for BTEX compounds in a fuel mixture have been determined in aerobic and anaerobic environments using field data from many fuel sites (Wiedemeier et al., 1995). Table 2.1 summarizes the published data.

Table 2.1 First-Order Biodegradation Rate Constants (days⁻¹) at Fuel Sites

	Chappell (1994)	Wilson et al. (1994)	Weidemeier et al. (1995a)	MacIntyre (1994)	Stauffer et al. (1994)	Aronson and Howard (1997)
total BTEX	0.01	0.186	0.01 to 0.031	--	--	
Benzene	--	--	0.029 to 0.043	0.007 to 0.012	--	
Toulene	--	--	0.023 to 0.039	--	--	
ethylbenzene	--	--	0.009 to 0.029	--	--	
Xylenes	--	--	0.006 to 0.029	0.01 to 0.02	0.01 to 0.019	
naphthalene	--	--	--	0.006 to 0.012	--	
Styrene						0.016

The range of degradation rates constants reported for benzene at fuel sites may be quite different for benzene at MGP SITES. Rate constants for MGP contaminants as a mixture in anaerobic environments have not been reported in the literature. Additionally, at MGP sites there is no mobile recalcitrant tracer compound whose transport can be readily compared to the biodegradable fraction of the plume. Therefore, the first-order degradation constants must be calculated using the method of Buscheck and Alcantar.

Prediction of the migration and degradation of a dissolved contaminant plume using a solute transport model is an important component of the intrinsic remediation demonstration. Although models can be used to estimate contaminant transport and attenuation, the results are only as good as the ability of the model to describe the underlying phenomena and the data used to calibrate the model. The hypothesis is that microorganisms will utilize nitrate, sulfate, iron III and/or carbon dioxide as electron acceptors in anoxic MGP plumes. However, it is not clear whether first-order decay constants, or transport-limited instantaneous reaction, best describe the processes observed at these sites. Certain types of solute transport models (such as BIOPLUME II, Bio Trans[®] and Bio 1D[®]) allow for the simulation of aerobic and anaerobic degradation by a first-order rate constant, while models such as BIOSCREEN and BIOPLUME III allow simulation of both first-order biodegradation and instantaneous reaction between electron acceptors and contaminant. It is important to determine which type of model best describes the behavior of the MGP plume in sandy aquifers.

The second line of evidence involves the use of chemical analysis in mass balance calculations to show that a decrease in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic byproduct concentrations. While the

numerous studies conducted at over 40 Air Force sites have shown this correlation to be true at fuel sites, this second line of evidence has never been demonstrated adequately in the literature for MGP plumes. Although there have been studies in which electron acceptor data are mapped and compared to contaminant concentrations, results are only qualitative. No quantitative determinations have been made regarding whether the ratio of electron acceptor to contaminant is adequate for significant contaminant reduction via anaerobic pathways.

Microcosm studies at aerobic fuel sites are generally not necessary because regulatory authorities generally accept aerobic biodegradation of fuel constituents. However, microcosm data is necessary at anaerobic MGP sites because of lack of acceptance by regulatory authorities of aerobic biodegradation processes.

2.3 NJDEP Criteria

All of the contaminants found at the MGP sites in this study were compared to NJDEP Soil Clean Up Criteria (Table 2.2). The applicability of the Unrestricted Use Criteria (UUC) and the Restricted Use Criteria (RUC) are dependent on the final remedy for the site. For example if the site is to be used for residential housing with no deed restrictions, the UUC will apply. If the site is to be used for some other purpose and access to the contaminants is restricted, than the RUC may apply. The Impact to Groundwater Standards (IGW) apply only in the unsaturated zone. For most of the sites, it is not yet known whether the UUC or the RUC will apply because the remedial strategy has not yet been finalized. The Egg Harbor site was cleaned up to either the UUC or the IGW

criteria, whichever was more stringent. The remedial strategy at all the sites will most likely include remediation of the unsaturated zone to the IGW standards.

Table 2.2 NJDEP Soil Clean Up Criteria (ppm)

Contaminants	UUC	RUC	IGW
Benzene	3	13	1
Toluene	1000	1000	500
Ethylbenzene	1000	1000	100
Xylenes	410	1000	67
Styrene	23	97	100
Naphthalene	230	4200	100
Acenaphthene	3400	10000	100
Fluorine	2300	10000	100
Anthracene	10000	10000	100
Fluoranthene	2300	10000	100
Pyrene	1700	10000	100
benzo(a)anthracene	0.9	4	500
Chrysene	9	40	500
benzo(b)fluoranthene	0.9	4	50
benzo(k)fluoranthene	0.9	4	500
benzo(a)pyrene	0.66	0.66	100
indeno(1,2,3-cd)pyrene	0.9	4	500
dibenz(a,h)anthracene	0.66	0.66	100

All groundwater data were compared to the higher of the Specific Groundwater Criteria [2A Aquifers, or the Practical Quantitative Levels (PQLs)]. These criteria were obtained from the September 25, 1998 revision of Table 1 of the Groundwater Quality Standards (N.J.A.C. 7:9-6). Any compounds for which groundwater quality criteria (GWQC) were not established in Table 1, were compared to the higher of the interim specific groundwater quality criteria, or interim generic groundwater criteria (if interim specific criteria have not been developed), or PQLs. Table 2.3 summarizes these standards.

Table 2.3 NJDEP Groundwater Quality Standards (ppb)

Contaminants	Higher of PQLs or GWQC with Interim Criteria
Benzene	1
Toluene	1000
Ethylbenzene	700
Xylenes	1000
Styrene	100
Naphthalene	300
Acenaphthene	400
Fluorine	300
Phenanthrene	100
Anthracene	2000
Fluoranthene	300
Pyrene	200
benzo(a)anthracene	0.2
Chrysene	5
benzo(b)fluoranthene	0.9
benzo(k)fluoranthene	1
benzo(a)pyrene	0.2
indeno(1,2,3-cd)pyrene	10
benzo(g,h,i)perylene	100

CHAPTER 3

SITE SUMMARIES

The following site summaries were developed for the eight MGP sites examined, utilizing data collected during remedial investigations (RIs) over the past decade. Table 5.3 (Chapter 5) summarizes the hydrogeology parameters. As an example typical of all eight sites, Appendix A includes BTEX/TEA isopleths, groundwater elevation contour map, geologic cross section, and site maps showing soil and groundwater contaminant concentrations at Pleasantville.

3.1 Egg Harbor

This former site is under an Administrative Consent Order (ACO) signed January 31, 1990 by representatives of the New Jersey Department of Environmental Protection (NJDEP or Department) and the Owner.

The MGP residuals were first identified in 1991 during a Phase I RI and later evaluated through the implementation of a Phase II RI and a Supplemental Remedial Investigation (SRI). A Remedial Action Workplan (RAWP) was submitted to the Department in June of 1999; and remediation was conducted during 2000.

3.1.1 Site Setting

According to the United States Geological Survey (USGS) Quadrangle map, the Site is generally situated 58 feet above mean sea level (MSL). The site is located inland in the New Jersey Coastal Plain. The nearest body of water is a creek, which is located 2,300-feet northeast of monitoring well MW-17-52 (i.e., the most downgradient monitoring

well where groundwater impacts have been detected), and about 1,000 feet downgradient of the two sentinel wells.

The former MGP site is located in a light industrial area of a city in Atlantic County, New Jersey. The site encompasses an area of approximately 1.5 acres and is bounded on the north, west and east by city streets, and on the south by a rail line and train station. No above ground structures exist on-site, and a seven foot high chain link fence with locking gates secures the site.

3.1.2 Operational History

The site was consigned in 1904 to the Enterprise Gas Company, Inc. (EGC) for the purpose of constructing a manufactured gas plant. Between 1904 and 1906, EGC constructed or installed the following facilities on-site:

- coal shed
- one story brick structure housing the boiler, generator, compressor, and pump rooms (near the center of the site)
- separator, three purifiers, and condenser units (adjacent to the generator room)
- booster house
- 10,000 gallon underground oil storage tank (northeast side)
- two 11,500 ft³ gas holder tanks (southern corner)
- 25,000 ft³ relief holder (northern corner)
- 51,000 ft³ storage holder (eastern corner).

Between 1906 and 1927, the site was used for the manufacturing and distribution of both coal gas and water gas. Coal gas was manufactured through the thermal

decomposition of the volatile matter in coal, producing a gas high in hydrogen and methane. Water gas was manufactured by passing steam over an incandescent bed of hot coke, coal or other carbonaceous material. Following the generation of the gas, the heat was extracted from the gas, and condensate was removed. The gas was then stored in one of the gas holders or storage tanks located on-site.

Between 1927 and 1947, the coal shed and gas manufacturing facilities were removed, with the exception of the one story brick building and two 11,500 ft³ gas holder tanks. In 1947, a meter house and 65,450 ft³ Hortonsphere (high-pressure gas storage vessel) were constructed. The site was used for gas storage and metering until 1961.

In 1961, the one story brick building and the Hortonsphere were removed from the site, leaving the meter house and two 11,500 ft³ gas holder tanks. By 1977, all above ground structures were removed.

3.1.3 Geology

Cross-sections of the on-site soils prepared from RI data collected during all phases of the investigation indicate six major stratigraphic units underlying the investigation area. The units (from the surface down) are as follows (the layers are of uneven depth, and sometimes run together):

- Surface to approximately 5-ft bgs: grayish brown fill and reworked native material. This layer is continuous across the entire investigation area. Directly beneath the site, remnant materials indicative of former MGP operations, such as brick and concrete fragments, piping, asphalt material and clinker were evident.

- Approximately 5 ft bgs to 20 ft bgs: gray fine to medium sand, with very variable (trace to mostly) amounts of silt. Discontinuous lenses of clay or silty clay occupy a large portion of this unit from 5 to 15 feet bgs in the site vicinity.
- Approximately 15 ft bgs to 30 ft bgs: light gray fine sand. This unit exists beneath the site and extends in a northerly direction approximately 1080 ft off-site. A 1-3 foot thick silty clay layer separates this layer from the next lower unit over a majority of the site.
- Approximately 25 ft bgs to 54 ft bgs: brownish yellow fine to coarse sand with occasional trace gravel.
- Approximately 44 ft bgs to 70 ft bgs: brownish yellow fine to medium sand, with alternating layers of silt, clay and varying amounts of coarse sand and occasional gravel. This layer was noted to have a lower hydraulic conductivity than layers immediately above or below (see Section 3.32).
- Layer of unknown thickness (62 ft bgs to an unknown depth) consisting of yellow to orange brown fine to coarse sand. This unit has a minimum thickness of 34 ft.

3.1.4 Hydrogeology

Synoptic groundwater elevation measurements were collected from all monitoring wells within the investigation area. This information was utilized in determining the hydrologic flow regime of the water table aquifer across the entire investigation area. Groundwater elevation contour maps depict groundwater flow to the north-northeast.

3.1.5 Contaminant Distribution

Soils

Surface soils (0.0 to 2.0 feet bgs) containing PAHs (at concentrations exceeding the applicable standards) are present in approximately 1-1/2 acres on and around the site, and also contain cinders, coal fragments, clinkers, and demolition debris (from 0.0 to 2.0 feet bgs). Surface soil impacts extend less than 30 feet beyond the original site boundary to the east, a maximum of 25 feet to the north, 35 feet to the west, and as far as the rail line to the south of the site. Surface soil impacts attributable to former MGP activities consist of PAHs including benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, pyrene, and fluoranthene.

Subsurface soil samples collected from greater than 2.0 feet bgs contained volatile organic compounds (VOCs) and PAHs at concentrations above applicable soil standards. VOCs were exclusively located in the north/northwestern portion of the site. Xylene (total) was the common constituent located within this area. Styrene was the only compound detected deeper than 4 ft bgs. These soil impacts correspond with the location of the former relief holder. It is interesting to note that although the groundwater plume emanating from this site contains high concentrations of benzene, the source area seemed to be depleted of this contaminant.

Several PAH compounds (including benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene and indeno(1,2,3-cd)pyrene) were detected at concentrations above the standards throughout the site area at varying depths. Other semi-volatile organic compounds (SVOCs), including acenaphthene, anthracene,

dibenzo(a,h)anthracene, fluoranthene, fluorene, naphthalene, and pyrene, were detected within the north/northwestern portion of the site. As with the VOC exceedances, many of these SVOCs were located in the vicinity of the former relief holder. Both analytical and visual data indicated impacts to a depth of approximately 25 ft bgs.

Visual evidence of contamination (i.e. free or residual product) extend vertically to a maximum depth of approximately 25 ft bgs, with the heaviest impacts focused in an irregular shaped area in the northern corner of the site in the vicinity of the former relief holder and generator building. This area is approximately 140 feet long (north to south) and 160 feet wide (east to west) and contains heavily impacted soils with free and/or residual product. Additional impacts beyond this area consist of varying degrees of residual product including staining and thin stringers of product.

Groundwater

Analytical results obtained during the two groundwater sampling studies conducted as part of the RI indicated that groundwater affected by the presence of source material in the subsurface soil has migrated in the direction of groundwater flow to the north-northeast, resulting in a plume of impacted groundwater extending approximately 2,500 to 3,000 ft off-site. Constituents include both VOCs and SVOCs.

VOCs were detected at levels exceeding the applicable groundwater quality standards (GWQS) in samples analyzed from monitoring wells on and downgradient of the site. These compounds included benzene, styrene, toluene, and xylene. Of these VOCs, benzene appears to be the primary MGP-related constituent of concern given its higher frequency of detection, higher toxicity, and broader distribution throughout the investigation area. The highest concentrations of benzene were detected at monitoring

well MW-2I-25, located in the northwest corner of the Site. Benzene was detected above the applicable standards as far downgradient as monitoring well MW-17-52 (1,850 feet downgradient) and groundwater screening location SB-72-86 (2,500 feet downgradient). The higher concentrations of styrene, toluene and xylenes were detected at MW-2I-25 (on-site) and MW-14-38 (located approximately 400 feet downgradient of the site). No MGP-related VOCs were detected in the two pairs of sentinel wells located approximately 3,100 feet downgradient of the site.

Naphthalene was the only SVOC detected at concentrations above the applicable standards during the two sampling events. Naphthalene concentrations exceeding the GWQS were detected in monitoring wells on and downgradient of the site. The highest naphthalene concentration (9600 ppb) was detected in monitoring well MW-2I-25 (on-site). Naphthalene was detected above the standard as far downgradient as monitoring well MW-17-52 (1,850 feet downgradient) and groundwater screening location SB-72-86 (2,500 feet downgradient).

3.1.5 Remediation

The remedial action selected for site soil was excavation and thermal desorption. The excavation depths extended from approximately 2 to 25 feet bgs. Due to the shallow water table (encountered at approximately 5.0 feet bgs) and depth of certain portions of the excavation, a sheet pile earth support and dewatering system were an integral part of this remedial strategy. Sixty foot lengths of sheet pile ensured penetration into the semi-permeable unit encountered at approximately 45 feet bgs for groundwater control, as well as providing adequate earth support where excavation depths exceeded 10 feet bgs.

The total volume of impacted material that was excavated was approximately 68,000 tons. Once soils were thermally treated they were returned to the site and used as backfill. The total dewatering volume of approximately 14,000,000 gallons was treated with activated carbon and discharged to the sanitary sewer. Once this soil remediation was complete, the down gradient groundwater plume will continue to be monitored for the occurrence of natural attenuation.

3.2 Hammonton

The Owner entered into an ACO with the NJDEP on February 9, 1993. An NJDEP-approved Phase 1 RI was conducted December 1993 through July 1994. The Phase 1 RI consisted of the following field activities:

- a geophysical survey to locate possible subsurface remnants of MGP structures
- installation of nine test excavations and 18 soil borings for soil sample collection to evaluate subsurface soil characteristics and quality including stratigraphy, hydraulic conductivity, and soil impacts from compounds potentially related to MGP activities
- installation of nine monitoring wells for water level monitoring and groundwater sampling to evaluate site hydrogeology, site groundwater flow, and groundwater impacts from compounds potentially related to MGP activities.

Compounds related to MGP activities were detected in on-site soil and groundwater samples in excess of the applicable NJDEP cleanup criteria. A Phase 1 RI report that included recommendations for further investigation was submitted to the NJDEP in March 1995.

A Phase 2 was conducted in 1997 with the following objectives:

- further characterize the extent and thickness of the Site-wide shallow clay layer
- delineate soils at the Site impacted by compounds potentially related to MGP activities at concentrations that exceed NJDEP Soil Cleanup Criteria
- determine if the nearby production wells have hydraulic influence on the unconfined aquifer beneath the site
- horizontally and vertically delineate compounds potentially related to MGP activities in groundwater.

3.2.1 Site Setting

This former MGP Site is located in a light industrial section of a city in Atlantic County, New Jersey. The site encompasses approximately 0.6 acres. The site is bounded on the east by commercial properties, on the west by commercial and residential properties, on the north by the local water department, and on the south by an electrical substation. No aboveground MGP structures presently remain on-site. The facility also contains two production wells operated by the City.

According to the USGS Quadrangle map, the Site is generally situated at 109 feet above mean sea level. The site is located inland in the New Jersey Coastal plain, the nearest body of water is a lake which is located approximately 2,800-feet east-southeast from the end of the area of groundwater impact.

3.2.2 Operational History

The site began operation in 1903 and was used for the manufacturing and distribution of water gas. Between 1923 and 1927, the gas works was still manufacturing gas and was expanding its facilities. In April 1927, the gas company merged with another entity and a gas plant from another location. At this time the operations were ceased.

Water gas was manufactured by passing steam over an incandescent bed of hot coke, coal or other carbonaceous material. The manufacturing equipment included a generator, waste heat boiler, and a wash box. The generator contained the coke or coal bed, the waste heat boiler was used to extract heat from the gas produced from the products of combustion when heating the coke bed, and the wash box was used to remove condensate from the gas produced.

Based on this type of gas manufacturing process, the manufacturing by-products generated at the Hammonton site may have included ash, clinkers, spent oxides, tars and light oils.

3.2.3 Geology

Immediately beneath the site, fill material was encountered, consisting primarily of reworked native sand and silt mixed with gravel. The fill material is underlain by a variegated clay layer which was encountered at approximately 8 to 11 feet bgs in all onsite borings. This clay layer ranged from approximately 3 feet in thickness in the northern portion of the site to 8 feet in thickness in the southern portion of the site. Thin sandy layers were observed within the clay layer in some borings. The clay layer thins to the east of the site to approximately 1 to 2 feet in thickness at depths ranging from 4 to 6

feet bgs. Further to the east, sand was encountered between the surface fill material and the clay layer (which thinned and eventually disappeared soon after).

The predominant stratigraphic unit encountered in all soil borings consists of fine to coarse sands and gravels identified as the Cohansey Sand. This sand unit is present beneath the clay layer at the site and to the east. Farther to the east, the Cohansey Sand is encountered at the ground surface. Throughout the area investigated, this unit extends to an average depth of approximately 120 bgs. Thin (less than 5 feet) discontinuous clay and fine sandy clay layers were encountered within the Cohansey Sand at several boring locations.

Beneath the site, and throughout most of the area investigated, the fine to coarse sand and gravel is underlain by fine to very fine sand and silt. The fine sand and silt ranges in thickness from approximately 15 to 30 feet. Approximately 900 feet east of the site, a 5-foot to 7-foot thick gray clay layer was encountered between the Cohansey Sand and the fine sand and silt.

3.2.4 Hydrogeology

The water table was generally encountered between approximately 26 to 32 feet bgs. Wet soils were noted above the site-wide clay layer in several soil borings. However, no significant perched groundwater zone was encountered. Only one water-bearing zone was encountered during this investigation. This zone extended from the water table to approximately 150 feet bgs, where a confining clay layer was encountered.

Several rounds of depth-to-water measurements were collected during the RI. Groundwater flows in an easterly direction in the vicinity of the site. The average hydraulic gradient in the upper portion of the aquifer (less than 70 feet bgs) was

calculated to be 0.0011 feet/foot. The average hydraulic gradient in the deeper portion of the aquifer (approximately 150 feet bgs) was calculated to be 0.0016 feet/foot. Assuming an effective porosity of 20 percent and hydraulic conductivity values calculated based on slug test data (see below), the groundwater seepage velocity is calculated to be 205 feet per year in the upper portion of the aquifer and 22 feet per year in the deeper portion of the aquifer.

The water table aquifer encountered beneath the site and study area ranges from approximately 28 feet bgs to approximately 150 feet bgs. Beneath the unconfined water bearing unit, a significant confining unit is present. The results of aquifer tests indicate that the aquifer consists of two zones with varying hydraulic conductivities. The first zone consists of predominately medium to coarse sand with some gravel and extends from the water table (~30ft bgs) to approximately 120 feet bgs. Below 120 bgs, the strata encountered grades to a fine sand with increased silt and clay content. The calculated hydraulic conductivity based on slug test results of the upper coarser grained sand ranges from 5.0×10^{-2} cm/sec at well MW-5-70, to 2.2×10^{-2} cm/sec at well MW-8-38. The calculated hydraulic conductivity based on slug test results of the lower finer grained sand and silt ranges from 4.8×10^{-3} cm/sec at well MW-3-150, to 6.4×10^{-4} cm/sec at well MW-5-150.

3.2.5 Contaminant Distribution

Soils

In the unsaturated zone, VOC and PAH compounds exceeding the applicable standards were discontinuously distributed throughout the site and were also reported for samples collected approximately 50 feet off-site to the east. VOC concentrations consisted

primarily of xylenes and benzene. PAHs include indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(k)fluoranthene, fluorene, acenaphthene, benzo(b)fluoranthene, benzo(a)anthracene, and benzo(a)pyrene.

Styrene was detected in saturated zone soils at concentrations in excess of the applicable standards in the eastern corner of the site (B-12-70) and to east of the site (B-26-80) at depths ranging from 43 feet bgs to 50 feet bgs. PAH exceedances were also reported for saturated soil samples collected off-site approximately 50 feet east of the site (B-26-80 and B-27-100) at depths ranging from 48.5 to 50 feet bgs. PAH exceedances were reported for naphthalene, chrysene, indeno(1,2,3-cd)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, and benzo(a)pyrene.

Groundwater

Benzene concentrations were observed in two offsite monitoring wells located approximately 900 feet (MW-39-70) and 1900 feet (MW-44-90) east of the Site. Benzene concentrations decrease to below detection limits prior to reaching the farthest downgradient well (MW-46-97). Naphthalene was detected in a shallow on-site groundwater monitoring well (MW-5-36). Off-site, naphthalene was reported above the GWQS in one monitoring well (MW-39-70) located approximately 900 feet east of the site.

3.2.5 Remediation

No remediation plan has yet been approved for this site.

3.3 Glassboro

This site is the subject of an ACO, entered into by the Owner and the NJDEP effective February 20, 1990. Work performed in accordance with the ACO includes a Phase 1 RI, a Phase 2 RI (with all addenda), a Phase 3, an Interim Remedial Action (RA) to remove an onsite tar pit, and an RA for unsaturated soil. These activities are briefly summarized below.

A Phase 1 RI was prepared to investigate possible impacts to soil and groundwater related to former MGP activities. The Phase 1 RI field activities were conducted between December 1990 and June 1991, and a report was presented to the NJDEP in August 1991. This report recommended an interim remedial action to remove a tar pit located at the northern border of the site. The NJDEP concurred with this recommendation and an Interim Remedial Action Work Plan (Interim RAWP) was developed. The field activities associated with the tar pit removal were conducted between June 1992 and July 1992, and a report was submitted to NJDEP in September 1992.

A Phase 2 RI, designed to delineate MGP related impacts identified during the Phase 1 RI, was prepared, and a work plan was submitted to the NJDEP in October 1992. Fieldwork associated with the Phase 2 RI was conducted between March and August 1993, and the results were presented in a report in January 1994. Two Addenda were submitted to the Phase 2 RI: Addendum 1, dated September 1994, addressed delineation of the unsaturated soils in an employee training area; and Addendum 2, dated July 1995, investigated and mapped subsurface geologic conditions.

An RA for unsaturated soils was conducted between May 1998 and April 1999, and included:

- excavation and off-site disposal of 1,560 tons of lead-contaminated soil
- excavation and off-site thermal treatment of 57,000 tons of BTEX- and PAH-contaminated soil
- backfill and restoration of excavated areas.

A Remedial Action Report (RAR) for Unsaturated Soils was submitted to the NJDEP in February 2000.

A Phase 3 Remedial Investigation was implemented between 1996 and 1999 and included:

- soil sampling from 25 new borings
- multi-level groundwater screening and soil sampling at 88 temporary locations
- installation of 76 permanent monitoring wells (in addition to the 13 already in place)
- two rounds of groundwater sampling and analysis from all 89 monitoring wells

The purpose of the investigation was to delineate the impacts to soil and groundwater associated with the former MGP. These impacts have migrated considerably from the original site, and the area investigated covers over 200 acres.

Based upon this extensive data set, a thorough understanding of the nature and extent of MGP-related impacts will provide the base of knowledge necessary to consider remedial alternatives for the site.

3.3.1 Site Setting

The site is located in a residential/light industrial section of a borough in Gloucester County, New Jersey. The site encompasses an area of approximately 5.5 acres. The site is bound by a street to the east, an active railroad right-of-way to the southwest, privately owned residential properties to the south, and an abandoned railroad right-of-way to the north. Surrounding land use consists primarily of single-family residential development. Light industrial land use exists approximately 1,000 feet west-southwest of the site.

The site is located inland in the coastal plain of New Jersey. A topographic survey of the site performed during the RI Phase depicts the site at an elevation of approximately 145 feet above MSL. The site slopes gently from west to east.

3.3.2 Operational History

There is little information available pertaining to the operational history of this former MGP, including when the plant was constructed and commenced manufacturing operations. Available information obtained from Sanborn Fire Insurance Maps (SFIMs) provide, to a degree, a historical perspective of the plant operations.

The SFIMs indicate the site operated as a water gas plant in 1910. From 1910 to 1923, the site was apparently enlarged and plant structures and facilities were expanded with the acquisition of property west and north of the original plant. Between 1923 and 1929, the facilities and structures were expanded.

Between 1923 and 1947, production of manufactured gas at the site using the coal gas process was continued. In 1947, production facilities were modified and production of manufactured gas using the oil gas process began. The facility operated on a full-time

basis until 1951. From 1951 onward, the gas plant operated on a standby basis only, until the termination of manufactured gas plant operations sometime in the late 1950's.

3.3.3 Geology

The RI was conducted within the following three stratigraphic units: the Bridgeton Formation, the Cohansey Sand, and the Kirkwood Formation. The Bridgeton Formation consists of yellowish-brown and light gray, medium to coarse sand with occasional clay stringers and varying amounts of fine gravel. This formation ranges in thickness from approximately 42 feet in the central portion of the site to approximately 52 feet in the northeastern and southeastern portions of the site.

The Bridgeton Formation is underlain by the Cohansey Sand. The Cohansey Sand consists of reddish-yellow to dark gray, fine sand with varying amounts of silt. The Cohansey Sand ranges in thickness from approximately 22 feet across the northern portion of the site to approximately 28 feet across the southern portion of the site. Soil borings conducted on the site show the Cohansey Sand to consist of three distinct strata. The uppermost stratum is a reddish-yellow, wet, fine sand with varying amounts of silt. This stratum is approximately 14 feet thick under the site. The second stratum consists of slightly moist to dry dark gray, fine sand with silt and clay. For the purposes of this report, this stratum is being identified as the Cohansey dry zone. The Cohansey dry zone ranges in thickness from four feet to eight feet under the site and appears to act as an aquitard. The third stratum of the Cohansey Sand consists of a dark gray, wet, fine sand with traces of silt. This stratum ranges in thickness from approximately three feet along the northern portion of the site to approximately eight feet across the southern portion of

the site. The upper surface of the Cohansey Sand is an eroded surface that slopes down away from the site to the east and south.

The Cohansey Sand is underlain by the Kirkwood Formation. The RI activities did not extend below the top few feet of the Kirkwood Formation in the area of the site. The top of the Kirkwood Formation exists as dry, dense, dark brown clay with occasional fine sand stringers in the area of the site. Based on information obtained from driller's logs for wells installed in this area, the clay unit is approximately 100 feet thick.

Southern Groundwater Plume Geology

The formation and/ or lithologic units identified from soil borings installed south of the site consist of the Bridgeton Formation, Cohansey Sand, and Kirkwood Formation. The observed geology indicates the Bridgeton Formation thickens south of the site, becoming approximately 63 feet thick approximately 550 feet south of the site. From this point south, the Bridgeton Formation begins to thin to a minimum observed thickness of approximately 21 feet.

The surface of the Cohansey Sand slopes downward from the site to approximately 550 feet south of the site. At that location, the surface of the Cohansey Sand is approximately 63 feet bgs and the unit is approximately 20 feet thick. Further south, the Cohansey Sand thickens and the surface slopes up. Approximately 2,400 feet south of the site, the surface of the Cohansey Sand is approximately 20 feet bgs and the unit is greater than 46 feet thick. The upper stratum of the Cohansey Sand thins from west to east and pinches out east of the southern groundwater plume.

The surface of the Cohansey dry zone slopes down to the south. Approximately 550 feet south of the site, the dry zone reaches its greatest observed depth of

approximately 71 feet bgs and it is approximately 3.5 feet thick. From this point the Cohansey dry zone gradually begins to slope upward. Approximately 1,300 feet south of the site, the slope of the dry zone steepens, reaching a minimum observed depth of 41 feet bgs approximately 1,800 feet south of the site.

The surface of the Kirkwood Formation slopes gradually downward south of the site. Approximately 1,300 feet south of the site the top of the Kirkwood Formation is at its maximum observed depth of 82 feet bgs. From that point south the top of the Kirkwood Formation slopes upward, reaching its minimum observed depth of 64 feet bgs approximately 1,800 feet south of the site. Based on information obtained from driller's logs for wells installed in this area, clay zones within the Kirkwood Formation are believed to be at least 100 feet thick.

Northern Groundwater Plume Geology

The formations identified through soil borings installed north of the site also consist of the Bridgeton Formation, Cohansey Sand (upper wet Cohansey sand, Cohansey dry zone, and lower wet Cohansey sand), and Kirkwood Formation. The observed geology indicates the stratigraphy is similar to the site geology for approximately 2,100 feet north of the site.

Approximately 2,100 feet north of the site the Cohansey dry zone begins to thin and then pinches out. From this location on, the Cohansey Sand exists as a single wet, fine sand unit with varying amounts of silt and occasional clay. The upper portion of the Cohansey Sand is yellowish brown in color grading to olive brown or olive gray. Also at that distance, the top of the Kirkwood Formation becomes a dark greenish-gray, very fine, wet sand. This sand ranges in thickness from approximately 22 feet to 35 feet. The

uppermost clay layer apparently pinches out between SB-73-114 and SB-81-102. Dense, dry, dark brown clay is encountered below the very fine sand at depths ranging from 100 feet bgs at SB-73-114, to 55 feet bgs at the terminus of the northern plume.

Moving away from the site to the north, the Bridgeton Formation gradually thins. This thinning is primarily a function of the dropping surface topography. Approximately 6,500 feet north-northwest of the site (at SB-180-60) the Bridgeton Formation pinches out and the Cohansey Sand becomes the surface stratigraphic unit.

3.3.3 Hydrogeology

The water table was generally encountered between approximately 5 to 10 feet bgs. Two water-bearing zones were encountered. The uppermost, associated with the Bridgeton Formation and the upper unit of the Cohansey Sand, extends from the water table to approximately 64 feet bgs, where the Cohansey dry zone acts as an aquitard. The second is a thin zone of the Cohansey Sand situated between the Cohansey dry zone and the Kirkwood clay. From approximately 2,100 feet north of the site, where the Cohansey dry zone and the uppermost layer of the Kirkwood pinch out, to the northern terminus of the plume, the Bridgeton Formation, Cohansey Sand, and Kirkwood sand appear to act as one hydrogeologic unit.

Site Groundwater Flow

Shallow groundwater (water table) flow across the site is in a northeasterly direction. The average hydraulic gradient at the water table is approximately 0.0002 feet/foot. The groundwater elevation contour maps for the intermediate zone indicate that the site is situated on a slight mound with flow toward both the south and north. Deep groundwater flow (immediately above the Kirkwood clay) is also divided at the site. The divide of

this flow appears to be at the southern boundary of the site. The average hydraulic gradient to the north is approximately 0.0015 feet/foot; and the average hydraulic gradient to the south is approximately 0.0004 feet/foot.

Southern Plume Groundwater Flow

The southern groundwater plume exists as a thin zone of groundwater impact that appears to run along the top of the Cohansey dry zone (intermediate zone). Groundwater elevation contours indicate flow within the intermediate zone is away from the southern site boundary in a southwesterly direction at an average hydraulic gradient of approximately 0.0004 feet/foot. Approximately 1,550 feet south of the site the average hydraulic gradient increases to approximately 0.0014 feet/foot.

Northern Plume Groundwater Flow

Shallow groundwater (water table) flow immediately north of the site is in a northeasterly direction with an average hydraulic gradient of approximately 0.0002 feet/foot. Groundwater in the intermediate zone flows from the northern site boundary to the north-northeast with an approximate hydraulic gradient of 0.0005 feet/foot. Approximately 1,250 feet north of the site the average hydraulic gradient increases to approximately 0.0025 feet/foot. Approximately 3,500 feet north of the site groundwater flow shifts from the north to the northwest and then west-northwest and the average hydraulic gradient increases to 0.0033 feet/foot.

Groundwater in the deep zone flows from the northern site boundary to the north-northeast with an approximate hydraulic gradient of 0.0008 feet/foot. From a point approximately 1,600 feet north of the site the average hydraulic gradient increases to approximately 0.0021 feet/foot. Approximately 3,000 feet north of the site groundwater

flow shifts from the north to the northwest and then west-northwest and the average hydraulic gradient increases to 0.0044 feet/foot.

Hydraulic Characteristics

Hydraulic conductivity within the Bridgeton Formation in the vicinity of the site was estimated using slug tests. These tests were conducted in the immediate site area and showed hydraulic conductivity in the Bridgeton Formation to be in the range of 1×10^{-4} to 1×10^{-2} cm/sec. The grain size analyses indicate that similar values can be expected in the Bridgeton and Cohansey Formations throughout the area under study.

Two Shelby tube samples were collected from the Kirkwood clay under both the northern and southern plumes. Triaxial cell permeability tests were conducted on these samples. The tests showed hydraulic conductivity of 3.8×10^{-7} cm/sec for sample SB-103/88-90 (collected in the southern plume) and 3.15×10^{-8} cm/sec for sample SB-107/84-86 (collected in the northern plume). These values indicate that the Kirkwood clay acts as an aquitard preventing downward migration of groundwater impacts.

3.3.4 Contaminant Distribution

Soils

Benzene, toluene, ethylbenzene, styrene, total xylenes, naphthalene and other SVOCs were detected in saturated soils at concentrations that sometimes exceeded the applicable criteria at depths ranging from just below the water table (approximately 9.5 feet bgs) to just above the Bridgeton/Cohansey contact (approximately 45.5 feet bgs). The soil samples that exhibited these exceedances had a distinct MGP-like or mothball-like odor, visible tarry or oily product, and/or visual indications of product such as black staining or sheen.

The extent of DNAPL in saturated soils was determined to extend from 5 feet bgs to 40 feet bgs (immediately above the Bridgeton/Cohansey contact). DNAPL was not observed in any borings below the Bridgeton/Cohansey contact. It appears that the lithologic change from the medium to coarse sands of the Bridgeton Formation to the fine sands of the Cohansey Sand serves to halt the downward migration of DNAPL.

Groundwater

Results from RI studies indicated that groundwater impacts from MGP contamination extended to approximately 6,500 feet north of the site (northern plume) and approximately 2,250 feet south of the site (southern plume).

Southern Plume

Benzene and naphthalene were the only constituents exceeding applicable groundwater criteria. The highest benzene concentrations were identified above the Cohansey dry zone. Benzene was identified at a concentration of 4,600 ppb along the southern site boundary. Approximately 500 feet south of the site, benzene was identified at a concentration of 1,100 ppb. Benzene concentrations above the Cohansey dry zone remain consistent to a point approximately 1,300 feet south of the site. In the southernmost monitoring well installed approximately 2,300 feet south of the site, the benzene concentration was 5.5 ppb. Naphthalene was identified above the Bridgeton/Cohansey contact along the southern site boundary at a concentration of 1,300 ppb. Neither naphthalene nor any other SVOCs were identified in any of the off-site monitoring wells.

Northern Plume

The northern plume extends offsite in a northerly direction for approximately 3,500 feet before turning northwest and then west-northwest. The northern plume terminates approximately 6,500 feet from the northern site boundary.

Benzene and ethyl benzene were identified extending offsite to the north of the site. Immediately north of the northeast corner of the site, and above the Bridgeton/Cohansey contact, the concentration of benzene was 650 ppb, and of methylbenzene was 1,100 ppb). The farthest off-site concentration of ethyl benzene was identified approximately 500 feet north of the site at 1,500 ppb. This monitoring well also had the only off-site exceedances of toluene (1,600 ppb) and total xylenes (1,400 ppb) identified in the northern plume. Benzene exceedances were identified throughout the extent of the northern plume.

At the site and through the first approximately 2,100 feet of the northern plume the highest benzene concentrations were identified above the Cohansey dry zone. Between 1,500 feet and 2,100 feet north of the site, the Cohansey dry zone becomes discontinuous and ultimately pinches out. At approximately 1,500 feet north of the site, benzene was identified at 220 ppb (above the Cohansey dry zone) and at 1.1 ppb (above the Kirkwood clay). The 1.1 ppb benzene concentration was identified during the first groundwater sampling event.

Approximately 3,600 feet north of the site, benzene was measured at 6,800 ppb. Approximately 4,600 feet north of the site, benzene was 950 ppb in well MW-47-46, and 8.9 ppb approximately 34 feet deeper in well MW-47-80 (screened immediately above the Kirkwood clay). The northernmost benzene exceedance was a concentration of 16

ppb at well MW-50-36, located approximately 5,800 feet north of the site. The northern plume is delineated by the MW-52 monitoring well cluster, located approximately 6,500 feet north of the site, where no benzene exceedances were detected.

Naphthalene was the only SVOC compound identified exceeding the GWQS in the northern plume. Naphthalene was identified in well MW-12BB-51, located just north of the northeast corner of the site, at a concentration of 8,800 ppb. Approximately 1,500 ft north of the site, in well MW-26-60, naphthalene was identified at 420 ppb. The northernmost naphthalene exceedance was a concentration of 960 ppb identified in MW-42-60, located approximately 3,600 feet north of the site.

3.3.6 Remediation

A tar pit and all on-site unsaturated soils have been removed and thermally treated. However, there is as yet no remediation plan for the groundwater and saturated soils.

3.4 Florida Avenue

Effective September 9, 1992, the Owner entered into an ACO with the NJDEP regarding this site. The ACO requires that the Owner conduct remedial investigations, feasibility studies and, if necessary, remedial actions associated with the former MGP site.

The following environmental investigations were conducted at this site:

- a Phase 1 Remedial Investigation (RI) was conducted in June 1994
- a Phase 2 RI was conducted between October 1995 and February 1996
- a supplemental Phase 2 RI in September 2000.

The primary objective of these investigations was to identify the extent of impacts on this site in order to develop remedial action alternatives.

3.4.1 Site Setting

The site is located on a coastal barrier island and lies at an average of approximately 7 feet above MSL. The site is relatively flat, with survey information indicating a variation in elevation from 5 to 10 feet relative to the national Geodetic Vertical Datum (NGVD). It is approximately 4 acres in size, located in a city in Atlantic County, New Jersey. The site is bounded by city streets, and the Intracoastal Waterway is located across the street to the west.

There are several different land uses within a 1,000-foot radius of the site. To the north and northeast of the site, construction of infrastructure is ongoing. The land to the east and south of the site consists of a mix of commercial and residential properties. A school is located approximately 800 feet south of the site; a recreation area/playground is approximately 650 feet south/southeast of the site. Land to the southwest of the site exists primarily as a residential neighborhood with a small amount of commercial property. There are two areas of open space southwest of the site: one approximately 350 feet from the site and the other approximately 750 feet from the site. These two areas provide recreational access to the Intercoastal Waterway, which bounds the western side of the site. The waterway is 20 to 70 feet from the site and approximately 700 feet in width. The land on the opposite shoreline is open space and classified as a wetland.

3.4.2 Operational History

MGP operations first began at the site about 1900. Gas was manufactured using the carburated water gas (CWG) method. CWG production was a three-step process. First, hydrogen gas was generated by passing steam over a bed of hot coal. Second, these gases were passed to a superheater and mixed with carburated oil or naphtha vapor to improve

the luminosity of the gas. Various chemical reactions took place in the high-temperature conditions of the superheater, and the carburated oil was converted to a permanent gas. Finally, the gas was purified prior to being stored in gas holders. The gas purification process involved an initial step to remove condensable constituents such as tar by passing the gas through condensers or scrubbers filled with wood chips. Then ammonia was removed from the gas by scrubbing the gas with water, and finally sulphur and cyanide compounds were removed by passing the gas through purifiers consisting of lime or iron oxide mixed with bulking materials such as wood chips. Residuals formed during the CWG process included tar, tar/water emulsions, ammoniacal liquor (from the ammonia removal step), purifier residuals (spent lime or wood chips containing tar and/or sulphur and cyanide compounds), ash and clinker.

The original gas plant consisted of two above-grade gas holders and a gas generating building, which contained a generator house, purifying house and exhaust house. Additional structures later added to the plant include a larger (1 million cubic foot [cu/ft]) gas holder, fuel oil tanks, a boiler house, a maintenance and dry goods building, and additional boiler and governor houses that serviced the gas holder. The 80-foot-diameter gas holder in the southeastern corner of the site was later converted for fuel-oil storage.

The MGP continued to operate until 1918, when this gas plant centralized operations with another facility several blocks northeast of the site. As part of the consolidation of gas manufacturing operations, an 8-inch diameter pipeline was constructed to transport oil from a barge pier in the bay to the centralized facility. In

1922, a 1.5-million-gallon capacity fuel oil storage tank was erected in the northeastern corner of the site.

In 1947, the subject site operated as a liquid propane peak shaving facility, comprised of (liquid propane gas) LPG storage tanks, a LPG vaporizing unit, and a LPG peak-shaving station. Peak-shaving was conducted to supplement the gas supply and maintain pressure in the lines during times of peak gas usage. In addition, the site continued to be used as a storage facility for raw materials and gas. No information is available regarding the decommissioning of the site as a storage facility, nor is there any available information regarding the duration of LPG peak-shaving operations. However, the 1969 Sanborn map indicates that the propane storage tanks had been removed from the site by this time.

The only structures currently remaining on the site are an office building, the 1.5 million-gallon aboveground fuel storage tank (used for fuel storage by a subsequent owner), and remnants of the fuel barge dock.

3.4.3 Geology

The site is underlain by fill material and unconsolidated marine and fluvial deposits of clay, silt, sand, and gravel deposited during the Late Cretaceous and Tertiary Periods. As with many barrier islands in New Jersey, much of the site is comprised of a layer of fill material either trucked in or deposited as part of dredging operations to allow for expanded development on the island. Fill material at the site ranges in thickness from about 1 to 12.5 feet, and is characterized as a fine to medium-grained sand with gravel and various debris.

Gray, fine to medium-grained sand underlies the fill material to depths greater than 72 feet bgs. This unit was encountered across the entire area of investigation. A separate gray medium to coarse-grained sand is present in portions of the site below the layer of gray fine to medium-grained sand. The layer appears to dip down toward the east and was not detected east of the site.

Three separate clay units and a dense silt unit are present interbedded within the two subsurface sand lithologies described above. The first clay unit, referred to as the shallow clay, extends horizontally across the site from approximately 7 feet bgs to 11 feet bgs, and ranges from lenses less than 0.5 foot thick to a layer up to 7 feet thick. A second clay unit, referred to as the intermediate clay, is encountered beneath the site approximately 23 to 29 feet bgs and ranges in thickness from less than 1 foot to 4 feet. The third clay unit, referred to as the deep clay, is encountered between 58 and 68 feet bgs. No borings have been advanced through this clay so its thickness is unknown. The deep clay is present beneath the northwestern portion of the site and appears to dip down toward the east (similar to the above-lying coarse to medium-grained sand). It was not encountered beneath the eastern portion of the site.

In addition to the three separate clay units, a dense clayey silt to sandy silt unit was encountered immediately east of the Intercoastal Waterway. This unit was encountered approximately 12 feet bgs and ranges in thickness between 4.0 feet and 7.5 feet. The sand content of this silt unit increases toward the site, while the clay content increases toward the waterway.

3.4.4 Hydrogeology

Information gathered during the investigations conducted across the site indicates three separate hydrogeologic systems. These systems are designated as shallow, intermediate, and deep. The shallow system includes the water-bearing unit between the water table and the shallow clay (or equivalent interval where the shallow clay is not present). The intermediate system includes the water-bearing unit between the shallow clay and the intermediate clay (or equivalent interval where either of the clay units are not present). The deep system includes the water-bearing unit between the intermediate clay and the deep clay (or equivalent interval where either of the clay units are not present).

Three rounds of depth to water measurements, conducted during groundwater sampling events, have been performed as part of RI activities. The shallow groundwater contour maps indicate groundwater flow away from an apparent north/south trending groundwater divide. The divide is located beneath the center of the site and is oriented parallel to the Beach Thorofare. Groundwater is flowing away from the divide toward the Atlantic Ocean (east) and the Intercoastal Waterway (west).

The intermediate water bearing zone indicates a broad groundwater divide traversing the site in an east-west orientation. Groundwater flow north of this divide is generally towards the northwest at an average horizontal hydraulic gradient of 0.005 feet/foot. Groundwater flow south of the divide is generally towards the southwest at an average horizontal gradient of 0.0057 feet/foot. The overall groundwater flow in the intermediate zone under the site still appears to be generally in a southwest direction.

Hydraulic conductivity testing was conducted as part of the RI. Hydraulic conductivities were calculated using visual curve matching of the late-time recovery data

to filter out data not representative of the native shallow water-bearing system; early time data collected during the rising head analysis often reflects the hydraulic conductivity of the well's sand pack and not native soil. Hydraulic conductivities calculated for monitoring wells in the shallow water bearing zone ranged from 2.5×10^{-4} to 3.15×10^{-4} cm/sec.

As part of RI activities, nine samples were collected and submitted for grain size analysis. The samples were collected from shallow, intermediate and deep water-bearing systems within the intervals that were screened during well installation. The grain size analysis data were used to estimate hydraulic conductivities of the screened intervals. The results indicated estimated hydraulic conductivities typical of clean sands, which are reported to range from 10^{-4} to 1 cm/sec (Freeze & Cherry, 1979).

In addition, one Shelby Tube was collected from an interval within the deep clay unit (approximately 65.0 – 67.0 feet bgs), and one Shelby Tube was collected from the silt unit (approximately 15.0 – 17.0 feet bgs) encountered immediately adjacent to the Intercoastal Waterway. The Shelby Tubes were submitted for triaxial permeability testing. The results from triaxial permeability testing indicate a hydraulic conductivity of 4.4×10^{-7} cm/sec for the deep clay unit and 1.04×10^{-7} cm/sec for the silt unit. These hydraulic conductivities are typical of confining units with very low permeability.

Two tidal influence studies were conducted as part of the RI. Data from the two tidal studies show a tidal transition period in the Intercoastal Waterway of approximately 6.2 hours, with an average maximum change in surface water elevation of 0.84 feet for the first study and 0.91 feet for the second study. Tidal influence was greater in the intermediate water bearing zone than the shallow zone. Tidal influence on the shallow

water bearing zone ends between 140 feet and 210 feet from the Intercoastal Waterway. Tidal influence was reflected in all of the intermediate wells monitored during both studies. The magnitude of the tidally induced groundwater elevation decreased with distance from the waterway.

3.4.5 Contaminant Distribution

Soils

Based on the review of the previous investigation reports prepared for this site, it is apparent that soil impacts identified at the site are attributable to three known sources: the former MGP facility, a fuel company which currently owns the property, and an underground storage tank which was originally used to fuel service vehicles but no longer exists. It appears that impacts associated with these sources are co-mingled, particularly in unsaturated and shallow saturated soils, and are difficult to differentiate.

The results of the numerous investigations indicate exceedances of applicable criteria for benzene, xylenes, and numerous PAH compounds. The investigation also identified a light non-aqueous phase liquid (LNAPL) associated with the 1.5 million-gallon bulk storage tank located on the fuel company property.

DNAPL associated with the MGP resulted in concentrations of BTEX and PAHs identified in soils situated above the shallow clay, and between the shallow clay and the intermediate clay.

Groundwater

Groundwater samples were collected from 26 wells installed as part of the RI. The investigation identified impacts to both the shallow (water table) and intermediate groundwater (above the intermediate clay).

The shallow water bearing zone had measurable concentrations of VOCs, SVOCs, cyanide, arsenic, and lead. Impacts from VOCs appear to extend across the site. The highest VOC exceedances are concentrated around the fuel company property. SVOC exceedances (primarily naphthalene) were identified in the southern portion of the former MGP site.

The intermediate water-bearing zone (above the intermediate clay) exceeded the applicable criteria for VOCs, SVOCs, cyanide, and arsenic. VOC exceedances consisted primarily of benzene; however, ethylbenzene, toluene, and xylenes were also identified. Naphthalene was the predominant SVOC noted in the intermediate water-bearing zone.

3.4.6 Remediation

There is as yet no approved remediation plan for this site.

3.5 Bridgeton

The Owner entered into a MOA with the NJDEP on 25 February 1993. Pursuant to the MOA, the Owner is to conduct a RI and RA to mitigate impacts of the former MGP at the site. An RI workplan was submitted to the NJDEP in January 1994. The Phase I RI was subsequently initiated in September 1994 in an effort to confirm the presence of former MGP structures, to determine subsurface stratigraphy, soil conditions in the saturated zones throughout the site, groundwater quality in the upper water-bearing zones, and the

groundwater flow direction in the subsurface. Based on the preliminary results of the Phase I RI, a supplemental phase of investigation was conducted in late 1995 and early 1996. The supplemental phase was implemented to more fully delineate the extent of soil contamination at the site and off-site and to further characterize groundwater quality at the site. The Phase I RI Report (including the supplemental phase of investigation) was submitted to NJDEP in August 1996.

3.5.1 Site Setting

This former MGP site is located in a city in Cumberland County, New Jersey. The site encompasses an area of approximately 2 acres located within a mix of commercial and light industrial properties (to the north, east and south), and residential properties (to the west). A river borders the site property to the east.

The site property is located at surface elevations ranging from approximately 40 feet above MSL in the western portions of the site to approximately 6 feet MSL in the eastern portion of the site along the Cohansey River. Surface water runoff from the western portion of the site drains towards a street and a storm water collection system that discharges into the river. Surface water runoff from the eastern portion of the site flows to the east towards the river.

3.5.2 Operational History

The operational history for this site is unknown.

3.5.3 Geology

A mixture of unconsolidated sediments that comprise four distinct stratigraphic units underlies the subsurface of the site. The majority of the site is covered with several inches of asphalt with the exception of one area that is covered with gravel. A fill material that ranges in thickness from approximately 1 foot to 10 feet underlies the asphalt and gravel veneer. The fill material varies across the site and generally consists of brown, orange, gray and tan silt coarse to fine sand and gravel, organic material (roots and wood fragments), manmade materials such as brick and concrete fragments, and some MGP-related materials (cinders, ash, clinker and coal fragments).

The fill material is underlain by light colored very fine to coarse sand and gravelly sand with occasional silt, very fine sand with clay lenses and occasional ironstone and lignite layers. This unit, which is characteristic of Cohansey sand, measures approximately 80 feet in thickness, and contains the water table surface within the upper portion.

Beneath this formation is a layer of gray dense clay with silt stringers at a depth of approximately 82 feet bgs. Three deep soil borings were advanced approximately 7 feet to 25 feet within this layer, but the total thickness was not determined.

3.5.4 Hydrogeology

Depth to groundwater in the site subsurface measures approximately 4 to 5 feet below ground surface (bgs). Groundwater flow direction across the site is to the east towards the river, paralleling the natural topography of the site. Groundwater levels at the site are influenced slightly by tidal fluctuations in the river. Measurements of these tidal

fluctuations indicated that a slightly increased water table gradient is observed during low tidal conditions and a slightly decreased water table is observed during high tidal conditions.

The shallow groundwater wells indicated an average horizontal flow gradient of approximately 0.015 feet/foot across the entire site, with a higher gradient (approximately 0.03 feet/foot) toward the east approaching the river. The deep groundwater monitoring wells indicated a steady horizontal hydraulic gradient across the site of 0.007 feet/foot. In general, vertical hydraulic gradients across the site indicated a downward trend ranging from 0.007 to 0.017 feet/foot.

The saturated zone of the site subsurface extends from the fill material in the Cohansey sand to a depth of approximately 85 feet bgs. A clay unit was encountered across the site at a similar depth (approximately 73 feet below MSL) and was a minimum of 7 to 25 feet thick. Based upon results of conducted permeability tests and the minimum thickness of the clay unit, it was determined that the clay horizon is acting as a confining unit in the subsurface. A potential semi-confining layer consisting of unsaturated very fine sand and silt was encountered below the water table (approximately 10 feet to 15 feet bgs) within the northern end and western portions of the site. This layer was discontinuous across the site, thinning and pinching out to the south and east.

Results of aquifer permeability tests indicated that hydraulic conductivities in the shallow monitoring wells ranged from 1.06×10^{-2} cm/sec to 1.03×10^{-4} cm/sec. In the deep monitoring wells, hydraulic conductivities ranged from 1.96×10^{-3} cm/sec to 4.52×10^{-3} cm/sec.

3.5.5 Contaminant Distribution

Soils

The site contains the remnants of former MGP structures, including three surface gasholders, a subsurface gasholder, a tar vessel, and several building foundations and miscellaneous piping. MGP residuals were noted in the soils adjacent to the former gasholders. The tar vessel, located in the west-central portion of the site, may be acting as a continuing source of residual impact to the surrounding soils and groundwater.

The soil investigation phase of the Phase I RI indicated that residual compounds characteristic of MGP operations have impacted the soils across the site. Several compounds of concern, including VOCs, SVOCs and metals, were detected in both the unsaturated and saturated zones of the site subsurface at concentrations exceeding the applicable criteria.

Groundwater

Results of the groundwater investigation phase of the RI indicate that groundwater degradation has occurred in the site subsurface. Contaminant compounds (benzene and xylenes) were detected in groundwater samples collected from both the shallow monitoring wells and intermediate monitoring wells at concentrations that exceeded the applicable criteria.

The analytical results indicate that VOCs were only detected downgradient of the central portion of the former MGP. No evidence of LNAPL or DNAPL was detected during the Phase I RI.

3.5.6 Remediation

There is as yet no approved plan for remediating this site.

3.6 Salem

In 1990, the United States Environmental Protection Agency (EPA) conducted an inspection at the Salem site. Results of the investigation indicated the presence of MGP-related impacts. In 1992, the company entered into an MOA with the NJDEP to investigate and, if necessary, remediate the Salem site. A Phase I remedial investigation RI was conducted to evaluate potential MGP impacts at the site. The Phase I investigation, conducted in 1994, indicated that levels of MGP-related contaminants in site soils and groundwater exceed applicable NJDEP criteria. In 1996, a Phase II investigation was conducted at the site, primarily to determine the nature and extent of MGP-related impacts off-site.

3.6.1 Site Setting

This MGP site is located in Salem County, New Jersey, approximately 2.5 miles east of the Delaware River. The nearest body of water is a large creek, located approximately 400 feet west and north of the site. The site is approximately 1.2 acres in size and is divided by a street into two sections, referred to herein as Parcel 1 and Parcel 2. Both parcels are entirely enclosed by fencing and are inaccessible to the public.

Parcel 1 of the site is 0.9 acres, bounded by streets, and consists of a paved, empty storage lot. The only structure is a metal building located on the northernmost portion of property, separated from the storage lot by a fence.

Parcel 2 of the site is 0.3 acres, bounded to the south by residential properties, to the east by a vacant lot, and to the west by a street. Remnants of the former MGP facility,

including a partial gas holder ringwall and the foundation supports for a former gas holder, are visible on this lot.

3.6.2 Operational History

Not much is known about the MPG operations at this site. However, it is known that the operations first began at the site on or about 1885. The MGP facility was later expanded some time prior to 1891. The site most likely operated as a water gas facility. All MGP operations were discontinued by 1955, and a liquid propane gas plant began operating on Parcel 1. By 1959, all of the former MGP structures on Parcel 1 had been removed, and a gas meter station was constructed on Parcel 2.

3.6.3 Geology

The site is underlain by approximately 2 to 8 feet of fill material, primarily composed of fine to coarse sand with silt and fine gravel and debris (brick, clinker, ash, wood, etc.). The fill is underlain either by sandy soils (0 to 18 feet thick) or by a peat-rich silt and clay (0 to 46 feet thick). These units are underlain by the Hornerstown Formation, which consists of two glauconitic units. The upper unit is a glauconitic silt and clay which ranges from 4 to 6 feet in thickness. This unit appears to act as a confining unit beneath the site and adjacent off-site properties.

The lower unit of the Hornerstown Formation consists of 5 to 8 feet of glauconitic fine- to medium-grained sand with some clay and silt. The Hornerstown Formation was encountered in all soil borings completed on site and off site, with the exception of one boring located north of the site, adjacent to Fenwick Creek. The Hornerstown Formation is underlain by the fine sands and silts of the Navasink Formation, which ranges in

thickness from 14 to 28 feet. Below the Navasink is the Mount Laurel Formation, consisting of fine to medium gray sands. The bottom of this formation was not encountered in either the Phase I or Phase II investigations; geologic literature for Salem County indicates that it is approximately 90 feet thick.

3.6.4 Hydrogeology

Two aquifers were encountered in the overburden beneath the site. The shallow aquifer present in the sandy soils overlying the glauconitic clay confining unit is otherwise unconfined. The fine to medium sands of the Mount Laurel Formation comprise the deep aquifer, which is confined. Both the shallow and deep aquifers appear to flow west, toward the large creek, and are influenced by the creek's tidal flow. Tidal influences were observed in all wells monitored during the study, although one shallow well located southeast of the site, approximately 250 feet from the creek, exhibited minimal effects. In general, tidal influence was stronger in the deep aquifer than the shallow aquifer.

3.6.5 Contaminant Distribution

Soils

The most heavily impacted soils were encountered in Parcel 1. Tar was noted throughout subsurface soils on Parcel 1, and several MGP-related compounds were in excess of NJDEP criteria in Parcel 1 surface and subsurface soils. Tar was also noted in association with a gas holder located on Parcel 2 and in test excavations along the street east of Parcel 1. Isolated exceedances of NJDEP criteria were detected in soils on Parcel 2 and on off-site properties adjacent to the site's eastern and western boundaries. No

physical evidence of impacts or exceedances of NJDEP criteria were noted in soils beneath the glauconitic clay confining layer.

Groundwater

MGP impacts were detected in shallow groundwater collected from on-site monitoring wells. No MGP-related compounds were detected in off-site shallow groundwater at levels in exceedance of NJDEP criteria. However, cyanide detected in on-site shallow monitoring wells exceeded the NJDEP criteria, and cyanide analysis was not performed on samples from off-site wells. No MGP-related impacts were detected in deep groundwater.

3.6.6 Remediation

Preliminary plans include excavation and thermal desorption of soils, and natural attenuation of groundwater.

3.7 Pleasantville

Effective 4 June 1993, the Owner entered into a MOA with the NJDEP to perform a RI, feasibility study, and if necessary, remedial action at the site. A Phase I RI and subsequent report were completed in March 1995. A Phase II RI Work Plan was submitted to and approved by the NJDEP in early 1996. Implementation of the Phase II RI commenced in July 1996. A Phase II Remedial Investigation was subsequently conducted in response to on-site MGP-related environmental impacts identified during Phase I activities. Objectives of the Phase II Remedial Investigation include the further characterization and delineation of soil and groundwater contamination, the investigation of the former Gas Holder No. 4 in Parcel 1 (previously identified as the Circular Oil

Tank), and the investigation of potential upgradient (off-site) sources of soil and groundwater contamination.

3.7.1 Site Setting

This former MGP site is located in Atlantic County, New Jersey. The site is divided into two separate parcels. Parcel 1 is 0.51 acres, and formerly contained the main gas manufacturing building, a relief holder (Holder 3), tar tanks, two oil tanks and a coal shed. A masonry garage and a metal garage are currently the only structures located on Parcel 1. The remaining area of the parcel is partially paved. Parcel 2 is 0.55 acres, and currently contains a small masonry building, open bins (for pipe storage), and an active gas metering station. A concrete pad is located on the southeast corner of the parcel, which formerly housed a metering station. The remaining area of Parcel 2 is paved. The parcel formerly contained Gas Holders 1 and 2, and the Compressor House. Both parcels are currently secured by fencing.

The site is separated by a road, which runs east to west between the two parcels. A petroleum product storage and distribution facility neighbors the property immediately to the west of Parcel 1. Railroad tracks border the site to the south. An auto repair and tire shop is located to the west of Parcel 2.

Surface topography of the site is relatively flat with a slight downward slope to the east. Ground surface elevations at the site range from 18.6 feet to 25.3 feet above mean sea level (MSL). A large bay, which is located approximately 3,000 feet to the southeast of the site, separates the mainland from the barrier islands to the east.

3.7.2 Operational History

There is no operational history available for this site.

3.7.3 Geology

RI investigative efforts revealed that a mixture of unconsolidated sediments, which comprise the following lithologic unit, underlies the subsurface of the site:

- the near surface consists of fill material of coarse to fine sand and varying amounts of gravel, silt, and miscellaneous debris, with an average thickness of approximately six feet
- the fill material is underlain by a layer of light brown to gray coarse to fine sand with varying amounts of gravel and trace silt. In two deep soil borings completed on-site, a lens of fine sand and silt was noted within the sandy unit at 60 to 65 feet bgs. The sand layer extends to a depth of approximately 97 feet bgs.
- a layer of gray silt and clay was encountered at 97 feet bgs in one deep soil boring completed on site. This layer was not penetrated, so its thickness is unknown. This silt and clay layer was not encountered in two off-site borings completed to comparable depths.

3.7.4 Hydrogeology

Depth to water in the site subsurface ranges from 12 to 16 feet bgs. The hydrology in Pleasantville is dominated by the Kirkwood-Cohansey Aquifer. The groundwater flow direction across the site is to the southeast towards the bay, with an average hydraulic gradient of 0.00155 feet/foot. The interpreted direction of flow parallels the natural surface topography of the site.

Field permeability tests were conducted on all six of the on-site monitoring wells, however the results are suspect. Grain size analyses performed on soil samples collected during the Phase I RI indicated that the aquifer consists of poorly sorted coarse to medium sands with less than 10 percent silt. For the table of hydraulic characteristics in Chapter 5, published references were used for the range of hydraulic conductivities typical of these types of sediment.

3.7.5 Contaminant Distribution

Soils

On Parcel 1, results of chemical analysis of soil samples indicate compounds possibly related to MGP operations were detected at concentrations above NJDEP soil cleanup criteria from 0 feet bgs to approximately 17 feet bgs. Tar and pieces of wood and brick were encountered at a depth of approximately 3 to 5 feet bgs in the vicinity of the Tar Tanks. Benzo (a) pyrene was the only PAH detected in excess of NJDEP soil cleanup criterion in the surface soil samples collected from the area.

Additional contamination was located on Parcel 1 near the former Circular Oil Tank and Tower, including exceedances of several PAHs detected in surface and near surface soils. Cadmium exceeding the NJDEP criterion was also found in the vicinity of the former coal shed.

Contamination on Parcel 2 was located primarily in surface soils in the vicinity of the former Gas Holder No. 2 and Compressor House. Laboratory analytical results from the collected surface soil samples indicated the presence of PAH compounds above the NJDEP soil cleanup criteria at a depth of 0 to 2 feet bgs. Soil samples collected from only one of the soil borings (SB2-02) yielded contaminant concentrations (VOCs and

naphthalene) that exceeded NJDEP soil cleanup criteria. The reported concentrations were detected in the soil samples collected at a depth of 14 feet bgs. Tar was encountered in saturated soils in one soil boring completed near the location of the former Compressor House.

Groundwater

Analytical results of groundwater samples collected from the upgradient monitoring wells indicated the presence of VOCs above NJDEP groundwater quality criteria, which suggests the presence of an off-site source. Results of samples collected from the downgradient monitoring well (MW2-02) indicated the presence of BTEX compounds and naphthalene.

3.7.6 Remediation

There is as yet no approved remediation plan for this site.

3.8 Millville

Effective October 15, 1992 SJG entered into a Memorandum of Agreement (MOA) with the New Jersey Department of Environmental Protection (NJDEP). Upon NJDEP approval of the Phase 1 RIWP, the Phase 1 RI and a Supplemental Phase 1 RI were conducted from October 1994 through April 3, 1996. Results of the Phase 1 RI and the Supplemental Phase 1 RI were summarized in a report entitled "*Comprehensive Phase 1 Remedial Investigation Millville, Former Gas Works*" dated October 1996. The Phase 1 RI and Supplemental Phase 1 RI consisted of the following field activities:

- a geophysical survey and 30 test excavations to locate possible subsurface remnants of MGP structures

- installation of 35 soil borings to evaluate subsurface soil characteristics, including stratigraphy, hydraulic conductivity, and soil impacts from compounds potentially related to MGP activities
- installation of 19 monitoring wells, and 4 temporary monitoring clusters, for water level monitoring and groundwater sampling to evaluate site hydrogeology, site groundwater flow, and groundwater impacts from compounds potentially related to MGP activities
- in-situ aquifer permeability tests on each of the shallow and intermediate monitoring wells.

A Phase 2 RIWP dated October 1997 was prepared and submitted to the NJDEP, which addressed their comments and proposed additional RI activities. The objectives of the Phase 2 RIWP were as follows:

- characterize saturated and unsaturated zone soil quality with regard to the NJDEP Soil Cleanup Criteria (SCC)
- determine the groundwater impact with regard to the Groundwater Quality Standards
- collect groundwater samples necessary for the selection of remedial alternatives
- investigate surrounding industrial sites and their potential contribution to the soil and groundwater quality.

3.8.1 Site Setting

The former MGP site is located in the city of Millville, Cumberland County, New Jersey. The site encompasses 7.64 acres and currently contains a single brick structure, which serves as an office and warehouse facility.

Land use in the immediate vicinity is mixed commercial and industrial. The site is bounded to the north by an automobile dealership, to the west by a street, to the south by a substation, and to the east by an active railroad right-of-way. Further east, across the right-of-way, is a glass manufacturing facility. Land use south of the site consists primarily of small commercial establishments and residential properties.

According to the United States Geological Survey (USGS) quadrangle, the site is generally situated approximately 45 feet above mean sea level. A survey plan revealed approximately 6 feet of relief over the site. Elevations range from 43 feet above mean sea level in the southwestern corner of the site, to 49 feet at the northeastern corner of the site. Off-site, the land gradually slopes to the southwest.

3.8.2 Operational History

By 1915, the property was occupied by a gas light company, which manufactured gas using coal gas and carbureted water gas processes. By 1923, the gas light property encompassed approximately 16.5 acres. Site operations were converted in 1950 from coal gas and carbureted water gas to an oil gas process. All gas manufacturing operations were discontinued in 1952. By 1961, the current owner operated a liquefied petroleum storage and distribution plant on the property. During the period between 1979 and 1980, all structures associated with the MGP operations were demolished.

3.8.3 Geology

One hundred and four (104) borings were conducted during the Phase 2 RI. Data obtained from the boring logs indicate that numerous fluvial, beach, and marine deposits underlie the site and vicinity.

The site surface consists of 2 to 6 feet of fill material. Underlying the fill are sands and gravelly sands of the Bridgeton Formation, which extend to approximately 40 feet bgs. The upper portion of the Bridgeton Formation, extending from beneath the site fill to approximately 20 feet bgs, consists of a brownish-yellow, well-graded sand. Below this sand is a unit of coarse sand and fine to medium gravel. This unit extends to depths of approximately 35 feet bgs, with thickness varying between 10 and 25 feet. Generally, this unit is poorly graded, with some localized fine sands, silts, and clays appearing within the matrix.

Underlying the Bridgeton Formation is a silty sand unit. This unit is interpreted to be the top of the Cohansey Formation. The Cohansey Formation contains two silty sand units, as depicted on the cross-sections. These units are both fine to medium grained sands. The upper silty sand unit is a light-colored fine to medium sand with interbedded fine sand and silt layers. This sand extends to a depth of approximately 45 feet bgs. The second silty sand unit is a brownish-yellow fine to medium sand, with silt and occasional interbedded layers of clay and/or fine gravel. This unit is characterized as having a higher silt content than the upper silty sand and extends to a depth of approximately 85 feet bgs. A varved sandy clay unit separates the two silty sand units. This varved clay unit is characterized by tightly packed, light gray to white clay varves separated by yellowish-brown sand and silt lenses that are less than 1/10 of a foot in thickness. The beds of clay varves are generally less than 1 foot in continual thickness. Although this unit was seen in all of the on-site Phase 2 RI borings, it appears that this unit is not laterally extensive and thins out to the south and west of the former site.

The lowermost unit of the Cohansey formation is characterized as poorly graded, heavily iron-stained, coarse sand, with interbedded medium sands and fine gravels. Found beneath the site, and throughout most of the investigated area, this unit is encountered at depths greater than 85 feet bgs.

Beneath the Cohansey Formation exists a dark gray silt and fine sand unit that is interpreted as being the uppermost unit of the Kirkwood Formation. Only two soil borings were advanced deep enough to encounter the Kirkwood Formation (SB-32-182 installed approximately 400 feet north of the site, and SB-65-180 installed approximately 250 feet south of the site). At SB-32-182, the Kirkwood was encountered approximately 130 feet bgs, and persisted to the terminus of this boring at 182 feet bgs. At SB-65-180, the Kirkwood was encountered at approximately 140 feet bgs, and persisted to the terminus of this boring at 180 feet bgs.

Off-site geology is consistent with the on-site geology. The only significant difference is the existence of intermittent layers of organic silty clays. These highly organic deposits are characterized as localized, olive to very dark gray silts with interbedded clays and sands containing peat and wood fragments. The maximum thickness encountered per formation is approximately 20 feet, although a thickness over 40 feet have was observed in SB-81-120.

3.8.3 Hydrogeology

The following summary of site hydrogeology was developed using monitoring well groundwater data collected during the Phase 1 and Phase 2 RIs. The monitoring wells include 20 shallow wells (13 on-site and 7 off-site) screened to a depth of 12' to 42' bgs;

21 intermediate wells (6 onsite and 15 offsite) screened to a depth of 42' to 94' bgs; and 5 deep wells (1 on-site and 4 off-site) screened to a depth of 94' to 135' bgs.

The water table was generally encountered between 9 and 21 feet bgs. Generally, only one water-bearing zone was encountered during this investigation. This zone extended from the water table to 130 feet bgs, where a semi-confining unit (silty-clay) was encountered.

Shallow and intermediate zone contour maps indicate a groundwater flow in a south-southwesterly direction. The groundwater impact plume identified emanating from this site appears to move along in the direction of groundwater flow.

The average hydraulic gradient across the site, down to 94 ft bgs in the aquifer, was determined to be 0.0036 feet/foot.

3.8.5 Contaminant Distribution

Soils

During the Phase 1 RI, exceedances of the NJDEP clean up criteria for benzene, toluene, ethylbenzene, total xylenes, and styrene were identified in the east-central portion of the site, and off-site to the west and southwest. Exceedances for total xylenes were also identified extending into the northeast quadrant of the site, and an apparently isolated benzene exceedance was identified near the western site boundary.

Exceedances of the soil clean up criteria for SVOC compounds were identified throughout the site, and at off-site locations during the Phase 2 RI. On-site naphthalene exceedances appear to be largely confined to the central and northern portions. Exceedances of polyaromatic hydrocarbons (PAHs): benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene,

and dibenz(a,h)anthracene were identified throughout the site and extending off-site to the north, west, and south.

Off-site to the north and southwest of the site, SVOC exceedances were associated with visual or olfactory indications of residual impact. These samples had a naphthalene-like odor, and generally had visual impacts such as staining or interstitial product.

Most impacted soils in the saturated zone were associated with the presence of DNAPL (i.e. free or residual product, heavy sheen). On-site the soil impacts were found in three distinct impacted layers in the saturated zone. The first zone is located at or within two feet of the water table (zone of fluctuation). The middle impacted zone is located at a change in lithology from the coarser sands of the Bridgeton Formation to the finer sands of the Cohansey Formation. The deepest soil impact zone is found between 45 feet and 55 feet bgs, along the top of a varved clay unit underlying the site within the Cohansey Formation.

The shallowest zone DNAPL is closely associated with the water table. Observed impacts were noted at the water table or within the apparent zone of water table fluctuation. Shallow DNAPL impacts extend off-site as far as 115 feet to the southwest and 175 feet to the north.

The majority of saturated soil impacts identified during this investigation exist within the Bridgeton Formation. The interface between the Bridgeton Formation and the underlying Cohansey Formation appears to retard the downward migration of most of the saturated soil impacts associated with this Site. The majority of DNAPL identified during this investigation was observed immediately above the top of the Cohansey

Formation. The widest horizontal distribution of saturated soil impacts and DNAPL, including offsite migration to the west and south, occurs immediately above the top of the Cohansey Formation.

The middle zone of DNAPL is located at the interface between the Bridgeton Formation and Cohansey Formation at approximately 40 feet bgs. DNAPL extends the most laterally (as far as 300 feet off-site) immediately above the Cohansey Formation.

The deepest product zone is found between 45 and 55 feet bgs, above a varved clay unit identified within the Cohansey Formation. This zone of DNAPL was identified only in the south-central portion of the site. No evidence of soil impact exists below the varved clay unit.

Groundwater

The groundwater investigation consisted of the installation and sampling of temporary groundwater screening wells and permanent groundwater monitoring wells.

Groundwater screening was conducted to delineate the extent of groundwater impacted by compounds potentially related to MGP activities, and to aid in the selection of locations for permanent groundwater monitoring wells. Groundwater screening samples were collected at 19 on-site boring locations and 47 off-site locations.

The groundwater screening program identified three apparently distinct groundwater plumes to the south and southwest. One of these plumes appears to be associated with the former MGP site. This plume extends along a corridor approximately 1,000 feet in width to the south west of the site. The apparent width of this corridor is consistent with the horizontal distribution of DNAPL and saturated soil impacts

identified at the site. The depth and vertical thickness of this plume is also consistent with the distribution of DNAPL and saturated soil impacts at the site.

Volatile organic compounds identified in groundwater at the site consist of benzene, toluene, ethylbenzene, styrene, total xylenes, and MTBE. Ethylbenzene and styrene were identified extending approximately 400 feet off-site to the southwest. Total xylenes exceeded the GWQS as far as 3,000 feet southwest of the site. Benzene is the most widespread VOC identified in this groundwater plume, measured above the GWQS as far as 4,000 feet south of the site. Benzene concentrations immediately southwest of the site are about 1,200 ppb, which decreases to 380 ppb approximately 2,500 feet southwest of the site, to 150 ppb 3,000 feet southwest of the site, and to 2.4 ppb approximately 4,000 feet southwest of the site.

Two PAH compounds (naphthalene and 2-methylnaphthalene) were identified exceeding the groundwater standards in the groundwater plume that extends southwest of the site. 2-methylnaphthalene was identified approximately 400 feet southwest of the site. Naphthalene was identified extending approximately 3,000 feet southwest of the site.

3.8.6 Remediation

There is as yet no approved remediation plan for this site

CHAPTER 4

EXPERIMENTAL METHODS

This research used the three lines of evidence, as developed for the AFCEE protocol to provide a better understanding of anaerobic biodegradation mechanisms at MGP sites. The first two lines of evidence (documented loss of contaminants at the field scale; and the use of chemical analysis in mass-balance calculations for potential biodegradation) require the analysis of field data, as described below under the heading *Field Data Analysis*. The third line of evidence, the microcosm study, will be discussed under the heading *Laboratory Microcosm Studies*.

4.1 Field Data Analysis

As stated earlier, a major reason why a research project of this nature is possible is a result of access to a large data set from eight well characterized MGP sites. These data were collected in conjunction with the RI efforts occurring at these sites.

In general, all of the sites are located within the Atlantic Coastal Plain Physiographic Province. This Province is composed of a seaward dipping wedge of unconsolidated sediments ranging in age from Cretaceous to Recent. These sediments consist of gravel, sand, silt, and clay. The Cretaceous and Tertiary sediments dip gently to the southeast at 10 feet to 60 feet per mile. These deposits thicken to the southeast from outcrops along the Delaware River to over 6,500 feet at the southern tip of Cape May.

Five of the MGP sites (Egg Harbor, Hammonton, Glassboro, Millville and Pleasantville) are located inland and three of the sites (Bridgeton, Salem and Florida

Avenue) are located adjacent to a salt or brackish body of water. Most of the sites are located in industrial areas with evidence of other sources contributing to the contaminant plume.

Soil Boring Methods

In order to investigate the subsurface conditions, soil borings were installed using hollow stem auger (HSA) and/or mud rotary drilling techniques. Soil borings were used to collect soil and groundwater screening samples. All soil borings were performed in accordance with the Subsurface and Percolating Waters Act, N.J.S.A. 58:4A-4.1 *et seq.*

Installation methods and techniques for advancement of the soil borings was determined based on the geology encountered. If a potential confining unit was encountered, double-cased drilling methods were initiated in order to minimize the potential for downward migration product or groundwater impacts. This was accomplished by setting a temporary four-inch steel casing a minimum of one foot into the confining layer. The steel casing was grouted in place with bentonite slurry to seal off the impacted horizon above the dry zone. Drilling was then continued through the “cased-off” dry zone using mud-rotary drilling techniques.

Continuous two-inch or three-inch split spoon samples were collected from all borings. The split spoon samplers were advanced using a 140-pound hammer dropped from a height of 30 inches. Upon opening the split spoon sampler, each sample was field characterized (logged) and screened with a calibrated flame ionization detector (FID) and/or photoionization detector (PID).

Soil samples collected during all phases of analysis were submitted to a New Jersey Certified Laboratory. All samples were collected in accordance with the Field Sampling Procedures Manual (FSPM) and the Technical Requirements for Site Remediation. The soil samples and appropriate quality assurance/quality control (QA/QC) samples (discussed below) were placed in a sealed, iced-cooler, and transported to the laboratory.

Groundwater Screening Methods

A dynamic groundwater screening program was implemented to delineate vertical and horizontal groundwater impacts related to former MGP activities. The results of the groundwater screening program were used to design the permanent groundwater monitoring well network. Groundwater screening samples were collected from temporary monitoring wells, which are typically constructed of 5 or 10 foot sections of two-inch diameter schedule 40 PVC screen (0.01 inch slots) and two-inch diameter PVC riser pipe. The PVC screen and riser were lowered through the hollow stem augers, or a temporary steel casing, after the desired drilling depth was reached. A silica sand pack was added to fill the annular space between the PVC riser and the inner wall of the borehole. This process was continued until the sand pack was at least two feet above the top of the well screen. A well seal was provided by pumping a bentonite slurry using a tremie pipe. The bentonite slurry was allowed to set for approximately a half hour prior to purging.

Prior to sampling, the temporary wells were purged using submersible pumps until the purge water was clear and relatively free of sediments or for a maximum

duration of one hour. If a well had insufficient yield to support use of the submersible pumps for well development, the well was hand-bailed, using dedicated polypropylene bailers, until at least three wet casing volumes were evacuated. The groundwater screening samples were collected using a dedicated, two-inch diameter, disposable Teflon™ or polypropylene bailer. The temporary wells were removed after sample collection and the borings were overdrilled to remove the remaining sand pack and bentonite seal. If the borings were not continued deeper they were tremie grouted from the bottom up with a cement-bentonite grout.

The groundwater screening samples were collected in accordance with the FSPM and the Technical Requirements, placed in the appropriate laboratory glassware, and stored in an iced cooler, before shipment to a New Jersey Certified Laboratory for analysis.

Permanent Monitoring Well Installation

Permanent monitoring wells were installed in locations where the highest concentrations of potential MGP-related compounds were identified by the groundwater screening results, and at corresponding out-of-plume locations (vertically and horizontally). Typically, monitoring wells were installed using HSA drilling methods, in some cases followed by mud rotary drilling methods, in accordance with NJDEP specifications. Monitoring wells were constructed of four-inch or two-inch inner diameter (ID) stainless steel riser, and five or 10 feet of stainless steel wire wrapped 0.01-inch slotted screen. Typically, four-inch wells were installed. However, when wells were double-cased, two-inch well material was used. All permanent monitoring wells consisted of five-foot

screens, except for water table wells, which were constructed with 10-foot screens with the screen positioned to straddle the water table. When the well installation depth was reached, the stainless steel screen and riser were lowered to the bottom of the boring through the hollow stem augers or steel casing set during the well installation process. A silica sand pack (No. 1 sand) was installed in the annulus between the borehole wall and the screen. The sand pack extended approximately two feet above the top of the screen. The sand pack above the well screen was graded down to a fine sand (No. 00 sand) to minimize grout intrusion. The borehole was tremie-grouted with a bentonite-cement grout from the top of the sand pack to 1.0 foot bgs.

Monitoring wells were secured with watertight locking well caps. The wells were completed with flush-mounted locking road boxes or with stick-up well protectors. The road boxes and stick-ups were secured in place within a minimum two-foot by two-foot concrete pad. Well permit numbers were marked on each well.

Groundwater Sampling Methods

Typically, all groundwater sampling was conducted in accordance with the NJDEP-approved low-flow sample collection methodology. Prior to each groundwater sampling event, the water level and distance to the bottom of the wells were measured to the nearest 0.01 feet. Headspace readings were also obtained using a PID prior to groundwater sampling. The water levels were measured with a field-decontaminated depth to water probe. The depth to bottom of the wells was measured using a field decontaminated oil/water interface probe to check for the presence of non-aqueous phase liquids. The depth-to-water measurements were used in evaluating groundwater flow

direction and, in certain instances, for purge volume calculations. The synoptic water level measurements were collected in one day prior to initiating the groundwater sampling.

Groundwater samples were collected using either a Keck Instruments, Inc. Model SPR submersible pump or a Fultz Pumps, Inc. Model SP-300R submersible pump. The pump intake was set at predetermined depths during sample collection. These depths were based on the following: the approximate middle of the screen interval for wells installed outside the groundwater impact plume; the depth exhibiting the highest PID reading recorded during well installation; or the depth exhibiting the highest PID reading during the advancement of the Phase 3 RI groundwater screenings conducted in the immediate area of the monitoring wells. The pumps were fitted with a YSI Environmental Monitoring Systems (YSI) Model 6820 Multi-Parameter Water Quality Monitor with a flow-through cell housing sensors reading temperature, pH, dissolved oxygen (DO), specific conductivity, turbidity, and oxidation-reduction potential (ORP). Readings were recorded electronically by a YSI 610-DM Data Logger. Additionally, the water level was continuously monitored using an electronic probe. The readings were also recorded at five-minute intervals on field sampling forms. Pumping rates were kept between 200 milliliters per minute (ml/min) and 500 ml/min. Groundwater drawdown was not allowed to exceed 0.3 feet over any three consecutive five-minute intervals. The YSI was calibrated twice daily (beginning and end of the day), in accordance with the manufacturer's specifications.

All monitoring wells were pumped for a minimum of 20 minutes prior to collecting groundwater samples at stabilized readings of pH, DO, specific conductivity,

turbidity, and ORP. Stabilization was achieved when the following allowable tolerances were observed for three consecutive five-minute readings:

<u>Parameter</u>	<u>Tolerance</u>
PH	± 0.1
DO	± 10%
specific conductivity	± 3%
turbidity	± 10%
ORP	± 10mv

Once three consecutive readings within the above tolerances were obtained, the well was considered to be within equilibrium and sample collection was initiated. Prior to sampling, the YSI was removed to avoid cross contamination and aeration. The groundwater samples were collected directly into the appropriate laboratory-supplied glassware, with the VOC sample fraction collected first, followed by the other fractions.

If monitoring well equilibrium was not obtained (i.e. YSI measured parameters did not come within allowable tolerances) within four hours of continuous pumping, this was noted on the field form and in a field book and the groundwater sample was collected as before.

If the maximum allowable well drawdown of 0.3 feet over three consecutive five-minute intervals (15 minutes) could not be maintained at the minimum flow of 200 ml/min, the well was determined to be a low-yield well. Low-yield wells were pumped until either a minimum of three wet casing volumes were evacuated from the well or until the water level in the well was drawn to the top of the sand pack. The well would then be closed and allowed to recharge overnight and the sample was collected the next day using the submersible pump, with the pump intake set at the predetermined depth.

QA/QC Sampling

Field QA/QC samples were collected during all field activities in accordance with the FSPM. The QA/QC samples included field duplicates, field blanks, trip blanks, temperature blanks, and matrix spikes/matrix spike duplicates (MS/MSD). All QA/QC samples were analyzed for the same parameters as the investigative samples, except for trip blanks (which were analyzed only for VOC). Field duplicate samples were submitted to the laboratory as "blind" samples, and were intended to check field sampling and handling procedures along with laboratory analytical procedures. Field duplicate samples were submitted for laboratory analysis at a minimum frequency of one for every 20 investigative samples (i.e. 5%).

During groundwater sampling, field blanks were collected and submitted at a rate of one field blank per day per sampling team. Field blank samples were intended to evaluate the adequacy of field decontamination procedures and ambient conditions. For soil samples, field blanks were collected in the sampling area by pouring laboratory-supplied deionized water over the field decontaminated sampling equipment, and collecting the water in the appropriate sample containers. For groundwater samples, field blanks were collected by pumping laboratory-supplied deionized water through the sampling pump and a section of discharge tubing.

Trip blank samples are intended to evaluate potential VOC contamination sources in the sample containers and field blank water, and to evaluate sample transport procedure. Trip blank samples were laboratory-prepared using deionized water and accompanied the sampling bottles (that were prepared at the laboratory) into the field and back to the laboratory, along with the collected investigative samples. Trip blanks were

submitted for VOC analysis at a rate of one trip blank for each shipment of aqueous samples to the laboratory.

Aquifer Permeability Testing

In-situ hydraulic conductivity testing was performed at selected wells at most of the sites. Rising-head data were then analyzed with groundwater modelling software (AQTESOLV), using the Bouwer and Rice rising head test analysis technique. Hydraulic conductivities were calculated using visual curve matching of the late-time recovery data to filter out data not representative of the native shallow water-bearing system. Early time data collected during the rising head analysis often reflects the hydraulic conductivity of the well's sand pack and not native soil.

Analytical Methods

Table 4.1 summarizes the analytical methods used for the various parameters sampled at the sites.

Table 4.1 Summary of Analytical Methods

Matrix	Parameter	Analytical Method
Soil		SW-846 Methods
	VOC	8240
	SVOC	8270
	Inorganics	6010
Ground water		EPA Methods
	VOC	624
	SVOC	625
	dissolved iron	200.7
	nitrate	353.2
	sulfate	375.4
	BOD	405.1
	COD	410.4
	Alkalinity	310.1
	Methane	3810

4.1.1 Calculation of First Order Rate Constant Via Buscheck and Alcantar Method

The first line of evidence (contaminant losses on a field scale) was documented by measuring the distance each plume traveled over time, as opposed to noting actual decreases in monitoring wells over time, because the source material is still in the ground. Additionally, since there is typically no compound present that can be used as a conservative tracer (such as TMB in fuel mixtures), the change in solute concentration in groundwater over time was determined by calculating a first-order decay rate constants as per Buscheck and Alcantar (1995).

This method involves a regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) and relating the result to an analytical solution for one-dimensional, steady-state, contaminant

transport that includes advection, dispersion, sorption and biodegradation. For a steady-state plume, the first-order decay rate is given by:

$$k = v \left[\frac{d(\ln S)}{dx} \right] \left\{ \left(\frac{D_x}{v} \right) \frac{d(\ln S)}{dx} - 1 \right\}$$

where: k = first-order biological decay rate (s⁻¹)
 v = groundwater velocity in the x direction (cm/s)
 D_x = axial dispersivity (cm²/s)
 d(lnS)/dx = slope of line formed by making a log-linear plot of
 contaminant concentration versus distance downgradient
 along flow path (cm⁻¹)

The first step in calculating first-order decay rate constants was to confirm that the contaminant plume for each site had reached a steady-state configuration. This was done by analyzing the historic data to make sure the plume is no longer migrating downgradient and contaminant concentrations are not changing significantly through time. This is generally the case for older spills where the source has not been removed (Weidemeir et al., 1999). The next step was to make log linear plots of contaminant concentration versus distance downgradient using the data collected during the RI investigations. Using linear regression, the slope of the line (d(lnS)/dx) was determined and entered into the equation and the first-order biological decay rate (k) was determined. Calculations were completed for each contaminant of concern at each of the eight sites.

4.1.2 Best Fit Kinetic Model Via BIOSCREEN

BIOSCREEN – Groundwater Contamination Natural Attenuation Model, Version 1.4 was used to determine if biodegradation kinetics at the MGP sites more closely follow first-order or transport-limited (instantaneous reaction) kinetics. BIOSCREEN is an analytical computer model operating in the Microsoft Excel® environment. The model was designed to simulate biodegradation by both aerobic and anaerobic processes and was

developed for the AFCEE Technology Transfer Division at Brooks Air Force Base by Groundwater Services, Inc., Houston, Texas. Since it was originally developed for fuel spills, it had to be modified to accommodate MGP site data. The model is based on the Domenico analytical solute transport model, and has the ability to simulate advection, dispersion, adsorption, and aerobic/ anaerobic biotransformation of petroleum constituents. Requisite model input parameters include the following site data gathered during the site characterization phase of the RI for each of the eight sites:

- hydrogeology
- dispersion
- adsorption
- biodegradation
- plume morphology
- source data
- field contaminant concentration data

BIOSCREEN assumes that biodegradation is consistent with either first-order kinetics or the instantaneous reaction model (where contaminants react with terminal electron acceptors instantaneously in accordance with the stoichiometry). In order to evaluate which model is more consistent with site data, BIOSCREEN results (assuming first-order kinetics, and then assuming instantaneous reaction) were compared to actual site data, laboratory microcosm data, and literature values (e.g. for fuel constituents, generated during the AFCEE natural attenuation initiative).

4.1.3 Evidence of Significant Terminal Electron Acceptors

The second line of evidence involves the use of chemical analyses and mass balance calculations to show that decreases in contaminant concentrations can be correlated with changes in electron acceptor concentrations. As part of the data reduction phase of the RI for each site, contaminant contour maps were constructed for contaminants of concern at each site, electron acceptors consumed (dissolved oxygen, nitrate, and sulfate), and metabolic byproducts produced [iron(II) and methane].

In cases where these contour maps suggest a qualitative relationship between a terminal electron acceptor and a contaminant, mass balance calculations were completed for that specific contaminant and metabolic pathway to quantify the relationship, and determine the assimilative capacity. "Assimilative capacity" refers to the natural ability of the groundwater system to attenuate contaminants such that they do not pose significant risk to potential receptors. Mass ratios were first calculated for each electron acceptor and contaminant of interest using the stoichiometry of each metabolic pathway (aerobic, iron, sulfate, and nitrate reduction, and methanogenesis). Since the mass ratios are very similar for BTEX and PAH compounds utilizing the same electron acceptor, the mass ratios were averaged to obtain a single value for a given electron acceptor. These were then multiplied by electron acceptor concentrations collected from monitoring wells located along the plume centerline. Summing over all electron acceptors resulted in a total assimilative capacity for the site, which was then compared to the actual mean contaminant concentration along the plume centerline to determine if there was sufficient electron acceptor present to affect a significant degree of natural attenuation.

Table 4.2 summarize the stoichiometry for the major contaminants and electron acceptors.

Table 4.2 Terminal Electron Acceptor Stoichiometry

Dissolved Oxygen		Mass ratio O₂/COC	Mass ratio COC/O₂
Benzene	$7.5\text{O}_2 + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$	3.08	0.33
Toluene	$9\text{O}_2 + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O}$	3.13	0.32
Ethylbenzene	$10.5\text{O}_2 + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow 8\text{CO}_2 + 5\text{H}_2\text{O}$	3.17	0.32
Xylene	$10.5\text{O}_2 + \text{C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow 8\text{CO}_2 + 5\text{H}_2\text{O}$	3.17	0.32
Naphthalene	$12\text{O}_2 + \text{C}_{10}\text{H}_8 \rightarrow 10\text{CO}_2 + 4\text{H}_2\text{O}$	3.00	0.33
MEAN		3.11	0.32

Nitrate Reduction		Mass ratio NO₃⁻/COC	Mass ratio COC/NO₃⁻
Benzene	$6\text{NO}_3^- + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 3\text{N}_2 + 6\text{OH}^-$	4.77	0.21
Toluene	$7.2\text{NO}_3^- + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow 7\text{CO}_2 + 3.6\text{N}_2 + 7.2\text{OH}^- + 0.4\text{H}_2\text{O}$	4.85	0.21
Ethylbenzene	$8.4\text{NO}_3^- + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow 8\text{CO}_2 + 4.2\text{N}_2 + 8.4\text{OH}^- + 0.8\text{H}_2\text{O}$	4.91	0.20
Xylene	$8.4\text{NO}_3^- + \text{C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow 8\text{CO}_2 + 4.2\text{N}_2 + 8.4\text{OH}^- + 0.8\text{H}_2\text{O}$	4.91	0.20
Naphthalene	$9.6\text{NO}_3^- + \text{C}_{10}\text{H}_8 + 0.8\text{H}_2\text{O} \rightarrow 10\text{CO}_2 + 4.8\text{N}_2 + 9.6\text{OH}^-$	4.65	0.22
MEAN		4.82	0.21

Iron Reduction		Mass ratio Fe²⁺/COC	Mass ratio COC/Fe²⁺
Benzene	$30\text{Fe}^{3+} + 12\text{H}_2\text{O} + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 30\text{Fe}^{2+} + 30\text{H}^+$	21.5	0.046
Toluene	$36\text{Fe}^{3+} + 14\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow 7\text{CO}_2 + 36\text{Fe}^{2+} + 36\text{H}^+$	21.9	0.046
Ethylbenzene	$42\text{Fe}^{3+} + 16\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow 8\text{CO}_2 + 42\text{Fe}^{2+} + 42\text{H}^+$	22.1	0.045
Xylene	$42\text{Fe}^{3+} + 16\text{H}_2\text{O} + \text{C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow 8\text{CO}_2 + 42\text{Fe}^{2+} + 42\text{H}^+$	22.1	0.045
Naphthalene	$48\text{Fe}^{3+} + 20\text{H}_2\text{O} + \text{C}_{10}\text{H}_8 \rightarrow 10\text{CO}_2 + 48\text{Fe}^{2+} + 48\text{H}^+$	20.9	0.048
MEAN		21.7	0.046

Table 4.2 Terminal Electron Acceptor Stoichiometry (Continued)

Sulfate Reduction	Mass ratio SO₄²⁻/COC	Mass ratio COC/SO₄²⁻
$3.75\text{SO}_4^{2-} + 7.5\text{H}^+ + \text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O} + 3.75\text{H}_2\text{S}$ Benzene	4.62	0.22
$4.5\text{SO}_4^{2-} + 9\text{H}^+ + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} + 4.5\text{H}_2\text{S}$ Toluene	4.70	0.21
$5.25\text{SO}_4^{2-} + 10.5\text{H}^+ + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow 8\text{CO}_2 + 5\text{H}_2\text{O} + 5.25\text{H}_2\text{S}$ Ethylbenzene	4.75	0.21
$5.25\text{SO}_4^{2-} + 10.5\text{H}^+ + \text{C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow 8\text{CO}_2 + 5\text{H}_2\text{O} + 5.25\text{H}_2\text{S}$ Xylene	4.75	0.21
$6\text{SO}_4^{2-} + 12\text{H}^+ + \text{C}_{10}\text{H}_8 \rightarrow 10\text{CO}_2 + 4\text{H}_2\text{O} + 6\text{H}_2\text{S}$ Naphthalene	4.50	0.22
MEAN	4.66	0.21

Methanogenesis	Mass ratio CH₄/COC	Mass ratio COC/CH₄
$4.5\text{H}_2\text{O} + \text{C}_6\text{H}_6 \rightarrow 3.75\text{CH}_4 + 2.25\text{CO}_2$ Benzene	0.77	1.30
$5\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow 4.5\text{CH}_4 + 2.5\text{CO}_2$ Toluene	0.78	1.28
$5.5\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow 5.25\text{CH}_4 + 2.75\text{CO}_2$ Ethylbenzene	0.79	1.26
$5.5\text{H}_2\text{O} + \text{C}_6\text{H}_4(\text{CH}_3)_2 \rightarrow 5.25\text{CH}_4 + 2.75\text{CO}_2$ Xylene	0.79	1.26
$8\text{H}_2\text{O} + \text{C}_{10}\text{H}_8 \rightarrow 6\text{CH}_4 + 4\text{CO}_2$ Naphthalene	0.75	1.33
MEAN	0.78	1.29

Note that the stoichiometric mass ratios are relatively constant for a given electron acceptor. Therefore, an average value can be used regardless of the specific contaminant composition at a given site.

Although cellular biomass production can be significant in the case of aerobic respiration (or denitrification), the stoichiometric calculations shown above do not consider contaminant assimilation into cellular biomass. The assimilative capacity only refers to *mineralization* of the contaminants (as per EPA and AFCEE usage), and is therefore conservative with regard to contaminant disappearance. A greater rate of biomass production will also accelerate the disappearance of contaminants. However, the stoichiometry is independent of the kinetics.

The following is an example calculation for the assimilative capacity at the Glassboro site (north plume). Note that the calculation represents the *potential* for biodegradation, not necessarily its reality, but it places an upper bound on the possibility of natural attenuation. Electron acceptor concentrations were first reduced by 70% to allow for other competing sinks and transport limitations, based on field experience.

Background oxygen at the site (outside the plume) was 4.5 mg/L. Reduced by 70%, this leaves 1.35 mg/L. When this value is multiplied by the mean mass of compound degraded per unit mass of oxygen (0.32), the result is the maximum mass of contaminants that can be degraded by this pathway (0.43 mg/L).

The highest iron (Fe^{+2}) concentration within the plume was 17.5 mg/L. Reduced by 70%, this leaves 5.25 mg/L, which when multiplied by the mean mass of compound degraded per unit mass of iron (0.046), results in the maximum mass of contaminants that can be degraded by this iron reduction pathway (0.24 mg/L).

The change in sulfate from the plume center to background was 203 mg/L. Reduced by 70%, this leaves 160.9 mg/L, which when multiplied by the mean mass of compound degraded per unit mass of sulfate (0.21), results in the maximum mass of contaminants that can be degraded by this sulfate reduction pathway (12.8 mg/L).

Nitrate was not detected in the contaminant plume or in the background groundwater; and methane was not analyzed for.

Therefore, the total expressed assimilative capacity can be calculated as follows. Since it exceeds the actual mean concentration of contaminants measured along the plume centerline, the possibility exists for natural attenuation to completely degrade the contaminant plume at this site.

Pathway	Assimilative Capacity (for COCs)
dissolved oxygen	0.43 mg/L
Iron	0.24
Sulfate	12.8
-----	-----
Total	13.5
actual mean COC	7.58

4.2 Laboratory Microcosm Studies

The third line of evidence, laboratory microcosm studies, were undertaken at Cook College, Rutgers University under the supervision of Dr. Lily Y. Young. The objective of these studies was to examine the ability of indigenous organisms, at the Glassboro Former MGP site (Glassboro) and the Florida Avenue Former MGP site (Florida Ave), to degrade representative MGP constituents (benzene, toluene and naphthalene) under nitrate reducing, iron-reducing and sulfate-reducing conditions. First-order decay constants were calculated from the microcosm data.

Soil and groundwater samples were collected from the Kirkwood-Cohansey aquifer system at two separate MGP sites in southern New Jersey: Glassboro and Florida Ave. Glassboro is located inland; therefore, the groundwater is fresh. Florida Ave is located on a barrier island; therefore, the groundwater is brackish. Soil and groundwater microcosms were made under various anaerobic conditions for each site.

The contaminant plume at Glassboro is approximately 4000 feet long and is found at a depth of 40 to 60 feet below ground surface. The aquifer matrix material mostly consists of a mix of fine gravel and coarse to fine sand. The predominant contaminants in the Glassboro plume are BTEX and naphthalene.

The extent of the (brackish) groundwater plume at Florida Ave. is approximately 1500 feet. The plume extends from the ground surface to a depth of approximately 45

feet below ground surface. The aquifer matrix at Florida Ave. consists of fine sand and silt. The predominant contaminants in the Florida Ave. plume are benzene and naphthalene.

Saturated soil and groundwater samples were collected from the anaerobic cores of both plumes. The contaminated aquifer soil samples were used as inocula to isolate cultures of benzene, toluene and naphthalene degrading microorganisms.

First, 4000 ml from Glassboro were divided into three 1800 ml flasks (A-C). Two flasks contained 1500 ml of site groundwater each (flask A and flask B), and 1 flask (flask C) contained 1000 ml of site water. 4000 ml from Florida Ave. were also divided into three 1800 ml flasks (D-F). Two flasks (flask D and flask E) contained 1500 ml of site groundwater each, and 1 flask (flask F) contained 1000 ml of site water.

Next, 300 ml of Glassboro aquifer sediments were added to each of two 1800 ml flasks containing groundwater from the Glassboro site (flasks A and B). 300 ml of Florida Ave. aquifer sediments were added to each of two 1800 ml flasks containing groundwater from the Florida Ave. site (flasks D, E). This gave a 20% soil to water ratio in each flask. Flasks A-F were degassed for 2 hours with a mixture of 70% nitrogen and 30% CO₂. Once degassed, 500 ml of site water was removed and set aside from flask C, and 500 ml of site water was removed and set aside from flask F for the purposes of making an iron hydroxide floc solution. To the 500 ml remaining in flask C (Glassboro), 350 ml of site aquifer sediments were added. To the 500 ml remaining in flask F (Florida Ave.), 350 ml of site aquifer sediments were added. Flasks C and F were degassed for an additional hour. 0.1 ml of 1% rosazurin was added to each flask (flasks A-F) as an indicator of oxygen contamination.

For each site the following five systems were set up: nitrate-reducing (flasks A and D), fortified nitrate reducing with vitamins and trace minerals (also flasks A and D), sulfate-reducing (flasks B and E), iron-reducing (flasks C and F), and unamended site water (also flasks B and E). The nitrate-reducing and fortified nitrate reducing systems were made for Glassboro by adding 3.664 grams of potassium nitrate to the slurry in flask A to make a 1240 ppm (20 mmol) nitrate solution. Six serum jars were filled with 150 ml of this slurry (G1-G6). To the remaining slurry in Flask A, one ml of vitamin solution and 0.5 ml of trace mineral solution were added. Six serum jars were filled with 150 ml of this fortified nitrate slurry solution (G7-G12). Florida Ave. nitrate reducing and fortified nitrate reducing systems were made by following the same procedures with the slurry contained in Flask D. Therefore jars F1-F6 represented the nitrate reducing conditions for Florida Ave, and jars F7-F12 represented the fortified nitrate reducing conditions for Florida Ave.

Six additional serum jars (G13-G18) were filled with 150 mls each of the unamended Glassboro site groundwater contained in Flask B; and six serum jars (F13-F18) were filled with 150 ml each of the unamended Florida Ave. site groundwater contained in Flask E. To prepare the sulfate-reducing system for Glassboro, 1.994 grams of sodium sulfate and 0.2 ml of 6.35 mg/L reducing agent were added to the remaining slurry in Flask B. Six serum jars (G19 – G24) were filled with 150 ml each of the sulfate reducing mixture. The same steps were followed for the remaining Florida Ave. groundwater contained in Flask E. The final concentration of the sulfate solution was 1920 ppm (20 mmol); therefore serum jars (F19-F24) represented sulfate reducing conditions for Florida Ave.

To prepare the iron-reducing system, an iron oxyhydroxide floc solution was prepared with the 500 ml of groundwater reserved from Flasks C and F prior to the addition of site aquifer sediments. The floc was prepared according to Mahadevia (1997). 75 ml of Glassboro groundwater slurry from Flask C was added to each of six serum bottles (G25-G30) and 75 ml of Florida Ave groundwater slurry from Flask F were added to each of six serum bottles (F25-F30). 75 ml of the iron oxyhydroxide floc prepared with Glassboro groundwater was added to serum jars G25-G30; and 75 mls of the iron hydroxide floc solution prepared with Florida Ave. groundwater was added to serum jars F25- F30.

Of the six serum jars for each electron acceptor, 3 jars were to be spiked with substrate, 1 was a sterile control and two were to contain no substrate (unspiked).

To prepare the substrate (benzene, toluene, and naphthalene) stock solution, each individual compound was weighed and dissolved in 1.48 ml of ethanol as follows: 0.114 grams of naphthalene, 0.096 grams of toluene, and 0.080 grams of benzene. To each of the jars, except the jars designated as unspiked, 25ul of the stock solution were added to bring the final concentration of each contaminant to 10 ppm. The bottles were sealed with Teflon-coated rubber stoppers and aluminum crimp-seals. Strict anaerobic techniques were used throughout all steps of microcosm preparation.

GC/MS analyses of slurry samples were performed periodically by a New Jersey State certified laboratory during the experiments to determine the utilization of benzene, toluene, and naphthalene. After 120 days, the microcosms were refed with benzene, toluene and naphthalene and then incubated, sampled, and analyzed in the same manner as described above.

The results from this microcosm study were used to corroborate the findings noted in the field data evaluations to add information in support of anaerobic mechanisms of natural attenuation. From the microcosm data, first-order degradation rate constants were calculated for benzene, toluene and naphthalene for each microcosm run in the laboratory. The results of the triplicate microcosms were averaged and the results from the sterile control were subtracted out. These results were compared to the field generated degradation constants, and the stoichiometric and spatial relationships noted in the field between electron acceptors and contaminants.

CHAPTER 5

RESULTS

5.1 Field Data

The following table summarizes field data at the sites:

Table 5.1 Summary of Field Data

Naphth. (mg/L)	benzene (mg/L)	sulfate (mg/L)	Iron (mg/L)	distance (ft)		site	round (date)	Well MW
				y	x			
6.400	0.780	5.0	16.9	493	0	Glassboro	1 (7/99)	24-54
0.098	0.790	69.7	1.29	4769	0	Glassboro	1 (7/99)	47-46
5.700	0.071	96.3	4.70	0	0	Hammonton	2 (3/97)	05-36
0.012		33.1	0.58	132	20	Hammonton	2 (3/97)	03-38
0.003		12.3	0.60	132	28	Hammonton	2 (3/97)	3-150
0.000		39.0	0.16	197	10	Hammonton	2 (3/97)	01-38
9.600	0.746	18.1	1.53	0	0	Egg Harbor	1 (7/97)	21-25
0.044	0.010	23.6	0.86	37	103	Egg Harbor	1 (7/97)	71-26
3.140	0.101	13.2	3.15	117	65	Egg Harbor	1 (7/97)	61-24
0.121	0.018	24.6	5.15	132	83	Egg Harbor	1 (7/97)	81-24
0.035	0.018	14.3	4.50	177	103	Egg Harbor	1 (7/97)	91-24
2.980		39.9	1.63	0	0	Pleasantville	1 (4/97)	02-17
4.340	0.668	22.2	4.08	0	0	Pleasantville	2 (2/98)	03-20
1.710		38.3	6.62	0	0	Pleasantville	2 (2/98)	02-17
0.090		15.5	0.18	253	149	Pleasantville	2 (2/98)	01-25
0.003		21.4	0.11	253	149	Pleasantville	1 (4/97)	01-25
6.400	0.322	0.0	18.3	392	70	Pleasantville	2 (2/98)	07-25
0.002		33.7	0.10	601	0	Pleasantville	1 (4/97)	02-25
0.000		27.6	0.00	601	0	Pleasantville	2 (2/98)	02-25
0.000		14.0	2.28	748	189	Pleasantville	2 (2/98)	08-33
0.002		20.6	0.00	908	0	Pleasantville	1 (4/97)	04-32
0.001		23.0	0.00	908	0	Pleasantville	2 (2/98)	04-32
0.300	1.200	0.07	2.62	92	91	Florida Ave.	1 (5/99)	10-38
0.069	0.019	0.0	1.91	102	0	Bridgeton	1 (7/98)	17-14

y is the distance from the pollution source in the direction of groundwater flow (along the plume centerline)

x is the distance perpendicular to y

- only complete data sets (with known values of sulfate, iron, x and y) are reported
- In some cases, data was not used because it appeared to be inconsistent (e.g. Egg Harbor, round 1, July 1997, well MW-14-38, unexplained spike in naphthalene concentration downstream from the source; and Pleasantville, round 2, February 1998, well MW-06-22, again unexplained spike in naphthalene concentration)

Benzene and naphthalene are the most prevalent organic contaminants in the plumes, and have the most complete data sets. Data for other contaminants is spotty from well to well, with many disappearing shortly beyond the source area, and as a result (although approximate isopleths can be developed) they are not shown in the above table.

Table 5.2 Hydrogeology Parameters

Site	Hydraulic Conductivity (cm/sec)	Gradient (ft/ft)	Porosity	Groundwater Velocity (cm/sec)
Egg Harbor	1.2×10^{-3} to 4.0×10^{-2}	2.7×10^{-3}	0.2	1.62×10^{-5} to 5.4×10^{-4}
Hammonton	6.4×10^{-4} to 5×10^{-2}	1.6×10^{-3} to 1.1×10^{-3}	0.2	3.5×10^{-6} to 4.0×10^{-4}
Glassboro	1×10^{-4} to 1×10^{-2}	2×10^{-4} to 4.4×10^{-3}	0.25	8×10^{-8} to 1.76×10^{-5}
Florida Ave	2.46×10^{-4} to 3.15×10^{-4}	5×10^{-3} to 5.7×10^{-3}	0.2	6.15×10^{-6} to 8.98×10^{-6}
Bridgeton	1×10^{-2} to 1×10^{-4}	3.0×10^{-2} to 7×10^{-3}	0.25	1.2×10^{-6} to 2.8×10^{-4}
Salem	8.3×10^{-3} to 2.4×10^{-4}	1×10^{-3} to 5×10^{-3}	0.1	7.2×10^{-6} to 4.15×10^{-4}
Pleasantville	1×10^{-1} to 1×10^{-3}	1.55×10^{-3}	0.2	7.75×10^{-6} to 7.75×10^{-4}
Millville	2.1×10^{-2} to 4.3×10^{-3}	3.6×10^{-3}	0.2	7.74×10^{-5} to 3.78×10^{-4}

The groundwater velocity was calculated from other parameters and is contemporary with the contaminant concentration profiles used in the equation below:
 groundwater velocity = (hydraulic conductivity)(gradient)/porosity

5.2 Calculation of First-Order Rate Constants (from Field Data)

The Buscheck and Alcantar (1995) method was used to estimate first-order rate constants (k) for each COC at each site:

$$k = v[d(\ln S)/dx]\{(D_x/v)d(\ln S)/dx - 1\}$$

where: k = first-order biodegradation rate constant (1/sec)
 v = average groundwater velocity in the x direction (cm/sec)
 D_x/v = longitudinal dispersivity (cm)
 $d(\ln S)/dx$ = slope of log-linear plot of contaminant concentration versus distance downgradient along the flow path (cm^{-1})

The following tables summarize the results. Specific COCs were chosen because they exceeded Class II groundwater standards at one or more wells. Longitudinal dispersivities

were estimated according to the equation given by Xu and Eckstein (1995) { longitudinal dispersivity = $3.28 * 0.83 [\log_{10} (\text{length of plume}/3.28)]^{-2.414}$ } and presented in Newell et al, 1996. Groundwater velocities are the average log values of the ranges shown above.

Table 5.2 (a) Egg Harbor

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	9E-05	1E04	-6.19E-04	4.00E-07	13
Naphthalene	9E-05	1E04	-9.27E-04	8.57E-07	27
Toluene	9E-05	1E04	-21.8E-04	44.7E-07	140
Xylenes	9E-05	1E04	-13.9E-04	18.6E-07	59

Table 5.2 (b) Hammonton

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	4E-05	1E03	-1.1E-03	9.24E-08	3
Naphthalene	4E-05	1E03	-1.7E-03	18.4E-08	6

Table 5.2 (c) Glassboro North Plume

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	2E-06	1.1E03	-2.4E-03	17.5E-09	0.6
Ethylbenzene	2E-06	1.1E03	-1.3E-03	6.32E-09	0.2
Naphthalene	2E-06	1.1E03	-2.9E-03	24.3E-09	0.8
Toluene	2E-06	1.1E03	-0.95E-03	3.89E-09	0.1
Xylenes	2E-06	1.1E03	-1.4E-03	7.11E-09	0.2

South Plume

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	8E-07	1.1E03	-1.4E-03	2.84E-09	0.1
Xylenes	8E-07	1.1E03	-3.E-03	10.3E-09	0.3

Table 5.2 (d) Florida Avenue

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	7E-06	500	-0.0146	8.48E-07	27

Table 5.2 (e) Bridgeton

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	6E-05	200	-0.0110	2.11E-06	67

Table 5.2 (f) Salem

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Benzene	3E-05	340	-0.0739	5.79E-05	1800
Toluene	3E-05	340	-0.0761	6.14E-05	1900
Xylene	3E-05	340	-0.0724	5.56E-05	1800
Naphthalene	3E-05	340	-0.0787	6.55E-05	2100

Table 5.2 (g) Pleasantville

North Plume

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
Ethylbenzene	8E-05	700	-0.0035	0.97E-06	30
Styrene	8E-05	700	-0.0147	13.3E-06	420
Xylene	8E-05	700	-0.0069	3.22E-06	100
Naphthalene	8E-05	700	-0.0030	0.74E-06	23

South Plume

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
benzene	8E-05	700	-0.0068	31.3E-07	99
ethylbenzene	8E-05	700	-0.0034	9.19E-07	29
naphthalene	8E-05	700	-0.0031	7.86E-07	25
xylenes	8E-05	700	-0.0036	10.1E-07	32

Table 5.2 (h) Millville

COC	groundwater velocity (cm/sec)	longitudinal dispersivity (cm)	slope $d(\ln S)/dx$ (cm^{-1})	1st order decay rate (1/sec)	1st order decay rate (1/yr)
benzene	2E-04	6.4E03	-7.E-04	76.7E-08	24
Toluene	2E-04	6.4E03	-23E-04	723.E-08	230
Styrene	2E-04	6.4E03	-2E-04	9.12E-08	3
naphthalene	2E-04	6.4E03	-15E-04	318.E-08	100
xylenes	2E-04	6.4E03	-16E-04	360.E-08	110

5.3 Determination of Best Kinetic Model Via BIOSCREEN

BIOSCREEN was run for each COC at each site to determine whether first-order kinetics or the instantaneous reaction model more closely predict conditions at the sites. The following tables summarize the results. An example of the BIOSCREEN input and output plots is shown in Figures 5.1 and 5.2.

Table 5.3 (a) Egg Harbor

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X		X	<ul style="list-style-type: none"> The benzene field data more closely match the no degradation line than the first order kinetics line Benzene continues to be detected over 600 feet from the source—the instantaneous reaction model shows no detects for that COC
Naphthalene	X		X	<ul style="list-style-type: none"> The naphthalene field data are generally located between the no degradation line and the first order kinetics line Naphthalene continues to be detected over 600 feet from the source—the instantaneous reaction model shows no detects for that COC
Toluene	X			<ul style="list-style-type: none"> The toluene field data more closely match the first order kinetics line than the no degradation line Toluene continues to be detected over 600 feet from the source—the instantaneous reaction model shows no detects for that COC
Xylenes	X		X	<ul style="list-style-type: none"> The xylenes field data are generally between the no degradation line and the first order kinetics line Xylenes continue to be detected over 600 feet from the source—the instantaneous reaction model shows no detects for those COCs

Table 5.3 (b) Hammonton

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X		X	<ul style="list-style-type: none"> The benzene field data more closely match the no degradation line than the first order kinetics line Benzene continues to be detected over 750 feet from the source—the instantaneous reaction model shows no detects for that COC beyond 500 feet
Naphthalene		X	X	<ul style="list-style-type: none"> The naphthalene field data more closely match the no degradation line than the instantaneous reaction model line Naphthalene continues to be detected over 750 feet from the source—the first order reaction model shows no detects for that COC beyond about 250 feet
Styrene			X	<ul style="list-style-type: none"> The styrene field data more closely match the no degradation line than either the first order kinetics or the instantaneous reaction model line

**Table 5.3 (c) Glassboro
North Plume**

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X		X	<ul style="list-style-type: none"> The benzene field data more closely matches the no degradation line than the first order kinetic line The no degradation line showed detections beyond 2000 feet in comparison to the first order model, which shows no detections after 500 feet from the source.
Ethylbenzene	X			<ul style="list-style-type: none"> The Ethylbenzene field data more closely matches the first order kinetic line than the no degradation line.
Naphthalene	X		X	<ul style="list-style-type: none"> The naphthalene field data more closely matches both the no degradation line and the first order kinetic line. The decay slope of both models matches that of the field data, but lags approximately 500 feet behind.
Toluene		X		<ul style="list-style-type: none"> The toluene field data more closely matches the instantaneous model line than either the first order kinetic line or the no degradation line.
Xylenes		X		<ul style="list-style-type: none"> The xylenes field data more closely matches the instantaneous model line than either the first order kinetic line or the no degradation line.

South Plume

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X			<ul style="list-style-type: none"> The benzene field data more closely matches the first order kinetics model line than either the instantaneous model or the no degradation line. The decay slope of the field data matches that of the first order kinetics model.
Xylenes	X			<ul style="list-style-type: none"> The total xylenes field data more closely matches the first order kinetics model line than either the instantaneous model or the no degradation line. The first order kinetics model shows dramatic decrease in concentrations that better match the field data. The no degradation and instantaneous model show concentrations orders of magnitude greater than field data.

Table 5.3 (d) Florida Avenue

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene		X		<ul style="list-style-type: none"> The benzene field data matches the first order and instantaneous reaction models almost identically. The instantaneous model is slightly more conservative and therefore is chosen to model the data.

Table 5.3 (e) Bridgeton

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X			<ul style="list-style-type: none"> The benzene field data more closely match the first order degradation model than the instantaneous reaction model. The instantaneous reaction model indicates complete degradation of the COC, which is inconsistent with known site conditions.

Table 5.3 (f) Salem

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X			<ul style="list-style-type: none"> The benzene field data more closely matches the first order kinetic line than the instantaneous reaction line
Toluene	X			<ul style="list-style-type: none"> The toluene field data more closely matches the first order kinetic line than the instantaneous reaction line. The no degradation shows significant concentrations beyond 200 feet from the source.
Xylene	X			<ul style="list-style-type: none"> The xylene field data more closely matches both the first order kinetic line. The no degradation line shows concentrations extending 200 feet beyond the source when in fact the field data indicate xylene concentrations do not exist much past the source area.
Naphthalene	X			<ul style="list-style-type: none"> The naphthalene field data more closely matches the first order kinetic line.

**Table 5.3 (g) Pleasantville
North Plume**

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Ethylbenzene	X			<ul style="list-style-type: none"> The Ethylbenzene field data match the first order degradation model more accurately than the instantaneous reaction model. The instantaneous model indicates Ethylbenzene will persist beyond 900 feet from the source, which is not consistent with present site conditions.
Naphthalene	X			<ul style="list-style-type: none"> The naphthalene field data match the first order degradation model more accurately than the instantaneous model. The instantaneous model indicates naphthalene will persist beyond 900 feet from the source, which is not consistent with present site conditions.
Styrene	X			<ul style="list-style-type: none"> The styrene field data match the first order degradation model more accurately than the instantaneous model.
Xylenes	X			<ul style="list-style-type: none"> The xylenes field data match the first order degradation model more accurately than the instantaneous model. The instantaneous model indicates xylenes will persist beyond 900 feet from the source, which is not consistent with present site conditions.

South Plume

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X			<ul style="list-style-type: none"> The benzene field data match the first order degradation model more accurately than the instantaneous reaction model. The instantaneous model indicates benzene will persist beyond 800 feet from the source, which is inconsistent with present site conditions.
Ethylbenzene	X			<ul style="list-style-type: none"> The Ethylbenzene field data match the first order degradation model more accurately than the instantaneous reaction model.
Naphthalene	X			<ul style="list-style-type: none"> The naphthalene field data match the first order degradation model more accurately than the instantaneous reaction model.

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Xylenes	X			<ul style="list-style-type: none"> The total xylenes field data match the first order degradation model more accurately than the instantaneous reaction model. The instantaneous model indicates xylenes will persist beyond 800 feet from the source, which is inconsistent with present site conditions.

Table 5.3 (h) Millville

COC	KINETIC MODEL			REMARKS
	First Order Kinetics	Instantaneous Reaction	No Degradation	
Benzene	X			<ul style="list-style-type: none"> The benzene field concentration data match the first order degradation model more accurately than the instantaneous reaction model (which predicts benzene will persist at concentrations much higher than field data indicate).
Toluene	X			<ul style="list-style-type: none"> The toluene field concentration data match the first order degradation model more accurately than the instantaneous reaction model (which predicts toluene will persist at concentrations much higher than field data indicate).
Naphthalene	X			<ul style="list-style-type: none"> The naphthalene field concentration data match the first order degradation model more accurately than the instantaneous reaction model (which predicts naphthalene concentrations will increase as the plume migrates farther from the source, contrary to field data).
Styrene	X			<ul style="list-style-type: none"> The styrene field concentration data match the first order degradation model more accurately than the instantaneous reaction model (which predicts styrene will persist at concentrations much higher than field data indicate).
Xylenes	X			<ul style="list-style-type: none"> The total xylenes field concentration data match the first order degradation model more accurately than the instantaneous reaction model (which predicts that xylenes will persist at concentrations much higher than field data indicate).

5.4 Estimation of Expressed Assimilative Capacity

5.4.1 Interpretation of Contaminant and Terminal Electron Acceptor Isopleths

In order to gain an understanding of the qualitative relationships prior to performing any quantitative analyses, it is important to examine contaminant isopleth maps and terminal electron acceptor (TEA) isopleth maps and overlay the data to look for trends. Although most of these isopleth maps were developed in conjunction with the RIs, the interpretations provided herein were performed exclusively for the purpose of this dissertation.

Isopleths were not developed based on strict linear data interpolations due to a variety of problems with the data sets (*e.g.*, paucity of data, apparent contradictions, lack of control points, *etc.*). Instead, the data were evaluated in the context of the natural attenuation processes presumably occurring at the site, and the contours were developed based on current understanding of contaminant biogeochemistry as well as linear interpolation. In certain instances, this required ignoring selected monitoring well data so that the figures showed a more cohesive overall spatial distribution of contaminants and electron acceptors.

Egg Harbor

DO

To develop the DO isopleths (for all sites), concentration data that did not fall within the typical range of about 0 to 8 milligrams per liter (mg/L) were ignored, as were anomalous data, such as widely varying concentrations for samples collected from two nearby monitoring wells. DO isopleth for the Egg Harbor site generally shows a decreasing trend toward the plume centerline. DO concentrations also generally decrease with increasing

distance from the COC source area. The spatial distribution of the DO data suggests that contaminants are undergoing biological degradation by aerobic respiration around the fringe of the plume. However, DO levels are too low within the core of the plume to support aerobic respiration.

Nitrate

A similar approach to the DO data was used for the nitrate data at all sites; anomalous nitrate data were ignored. Nitrate contours at the Egg Harbor site were generally similar to those for DO (i.e. concentrations decrease toward the plume centerline and were lower in the source area). The spatial distribution of the nitrate data suggests that COCs are also undergoing biological degradation by nitrate reduction.

Fe²⁺

The soluble iron (Fe⁺²) data across the site were highly variable, and as a result an isopleth was not developed.

Sulfate

Sulfate contours indicated that centerline concentrations were generally greater than those in background areas. However, because of the nature of the MGP processes and the raw materials utilized, dissolved sulfate is a common constituent of MGP related plumes. Therefore, it is possible that plume chemistry (related to the sulfate source) might be masking the typical visual patterns of sulfate reduction (i.e., the sulfate source strength may be significantly higher than just background).

Methane

The methane data across the site were highly variable, and as a result an isopleth was not developed.

Hammonton

DO

The DO isopleth generally shows a decreasing trend toward the plume centerline. The spatial distribution of the DO data suggests that contaminants are undergoing biological degradation by aerobic respiration in and around the plume fringe.

Nitrate

Nitrate contours were generally similar to those for DO (i.e. concentrations decrease toward the plume centerline and were lower in the source area). The spatial distribution of the nitrate data suggests that contaminants are undergoing biological degradation by nitrate reduction.

Fe²⁺

The soluble iron (Fe²⁺) data across the site were highly variable, and as a result an isopleth was not developed. However, it is possible that this pathway may be important for plume locations where oxidized iron is present because biological degradation has apparently proceeded to sulfate reduction.

Sulfate

Sulfate contours were generally similar to those for DO and nitrate (i.e. concentrations were lower in the source area). The spatial distribution of the sulfate data suggests that contaminants are undergoing biological degradation by sulfate reduction.

Methane

Methane data were not available for this site.

Oxidation Reduction Potential (ORP)

The distribution of the ORP data generally shows a decreasing trend (*i.e.*, progressively becoming chemically reducing) toward the plume source. The spatial distribution of these data indicates that conditions within the contaminant plume source area are more chemically reducing than within background areas.

Glassboro

DO

The DO isopleth generally shows a decreasing trend toward the plume centerline. The spatial distribution of the DO data suggests that contaminants are undergoing biological degradation by aerobic respiration in around the plume fringe.

Nitrate

Nitrate data were sparse and nitrate concentrations were not detected above the analytical practical quantification limit (PQL) for groundwater samples collected from many of the monitoring well locations. Therefore, the nitrate data were not contoured. However, given the fact that nitrate concentrations along the plume centerline were not detected above the PQL, whereas background concentrations were detected (albeit at low levels), suggests that nitrate reduction may be occurring and depleting that TEA.

Fe²⁺

The soluble iron (Fe²⁺) data across the site were highly variable, and as a result an isopleth was not developed. However, it is possible that this pathway may be important

for plume locations where oxidized iron is present because biological degradation has apparently proceeded to sulfate reduction.

Sulfate

Sulfate isopleths indicate that centerline concentrations were lower than those in background areas. The spatial distribution of the sulfate data indicates sulfate reduction may be a viable pathway for COC biodegradation.

Methane

Methane data were not available for this site.

Florida Avenue

DO

DO trends show *increasing* concentrations toward the source area, which makes the data highly suspect, particularly since the iron and sulfate data are consistent with anaerobic groundwater conditions.

Nitrate

Nitrate was not detected above its analytical practical quantification limit (PQL) at any monitoring well location.

Fe²⁺

Dissolved iron (Fe²⁺) concentrations increased toward the plume centerline, which is consistent with biological degradation via iron (III) reduction.

Sulfate

Due to the paucity of detectable sulfate concentrations, isopleths depicting a specific trend for this reduction pathway could not be generated. Sulfate was only detected at five of thirteen locations within the plume. However, the absence of detectable sulfate,

despite the fact it is commonly found in MGP plumes, suggests that sulfate reduction has been occurring at this site.

Methane

Methane data were not available for this site.

Alkalinity

Isopleths indicated alkalinity increased toward the plume centerline, which is consistent with the mineralization of BTEX compounds by biological degradation pathways.

Bridgeton

DO

The DO isopleth generally shows a decreasing trend toward the plume centerline. The spatial distribution of the DO data suggests that contaminants are undergoing biological degradation by aerobic respiration.

Nitrate

Nitrate contours were generally similar to those for DO (i.e. concentrations decreased toward the plume centerline and were lowest in the source area). The spatial distribution of the nitrate data suggests that contaminants are undergoing biological degradation by nitrate reduction.

Fe²⁺

Fe²⁺ contours indicated that centerline concentrations were generally greater than those in background areas. The spatial distribution of the Fe²⁺ data suggests that contaminants are undergoing biological degradation by iron reduction.

Sulfate

The sulfate data across the site were highly variable, and as a result an isopleth was not developed.

Methane

Methane contours indicated that concentrations were generally greater outside and downgradient of the source area. Therefore, the spatial distribution of methane is not consistent with biological degradation by methanogenesis, possibly because biological biodegradation has not proceeded beyond sulfate reduction.

Salem***DO***

The DO isopleth generally shows a decreasing trend toward the plume source area. The spatial distribution of the DO data suggests that COCs are undergoing biological degradation by aerobic respiration.

Nitrate, Fe²⁺, Sulfate

These data were highly variable across the site, and as a result isopleths were not developed.

Methane

Methane samples were not collected at the Salem site.

ORP

The distribution of the ORP data generally shows a decreasing trend (*i.e.*, progressively becoming chemically reducing) toward the plume source. The spatial distribution of these data indicates that conditions within the contaminant plume source area are more chemically reducing than within background areas, suggesting that the COC plume is

undergoing biological degradation, which is scavenging terminal electron acceptors (TEAs) and shifting conditions from chemically oxidizing towards chemically reducing.

Pleasantville

DO

A DO isopleth was not developed. Only six data points were available with values between 0 and 8 mg/L. Therefore, it is difficult to ascertain the relative importance of aerobic respiration as a natural attenuation mechanism for the site.

Nitrate

A nitrate isopleth was not developed because of a lack of available data. Therefore, it is difficult to ascertain the relative importance of nitrate reduction as a natural attenuation mechanism for the site. However, nitrate reduction may be occurring at locations where nitrate is present because of evidence for iron (III) and sulfate reduction (see below).

Fe²⁺

The distribution of Fe²⁺ data indicates higher concentrations of iron (II) within both plume source areas, as well as along the plume centerline directly downgradient of each source. Therefore, it appears that iron (III) reduction is occurring at this site.

Sulfate

The distribution of sulfate data indicates lower concentrations of sulfate within both plume source areas. Therefore, it appears that sulfate reduction is an important natural attenuation pathway at this site.

Methane

The distribution of methane data indicates higher methane concentrations within both plume source areas as well as along the plume centerline directly downgradient of each

source. Therefore, it appears that methanogenesis is an important natural attenuation pathway at this site.

Alkalinity

Isopleths indicated alkalinity concentrations increasing toward the plume source areas as well as along the plume centerline. Increasing concentrations may suggest the mineralization of BTEX compounds by biological degradation pathways.

Millville

DO

The DO isopleth generally shows a decreasing DO concentration toward the plume centerline. The spatial distribution of the DO data suggests that COCs are undergoing biological degradation by aerobic respiration.

Nitrate

Nitrate concentration contours were generally similar to those for DO (i.e. concentrations decreased toward the plume centerline and were lower in the source area). The spatial distribution of the nitrate concentration data suggests that COCs are undergoing biological degradation by nitrate reduction.

Fe²⁺

Iron (II) data were highly variable across the site, and as a result an isopleth was not developed.

Sulfate

A sulfate isopleth was not developed, since sulfate concentrations were greater within the plume than without. However, it is possible that plume chemistry, related to the sulfate source, might be masking sulfate reduction. Sulfate concentrations were compared to a

conservative tracer (total dissolved solids) that would primarily be affected by advection processes in groundwater. Sulfate concentrations decreased downgradient at a greater rate than the conservative tracer. This may be explained by sulfate reduction.

Methane

These data were highly variable across the site, and as a result a methane isopleth was not developed.

Alkalinity

Isopleths indicated alkalinity concentrations increasing toward the plume centerline. Increasing concentrations suggest the mineralization of BTEX compounds by biological degradation pathways.

5.4.2 Calculations of Expressed Assimilative Capacity

The approach presented by Wiedemeier et al. (1995) was used to calculate the assimilative capacity at each MGP site. The expressed assimilative capacity allows for the evaluation of the groundwater system's ability to naturally attenuate the COCs at each site. Information gleaned during qualitative analysis of the isopleth maps were used to crosscheck these calculations. The following tables present these results.

Table 5.4 (a) Egg Harbor

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
dissolved oxygen	0.32	1,050	336
nitrate	0.21	630	132
iron	0.046	2,040	94
sulfate	0.21	6,300	1,320
methanogenesis	1.29	65.4	84
Total Expressed Assimilative Capacity			1,970
Mean Observed Total COC Concentration along Plume Centerline			6,290

Table 5.4 (b) Hammonton

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
dissolved oxygen	0.32	1,080	346
nitrate	0.21	1,110	233
iron	0.046	1,880	86
sulfate	0.21	6,300	1,320
Total Expressed Assimilative Capacity			1,990
Mean Observed Total COC Concentration along Plume Centerline			5,530

**Table 5.4 (c) Glassboro
North Plume**

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
dissolved oxygen	0.32	1,350	432
iron	0.046	5,250	242
sulfate	0.21	60,900	12,800
Total Expressed Assimilative Capacity			13,500
Mean Observed Total COC Concentration along Plume Centerline			7,580

South Plume

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
dissolved oxygen	0.32	1,350	432
iron	0.046	950	44
sulfate	0.21	1,240	260
Total Expressed Assimilative Capacity			736
Mean Observed Total COC Concentration along Plume Centerline			2,120

Table 5.4 (d) Florida Avenue

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
sulfate	0.21	130	27
Total Expressed Assimilative Capacity			27
Mean Observed Total COC Concentration along Plume Centerline			600

Table 5.4 (e) Bridgeton

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
dissolved oxygen	0.32	930	298
nitrate	0.21	630	132
iron	0.046	19,400	892
Total Expressed Assimilative Capacity			1,320
Mean Observed Total COC Concentration along Plume Centerline			1,130

Table 5.4 (f) Salem

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product ($\mu\text{g/L}$)	expressed COC assimilative capacity ($\mu\text{g/L}$)
dissolved oxygen	0.32	5,300	1,700
nitrate	0.21	980	206
iron	0.046	30,000	1,380
sulfate	0.21	1,010	212
Total Expressed Assimilative Capacity			3,500
Mean Observed Total COC Concentration along Plume Centerline			3,460

**Table 5.4 (g) Pleasantville
North Plume**

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product (ug/L)	expressed COC assimilative capacity (ug/L)
nitrate	0.21	1,460	307
iron	0.046	490	23
methanogenesis	1.29	522	632
Total Expressed Assimilative Capacity			962
Mean Observed Total COC Concentration along Plume Centerline			3,100

South Plume

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product (ug/L)	expressed COC assimilative capacity (ug/L)
nitrate	0.21	530	111
iron	0.046	9,300	428
sulfate	0.21	2,200	462
methanogenesis	1.29	762	983
Total Expressed Assimilative Capacity			1,980
Mean Observed Total COC Concentration along Plume Centerline			3,100

Table 5.4 (h) Millville

TEA or degradation process	mean mass ratio COC / electron acceptor or product	mean concentration of electron acceptor or product (ug/L)	expressed COC assimilative capacity (ug/L)
dissolved oxygen	0.32	423	135
nitrate	0.21	548	115
iron	0.046	4,770	219
sulfate	0.21	1,020	214
methanogenesis	1.29	38	49
Total Expressed Assimilative Capacity			732
Mean Observed Total COC Concentration along Plume Centerline			1,910

5.5 Laboratory Microcosm Data

The objective of the third line of evidence, laboratory microcosm studies, was to examine the ability of the indigenous organisms at the Glassboro site and the Florida Avenue site to degrade representative MGP constituents (benzene, toluene and naphthalene) under

nitrate reducing, iron-reducing and sulfate-reducing conditions. From these microcosm data, first-order degradation rate constants were calculated for benzene, toluene and naphthalene, as summarized below. Unfortunately, much of the microcosm data were unusable. There was often considerable variation between runs, and in some cases, the lack of a consistent sterile control. Those runs in which the sterile control varied as much as the non-sterile replicates were discarded. Results are also shown in Figures 5.3 – 5.6.

Table 5.5 Naphthalene/Iron (Glassboro, Round 2) Results

	Microcosm 2	Microcosm 3	Sterile Control
Days	mg/L	mg/L	mg/L
0	8.86	5.76	9.25
14	3.19	4.55	2.17
28	9.00	11.9	11.2
42	6.80	11.4	19.8
70	not detected	1.00	9.20
98	not detected	not detected	5.00
First-Order Rate Constant (yr⁻¹)	29.1	48.8	5.48

Table 5.6 Naphthalene/Sulfate (Glassboro, Round 1) Results

	Microcosm 1	Sterile Control
Days	mg/L	Mg/L
0	58.7	15.0
8	4.76	10.4
18	0.800	12.9
24	0.312	14.9
40	0.055	3.06
First-Order Rate Constant (yr⁻¹)	62.6	12.4

Table 5.8 Benzene/Naphthalene/Sulfate (Florida Ave, Round 1) Results

days	Microcosm 1		Microcosm 2		Sterile Control	
	benzene (mg/L)	naphthalene (mg/L)	benzene (mg/L)	naphthalene (mg/L)	benzene (mg/L)	naphthalene (mg/L)
0	12.8	20.4	13.4	21.5	14.2	15.3
8	8.08	10.5	8.23	12.0	13.1	20.8
18	6.62	10.5	5.23	9.23	9.58	13.8
24	3.87	7.76	2.33	2.78	11.2	18.3
40	2.87	7.76	1.63	1.77	7.01	12.0
First-Order Rate Constant (yr⁻¹)	13.7	7.92	20.1	23.8	6.39	0.292

BIOSCREEN Natural Attenuation Decision Support System
 Air Force Center for Environmental Excellence

Pleasantville MGP
 Version 1.4 1 Year Timesheet
 Run Name

Data Input Instructions:
 1. Enter value directly... or
 2. Calculate by filling in grey cells below. (To restore formulas, hit button below.)
 Variable* Data used directly in model.
 Value calculated by model. (Don't enter any data.)

1. HYDROGEOLOGY
 Seepage Velocity* Vs 86.0 (ft/yr)
 or
 Hydraulic Conductivity K 2.9E-03 (cm/sec)
 Hydraulic Gradient i 0.0002 (ft/ft)
 Porosity n 0.2 (-)

2. DISPERSION
 Longitudinal Dispersivity* alpha x 22.2 (ft)
 Transverse Dispersivity* alpha y 2.2 (ft)
 Vertical Dispersivity* alpha z 0.0 (ft)
 or
 Estimated Plume Length Lp 800 (ft)

3. ADSORPTION
 Retardation Factor* R 1.8 (-)
 or
 Soil Bulk Density rho 1.8 (kg/l)
 Partition Coefficient Koc 83 (L/kg)
 Fraction Organic Carbon foc 1.0E-3 (-)

4. BIODEGRADATION
 1st Order Decay Coeff* lambda 6.7E+1 (per yr)
 or
 Solute Half-Life t-half 0.15 (year)
 or Instantaneous Reaction Model
 Delta Oxygen* DO 0 (mg/L)
 Delta Nitrate* NO3 0.53 (mg/L)
 Observed Ferrous Iron* Fe2+ 9.3 (mg/L)
 Delta Sulfate* SO4 2.205 (mg/L)
 Observed Methane* CH4 0.98 (mg/L)

5. GENERAL
 Modeled Area Length* 800 (ft)
 Modeled Area Width* 225 (ft)
 Simulation Time* 81 (yr)

6. SOURCE DATA
 Source Thickness in Sect. Zone* 25 (ft)
 Source Zones:
 Width* (ft) Conc. (mg/L)*
 20 0.764
 20 1.27
 80 2.81
 20 1.27
 20 0.764
 Source Hdlife (see Help):
 90 200 (yr)
 Inst. React. 1st Order
 Soluble Mass 1000 (Kg)
 In Source NAPL, Soil

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3

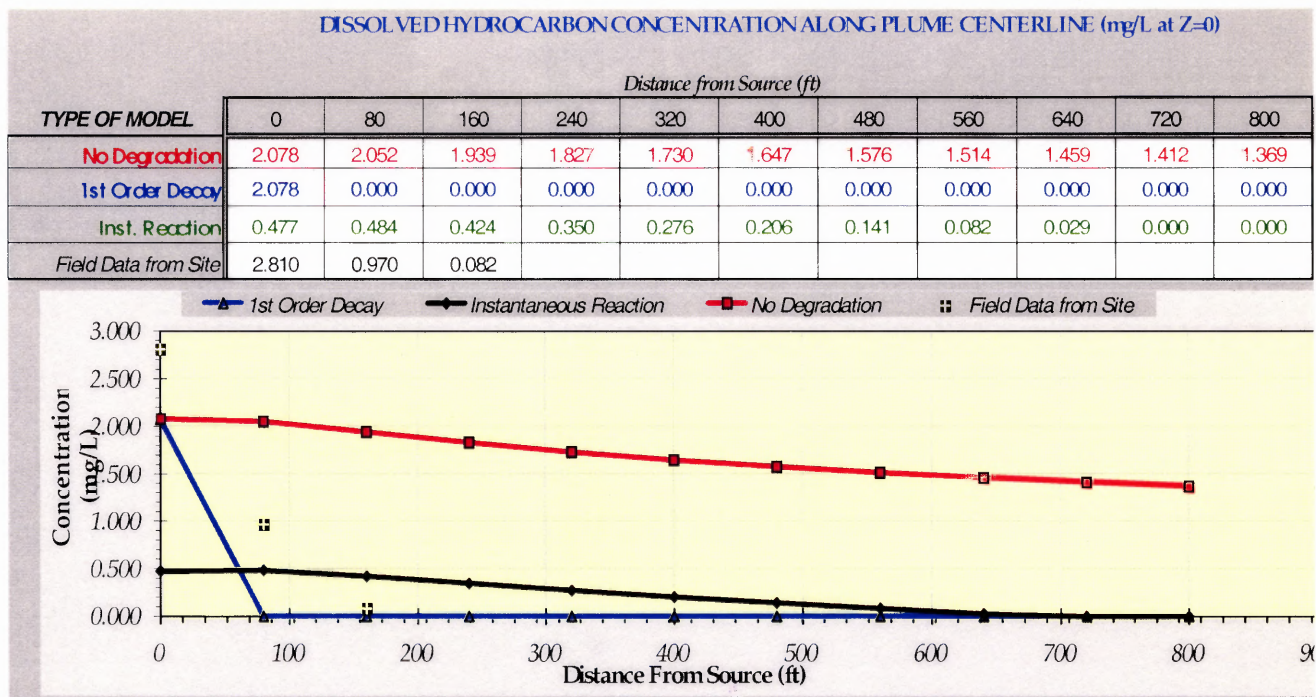
View of Plume Looking Down

Observed Centerline Concentrations at Monitoring Wells
 If No Data Leave Blank or Enter "0"

7. FIELD DATA FOR COMPARISON
 Concentration (mg/L) 2.81 .97 .082
 Dist. from Source (ft) 0 100 500 1000 2000 2080 2160 2240 2320 2400 2480

8. CHOOSE TYPE OF OUTPUT TO SEE:
 RUN CENTERLINE View Output
 RUN ARRAY View Output
 Help Recalculate This Sheet
 Paste Example Dataset
 Restore Formulas for Vs, Dispersivities, R, lambda, other

Figure 5.1 BIOSCREEN Input Sheet



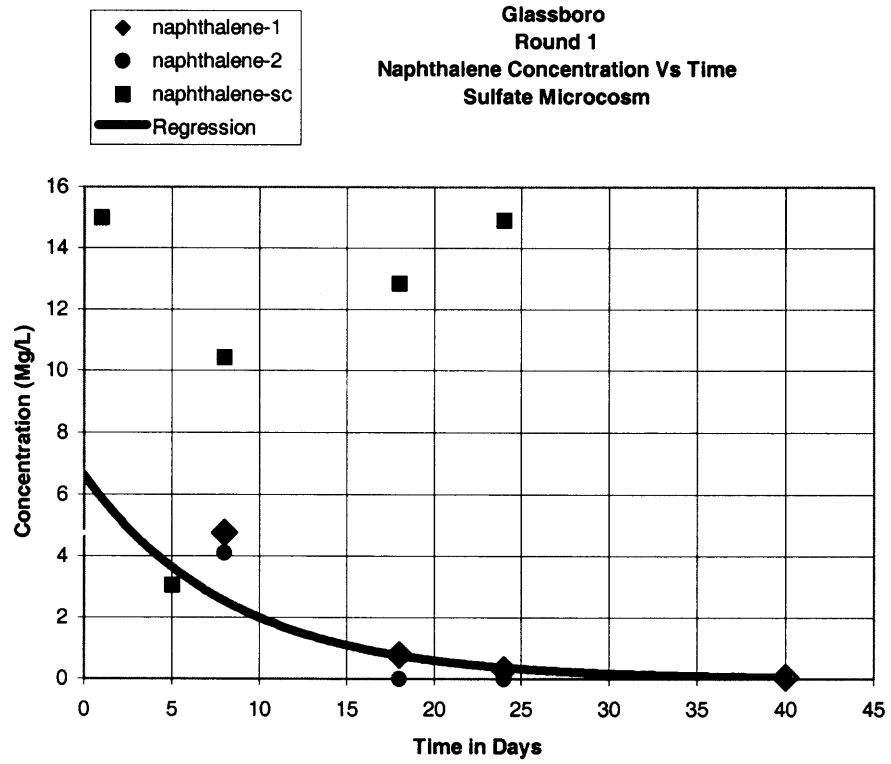


Figure 5.3 Sulfate Microcosm Data depicting Naphthalene Concentration vs. Time at Glassboro

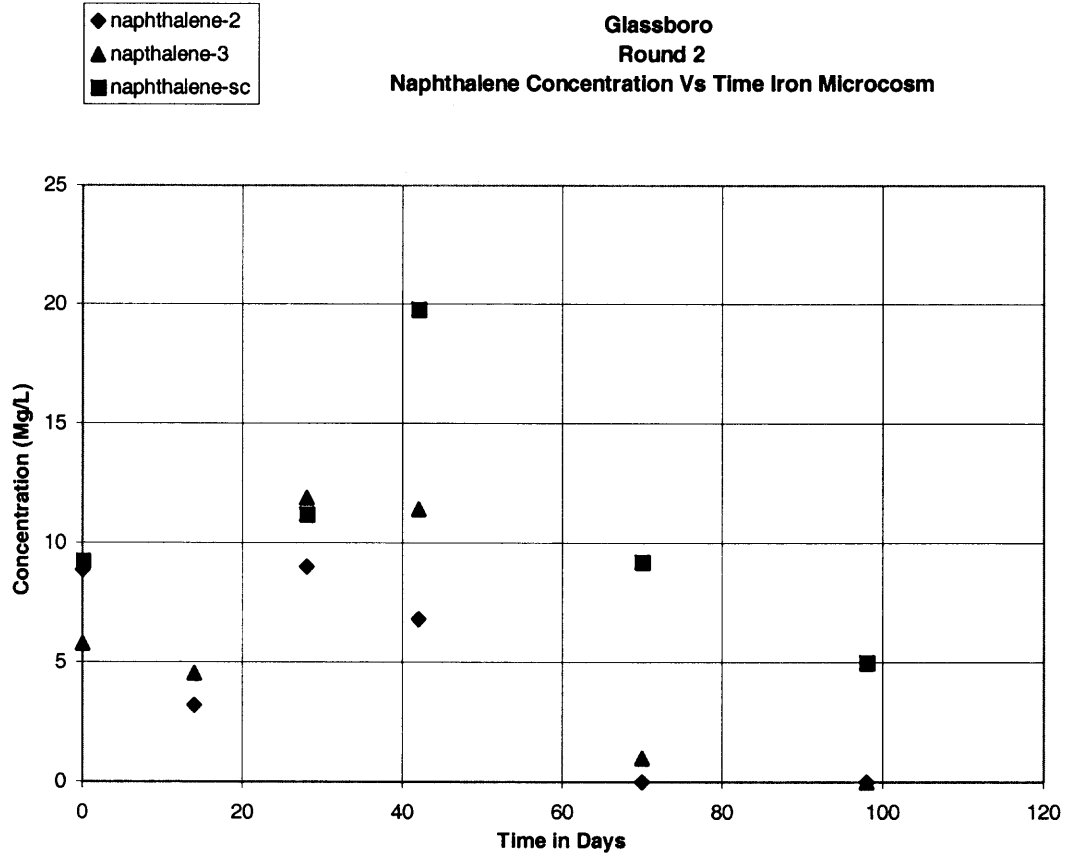


Figure 5.4 Iron Microcosm Data depicting Naphthalene Concentration vs. Time at Glassboro

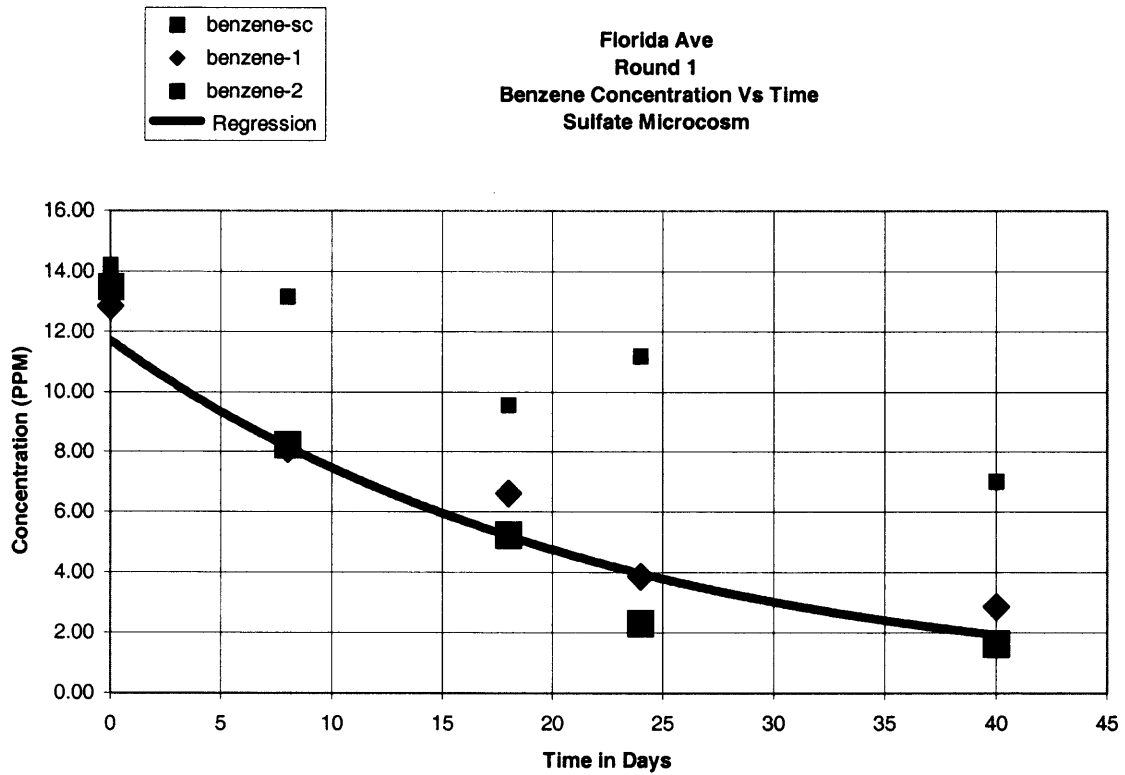


Figure 5.5 Sulfate Microcosm Data depicting Naphthalene Concentration vs Time at Florida Ave

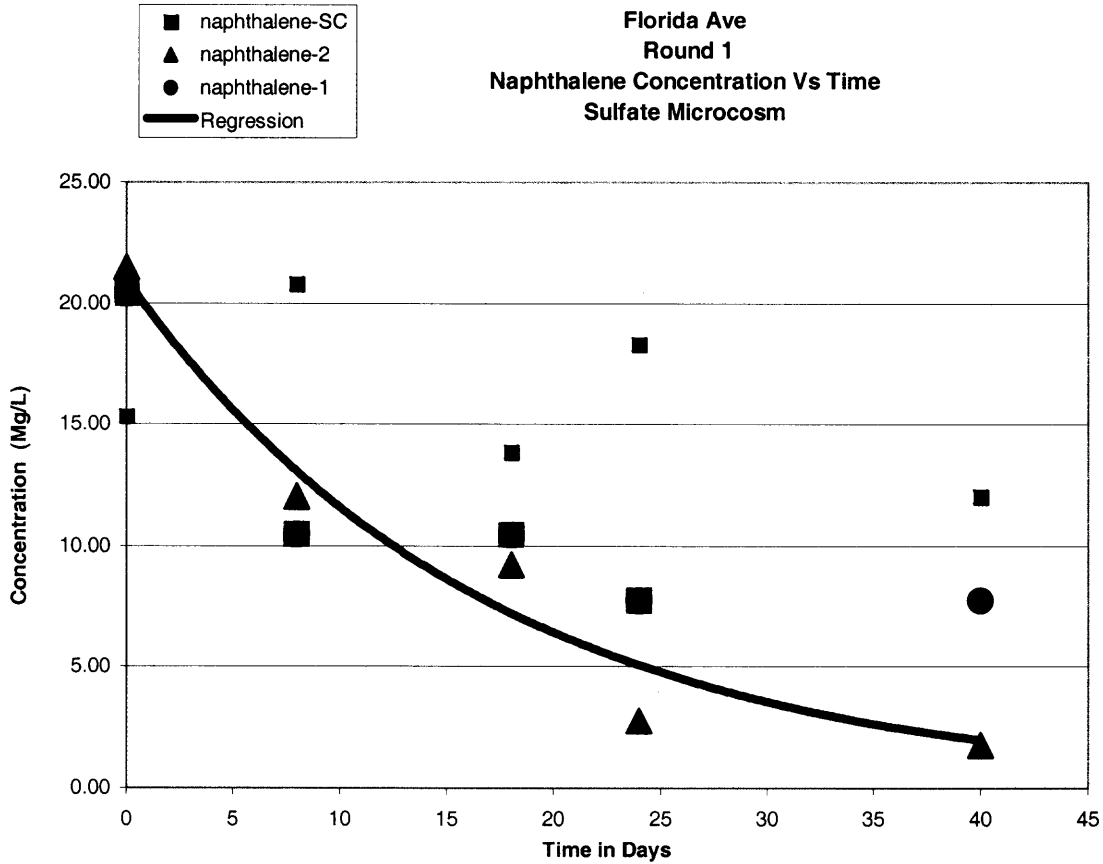


Figure 5.6 Sulfate Microcosm Data Naphthalene Concentration vs. Time at Florida Ave

CHAPTER 6

DISCUSSION

6.1 First-Order Rate Constants via Buscheck and Alcantar

Table 6.1 summarizes the first-order rate constants at the 8 MGP sites calculated via the Buscheck-Alcantar method, and compares the order-of-magnitude (OM) with the range of published values for the same contaminants at U.S. fuel sites (see Table 2.1). For the most part, the calculated values are within an order-of-magnitude of the published values.

Table 6.1 Calculated and Published First-Order Rate Constants (yr^{-1})

site	contaminant	Calculated k (yr^{-1})	published k (yr^{-1})	comparison
Egg Harbor	benzene	13	2.56 to 15.7	same OM
	naphthalene	27	2.19 to 4.38	+ 1
	toluene	140	8.40 to 14.2	+ 1
	xylenes	59	2.19 to 10.6	+ 1
Hammonton	benzene	3	2.56 to 15.7	--
	naphthalene	6	2.19 to 4.38	--
Glassboro North	benzene	0.6	2.56 to 15.7	- 1
	ethylbenzene	0.2	3.29 to 10.6	- 1
	naphthalene	0.8	2.19 to 4.38	--
	toluene	0.1	8.40 to 14.2	- 2
	xylenes	0.2	2.19 to 10.6	- 1
Glassboro South	benzene	0.1	2.56 to 15.7	- 2
	xylenes	0.3	2.19 to 10.6	- 1
Florida Avenue	benzene	27	2.56 to 15.7	--
Bridgeton	benzene	67	2.56 to 15.7	+ 1
Salem	benzene	1800	2.56 to 15.7	+ 2
	naphthalene	1900	2.19 to 4.38	+ 2
	toluene	1800	8.40 to 14.2	+ 2
	xylenes	2100	2.19 to 10.6	+ 2
Pleasantville North	ethylbenzene	30	3.29 to 10.6	--
	naphthalene	23	2.19 to 4.38	+ 1
	styrene	420	5.84	+ 2
	xylenes	100	2.19 to 10.6	+ 1
Pleasantville South	benzene	99	2.56 to 15.7	+ 1
	ethylbenzene	29	3.29 to 10.6	--
	naphthalene	25	2.19 to 4.38	+ 1
	xylenes	32	2.19 to 10.6	+ 1
Millville	benzene	24	2.56 to 15.7	--
	naphthalene	230	2.19 to 4.38	+ 2
	toluene	3	8.40 to 14.2	--
	styrene	100	5.84	+ 1
	xylenes	110	2.19 to 10.6	+ 1

6.2 BIOSCREEN Results

Table 6.2 Summary of BIOSCREEN Results

SITE	COC	KINETIC MODEL		
		First-Order Kinetics	Instant Reaction Model	No Degradation
Egg Harbor	Benzene	X		X
	Naphthalene	X		X
	Toluene	X		
	Xylenes	X		X
Hammonton	Benzene	X		X
	Naphthalene		X	X
	Styrene			X
Glassboro North Plume	Benzene	X		X
	Ethylbenzene	X		
	Naphthalene	X		X
	Toluene		X	
	Xylenes		X	
Glassboro South Plume	Benzene	X		
	Xylenes	X		
Florida Ave	Benzene		X	
Bridgeton	Benzene	X		
Salem	Benzene	X		
	Toluene	X		
	Xylene	X		
	Naphthalene	X		
Pleasantville North Plume	Ethylbenzene	X		
	Naphthalene	X		
	Styrene	X		
	Xylenes	X		
Pleasantville South Plume	Benzene	X		
	Ethylbenzene	X		
	Naphthalene	X		
	Xylenes	X		
Millville	Benzene	X		
	Ethylbenzene	X		
	Naphthalene	X		
	Xylenes	X		
	Toluene	X		
	Styrene	X		

* +1 signifies that calculated rate constant is about 1 order of magnitude greater than the published value.

Most of the compounds at most of the sites resembled first-order kinetics. The exceptions (where compound degradation more closely resembled instantaneous

reactions) are for naphthalene at Hammonton, toluene and xylenes at Glassboro (north plume), and benzene at Florida Ave.

6.1 Isopleths

6.1.1 Egg Harbor

DO and nitrate trends both show decreasing concentrations along the plume centerline, suggesting both pathways are likely being utilized in COC biological degradation. Aerobic respiration appears dominant along the plume periphery and leading edge, and nitrate reduction appears dominant within the core of the plume. These two processes appear to be the primary mechanisms driving biological degradation of site contaminants.

Sulfate concentrations were generally greater than those in background areas. However, because of the nature of the MGP processes and the raw materials utilized, dissolved sulfate is a common constituent of MGP related plumes. Therefore, it is possible that plume chemistry (related to the sulfate source) might be masking the typical visual patterns of sulfate reduction (*i.e.*, the sulfate source strength may be significantly higher than just background).

The soluble iron (Fe^{+2}) and methane data across the site were highly variable, and there were no clear patterns of biodegradation employing these pathways. Soil boring logs at the Egg Harbor site revealed yellow-brown to orange-brown layers, suggesting high iron content. In addition, the iron may be soluble in the groundwater due to the relatively low pH and anoxic conditions. However, no apparent trends can be discerned in the data to confirm iron reduction as an important natural attenuation process.

6.1.2 Hammonton

DO, nitrate, and sulfate concentrations are generally lower within the plume, relative to background levels, suggesting that these pathways are important for contaminant biodegradation. The data trend for Fe^{2+} was inconclusive.

6.1.3 Glassboro

DO and sulfate trends both show decreasing concentrations along the plume centerline, suggesting both pathways are likely being utilized in contaminant biodegradation. Aerobic respiration appears dominant along the plume periphery adjacent to the source area, and sulfate reduction appears dominant along the leading edge of the plume. It should be noted that for sulfate reduction to be important, nitrate and soluble Fe^{+3} concentrations must first have been depleted. RI data did not indicate the presence of iron in its oxidized form.

Methanogenesis is probably not occurring at the site. Sulfate concentrations are above detectable limits at all monitoring locations, indicating that this TEA has not been entirely depleted, a condition that must be met for methanogenesis to occur.

6.1.4 Florida Avenue

DO trends show *increasing* concentrations toward the source area, which makes the data highly suspect, particularly since the iron and sulfate data are consistent with anaerobic groundwater conditions.

Dissolved iron (Fe^{2+}) concentrations increased toward the plume centerline, which is consistent with biological degradation via iron (III) reduction.

Sulfate was only detected at five of thirteen locations within the plume. The absence of detectable sulfate, despite the fact it is commonly found in MGP plumes, suggests that sulfate reduction has been occurring at this site.

6.1.5 Bridgeton

DO and nitrate trends both show decreasing concentrations along the plume centerline, suggesting both pathways are likely being utilized in contaminant biodegradation. Fe^{+2} concentrations increase along the plume centerline, suggesting that biodegradation may also be occurring via iron reduction. Aerobic respiration and nitrate reduction appear dominant along the plume periphery and leading edge, while iron reduction appears to dominate within the core of the plume. Boring logs describe a portion of the site's stratigraphy as grayish orange, very fine to fine sand and silt, which would suggest the presence of significant oxidized iron (Fe^{+3}) within the formation.

Sulfate and methane concentrations were not consistent with biological degradation by either of these pathways. Since iron has not been depleted within the plume, this would normally preclude significant biodegradation via sulfate reduction or methane production.

6.1.6 Salem

DO concentrations decrease within the source area, suggesting that aerobic respiration is taking place. The iron and sulfate data were inconsistent. In addition, there is no mention of orange-brown staining within the soil profile, indicating limited presence of oxidized iron.

6.1.7 Pleasantville

DO and nitrate data were inconsistent, and as a result isopleths were not generated for these constituents. However, it is possible that both processes are being utilized at this site because there is strong evidence that both iron and sulfate reduction are occurring. Iron (II) concentrations increased within the north and south plumes, as well as along plume centerlines downgradient of the source. Sulfate concentrations were generally higher in background locations than within the source area. Methane concentrations increase toward the source area, suggesting that methanogenesis is occurring as well.

6.1.8 Millville

DO and nitrate concentrations both decrease along the plume centerline, suggesting both pathways are important biodegradation mechanisms. The nitrate pathway appears dominant within the source area, while DO appears dominant along the plume periphery and leading edge. Fe^{2+} concentrations were inconsistent, and isopleths were not developed.

Sulfate concentrations decrease more rapidly along the plume centerline, than a conservative tracer (TDS), which suggests that this pathway may also be utilized. Methanogenesis does not appear to be occurring at the site. Sulfate concentrations are above detectable limits at all monitoring locations, which would tend to preclude significant methanogenesis.

Table 6.3 Summary of Suggested Biodegradation Pathways Based on Field Data

Site	Plume		Unavailable Data
	Core	Periphery	
Egg Harbor	nitrate	aerobic	--
Hammonton	nitrate + sulfate	aerobic	methane
Glassboro	sulfate	aerobic	methane
Florida Ave.	sulfate	iron	methane
Bridgeton	nitrate + iron	aerobic	
Salem	?	aerobic	methane
Pleasantville	methanogenesis + sulfate	iron	--
Millville	nitrate	aerobic	--

6.3 Assimilative Capacities

The following table compares the calculated assimilative capacity to the mean contaminant concentration at each site in order to determine whether there is enough electron acceptor available to degrade the contaminant plumes.

Table 6.4 Summary of Assimilative Capacities

Site	Expressed Assimilative Capacity (a)	Mean COC Concentration (b)	(a) - (b)
Egg Harbor	1,970	6,290	- 4,320
Hammonton	1,990	5,530	- 3,540
Glassboro - North	13,500	7,580	+5,920
Glassboro - South	736	2,120	- 1,380
Florida Avenue	27	600	- 573
Bridgeton	1,320	1,130	+ 190
Salem	3,500	3,460	+ 40
Pleasantville - North	962	3,100	- 2,140
Pleasantville - South	1,980	3,100	- 1,120
Millville	732	1,910	- 1,180

Egg Harbor - The expressed assimilative capacity accounts for about a third of contaminant mass, which indicates that groundwater may take a long time to recover once source material is removed.

Hammonton - The expressed assimilative capacity also accounts for about a third of contaminant mass, which may also indicate why the plume extends for such a great distance.

Glassboro /North Plume - The expressed assimilative capacity is greater than the contaminant mass, which indicates that complete attenuation of the plume by natural processes may be attainable. However, the expressed assimilative capacity is skewed by the extremely high sulfate concentrations.

Glassboro /South Plume - The expressed assimilative capacity is less than the contaminant mass, which may be why contaminant concentrations are detected at distances much greater than those of the north plume.

Florida Ave - The expressed assimilative capacity accounts for five percent of the average contaminant mass. This plume is the largest of all those adjacent to a body of water (Bridgeton, Salem, Florida Ave.)

Bridgeton - The expressed assimilative capacity is approximately equal to the contaminant concentration, which may explain why the plume does not extend to the adjacent river.

Salem - The expressed assimilative capacity is approximately equal to the contaminant concentration, which may explain why the plume does not reach the river, despite the large contaminant mass on-site.

Pleasantville, North and South Plumes - The expressed assimilative capacities are much less than the contaminant concentration.

Millville - The expressed assimilative capacity is much less than the mean contaminant mass, which again may provide an explanation as to why the plume extends for such a great distance from the site.

6.4 Laboratory Microcosm Data

Table 6.5 presents the average first-order rate constants calculated from the laboratory microcosm data (corrected for the sterile control), and compares those values with field data at the Glassboro and Florida Ave. sites, and literature values for the same contaminants.

Table 6.5 Comparison of First-Order Rate Constants (yr^{-1})

		Microcosm	Buschek-Alcantar (field data)	Published (Table 2.1)
Glassboro	Naphthalene	39	0.7	2.2 to 4.4
Florida Ave.	Naphthalene	16	--	2.2 to 4.4
	Benzene	10	27	2.6 to 16

The microcosm rate constant for benzene is about the same order of magnitude as the value calculated from field data, and within the range of values reported in the literature at fuels sites. However, the microcosm rate constant for naphthalene is nearly two orders of magnitude greater than the value calculated from field data, and an order of magnitude greater than the range of values reported in the literature (albeit at a much more limited number of sites). This is consistent with the results of other investigators (Chiang et al., 1986; Rifai et al., 1995).

6.5 Application of AFCEE Protocol

Egg Harbor Site – The Egg Harbor site is located inland and the stratigraphy predominantly consists of fine to medium sands with occasional clay and silt lenses that are yellow to orange brown, indicating a high iron content. The highest contaminant concentrations are between 1,220 and 6,400, and the plume length is relatively long (1,700 ft). The mean observed COC concentration is higher than the expressed assimilative capacity. Aerobic respiration appears to be occurring at the plume fringe, with nitrate reduction occurring in the plume core. The best-fit kinetic model for all compounds is first-order decay, and the calculated field degradation rates are approximately an order of magnitude greater than the range of published values at fuel sites.

Hammonton - The Hammonton site is located inland and the stratigraphy predominantly consists of interbedded silty sands, sands and gravels and a clay layer around 6 feet bgs. The highest contaminant concentration is naphthalene at 5,620 ppb, and the plume length is relatively long (2,000 ft). The mean observed COC concentration is much greater than the expressed assimilative capacity. Aerobic respiration appears to be occurring at the plume fringe, with nitrate and sulfate reduction occurring in the plume core. The best-fit kinetic model for benzene is first-order decay, and for naphthalene is instantaneous reaction. The calculated field degradation rates are similar to published values at fuel sites.

Glassboro - The Glassboro site is located inland on a groundwater divide, with groundwater flowing in two directions from the site (to the north and to the south). The stratigraphy predominantly consists of well defined layers as follows from top to bottom:

yellowish-brown fine sand, brownish-yellow coarse to fine sand, fine sand, and a dark-gray clay and silt layer. The highest contaminant concentrations in the northern plume range from 1,400 to 9,900 ppb. The northern plume length is 2,600 ft, and the southern plume is 8,200 ft. The mean observed COC concentration is much less than the expressed assimilative capacity in the northern plume, but much greater than the expressed assimilative capacity in the southern plume. Aerobic respiration appears to be occurring at the plume fringe, with sulfate reduction occurring in the plume core. Sulfate reduction was also an important degradation mechanism in the microcosm studies for this site. The best-fit kinetic model for all compounds in both plumes is first-order decay, with the exception of toluene and xylene in the northern plume, which more closely resemble the instantaneous reaction. The calculated field degradation rates are about an order of magnitude less than those published at fuel sites, and up to two orders of magnitude less than the microcosm data from this site.

Florida Avenue - The Florida Avenue site is located adjacent to a body of salt water. The stratigraphy predominantly consists of two clay and peat layers at 14 feet bgs and 27 feet, with a layer of fine to medium sand in-between. The highest contaminant concentration is benzene at 2,900 ppb, and the plume length is 460 feet. The mean observed COC concentration is much greater than the expressed assimilative capacity. Sulfate reduction appears to be the dominant pathway, which is consistent with the microcosm studies. The best-fit kinetic model for benzene at this site is first-order decay, and the calculated field degradation rate is about the same order of magnitude as published values at fuels sites, and the microcosm data from this site.

Bridgeton - The Bridgeton site is located adjacent to a brackish river. The stratigraphy predominantly consists of grayish-orange fine to coarse sands with occasional silt; which may indicate a significant source of iron. The highest contaminant concentration at the site is benzene at 120 ppb, and the plume length is relatively short (112 ft). The mean observed COC concentration is approximately the same as the expressed assimilative capacity. Aerobic respiration appears to be occurring at the plume fringe, with nitrate and iron reduction occurring in the plume core. The best-fit kinetic model for benzene is first-order decay, and the calculated field degradation rate for benzene is about an order of magnitude greater than the published value at fuels sites.

Salem - The Salem site is located adjacent to a brackish river. The stratigraphy predominantly consists of interbedded peat and clay layers with silty fine sands. The highest contaminant concentrations at the site range from 1,300 to 7,400 ppb, and the plume length is relatively short (200 ft). The mean observed COC concentration is about the same as the expressed assimilative capacity. Aerobic respiration appears to be occurring at the plume fringe. The best-fit kinetic model for all compounds is first-order decay, and the calculated field degradation rates are about two orders of magnitude greater than those reported at fuel sites.

Pleasantville - The Pleasantville site is located inland. The stratigraphy predominantly consists of fine to coarse sands with occasional silt. The highest contaminant concentrations at the site are those for benzene and naphthalene. There are two plumes emanating from the site, one extending 900 feet to the north, and another extending 800 feet to the south. The mean observed COC concentrations are greater than the expressed assimilative capacity in both the north and the south plumes.

Methanogenesis seems to be an important pathway in both the north and the south plumes, with iron and sulfate reduction also occurring. The best-fit kinetic model for all COCs in both plumes is first-order decay, and the calculated field degradation rates are about an order of magnitude greater than those reported at fuel sites.

Millville - The Millville site is located inland. The geology primarily consists of fluvial, beach and marine deposits ranging from gravel to silty sands. Borings logs from the site indicate heavily iron stained soils in one or more of the encountered deposits. The plume length is approximately 3,300 ft. The mean observed COC concentration is much greater than the expressed assimilative capacity. Aerobic respiration appears to be occurring at the plume fringe, with nitrate reduction occurring in the plume core. The best-fit kinetic model for all compounds is first-order decay, and the calculated field degradation rates are about an order of magnitude greater than those reported at fuel sites.

CHAPTER 7

CONCLUSIONS

The objective of this study was to gain a better understanding of how anaerobic pathways contribute to the biodegradation of MGP contaminated plumes. A combination of laboratory and field studies was used to analyze the three lines of evidence, as developed for the AFCEE protocol to accomplish the objective.

The first line of evidence (documented loss of contaminants at the field scale) was measured using a first-order rate constant calculation via the method described by Buscheck and Alcantar for COCs at 8 MGP sites. The results of these calculations show that except for Glassboro, the first-order decay constants were either the same or somewhat greater than values reported for the same contaminants at fuel sites (Aronson and Howard, 1997; MacIntyre, 1994; Stauffer et al., 1994; Weidemeier et al 1995).

An additional objective was to determine whether the rates of degradation in the field could be better described by a classic first-order decay model, or by instantaneous reaction (i.e. transport limited) model. This is important because there are many commercially available models to simulate degradation based on either or both of the above described kinetic models. Using the BIOSCREEN program, which can compare the two models to field data, it was determined that at five of the sites (Egg Harbor, Bridgeton, Salem, Pleasantville and Millville), all of the compounds more closely resembled first-order decay rates. At the Florida Avenue site, where only benzene was a COC, the field data for benzene more closely resembled instantaneous reaction. Mixed results were noted at two of the sites, Hammonton and Glassboro, where the degradation

of some compounds more closely resembled first-order decay, while other compounds more closely resembled instantaneous reaction.

The second line of evidence involves the use of chemical analysis and mass balance calculations to show that changes in contaminant concentration can be related via the stoichiometry to changes in electron acceptor concentrations. As part of the RI for each site, isopleths were constructed for contaminants, electron acceptors (dissolved oxygen, nitrate, and sulfate), and metabolic products [iron(II) and methane]. In cases where these contour maps suggest a qualitative relationship between terminal electron acceptors and contaminants, mass balance calculations were made to quantify the relationship by determining the assimilative capacity (the natural ability of the groundwater system to attenuate contaminants). By comparing the total expressed assimilative capacity to the actual mean contaminant concentration, it can be determined if enough electron acceptor is available to degrade the contaminants at the sites.

The results indicate that at Egg Harbor, Hammonton, the south plume at Glassboro, Florida Avenue, Pleasantville, and Millville, there is a much greater concentration of contaminant than the total expressed assimilative capacity. At Bridgeton, Salem, and the north plume of Glassboro, the total expressed assimilative capacity is greater than the mean contaminant concentration. This may explain why the plumes at Bridgeton and Salem are very short considering the large amount of source material in the ground and the number of decades these contaminant have been present. When the total assimilative capacity is less than the contaminant load, the implication is that once source area is removed it will take a longer time for the plume to dissipate.

This also may provide an explanation as to why some of the plumes extend for such a long distance.

Nitrate reduction was significant at Egg Harbor, Hammonton, Bridgeton, and Millville, iron reduction at Florida Ave., Bridgeton, and Pleasantville. Sulfate reduction appeared to be a significant degradation pathway at Hammonton, Glassboro, Florida Ave., and Pleasantville. Methanogenesis was observed at Pleasantville, but methane data were absent at most sites.

These findings were corroborated in the microcosm studies done as the third line of evidence. Groundwater from the Florida Avenue and Glassboro sites, used in the microcosm studies, also indicated the importance of sulfate reduction at those sites. Furthermore, the rate constant calculated for benzene in the Florida Ave microcosms was about the same order of magnitude as the constant calculated from field data. However, the rate constant for naphthalene in the Glassboro microcosm was up to two orders of magnitude greater than the field data indicated, which has often been the experience of previous investigators (e.g. Chiang et al., 1986; Rifai et al., 1995).

On the whole, the AFCEE protocol provided an excellent methodology for analyzing the potential for natural attenuation at MGP sites, and the Buscheck-Alcantar method provides a means of quantifying the rate of plume attenuation.

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