

**Assessing Various Technologies  
to Remediate a Hydrocarbon Contaminated Aquifer**

by

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## **Abstract**

Releases of nonaqueous phase liquids (NAPLs) to groundwater systems are a serious and widespread problem throughout the United States. Research was conducted to determine if numerical groundwater flow and transport models could evaluate the effectiveness of alternative remedial strategies to reduce dissolved hydrocarbon contamination in aquifers, and therefore serve as tools to aid environmental managers in the remedial decision making process. A fuel distribution terminal in the Eastern United States was selected as the test site. A release of diesel and jet fuels from the terminal loading rack area contaminated the unconfined aquifer beneath the terminal and migrated off-site, impacting commercial and residential areas. In the analyses, groundwater flow and transport models were calibrated to site data. The calibrated models were applied to simulate four remedial options: (1) natural attenuation, (2) groundwater extraction, (3) groundwater flushing, and (4) microbial fences. Results of the predictive simulations indicated that the groundwater flushing remedial option provided the greatest reduction of benzene and TEX mass from the NAPL source as well as the lowest concentrations of benzene and TEX in the aquifer. The calibrated numerical models were able to predict the effectiveness of various remedial options and provide a basis for comparison. The modeling in conjunction with other factors, such as cost, were utilized to facilitate the decision making process.

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# 1. Introduction

Releases of nonaqueous phase liquids (NAPLs) to groundwater systems are a serious and widespread problem throughout the United States. As of June 1998, more than 350,000 releases from leaking underground storage tanks (USTs) were reported nationwide, and the United States Environmental Protection Agency (U.S. EPA) anticipated that additional releases will be identified during compliance with the December 1998 deadline to upgrade or replace substandard USTs (U.S. EPA, 1996; U.S. EPA, 1998). Each release has the potential to threaten human health and the environment. Once in the subsurface environment, NAPLs contaminate soil and groundwater and act as a source for dissolution of soluble hydrocarbon constituents. The contamination is further dispersed as the water soluble components flow with the groundwater. According to the U.S. EPA (1995), the cost for remediating sites with groundwater contamination can range from \$100,000 to millions of dollars.

How to effectively remediate aquifer and subsurface contamination from petroleum hydrocarbons is a common problem facing many environmental managers, as decisions on how to cleanup the hydrocarbon contamination in a timely and effective manner are required. Full-scale field implementation of a remedial technology can be costly and time consuming, especially at large sites covering many acres. Therefore, it is imperative that the appropriate remedial technology be selected, however, this can be an arduous task since site conditions vary and success of a remedial technology at one location does not guarantee success elsewhere. In addition, most NAPL impacted areas are under either federal or state regulatory control and environmental managers have to respond to these various regulatory demands.

How can environmental managers meet these demands and determine an effective remedial strategy for their NAPL impacted sites? To select an appropriate remedial strategy, environmental managers need a tool that can provide a means to evaluate the potential of various remedial technologies to reduce hydrocarbon concentrations and source mass. This research poses the question: Can computer models that simulate groundwater flow and contaminate fate and transport be utilized as tools to assess the potential effectiveness of remedial strategies to reduce hydrocarbon contamination in aquifers?

## 1.1 Objectives and Approach

The objective of this research is to evaluate, through the use of numerical groundwater flow and transport models, the potential of various remedial technologies to reduce dissolved hydrocarbon concentrations and source mass. To accomplish this objective, the following approach was applied:

- A hydrocarbon contaminated site was selected as a test case,
- Groundwater flow and transport models were calibrated to site data, and
- The calibrated computer models were utilized to evaluate various remedial options.

The selected test site is a fuel distribution terminal where a release of diesel and jet fuels contaminated the unconfined aquifer beneath the terminal and migrated off-site, impacting

commercial and residential areas. This site was selected because extensive site characterization and monitoring data were available for the development and calibration of the groundwater flow and transport models. In addition, an Administrative Order (AO) from the U.S. EPA was issued for this site requiring the development and evaluation of remedial options. Preliminary remedial options were selected and submitted in the Remedial Assessment Plan (RAP) (RETEC, 1994). After submission of the RAP, small-scale field studies and other site characterization activities were conducted to enhance understanding of the site and to assess the feasibility of several of the proposed remedial options. These activities provided information about the geology, aquifer properties, groundwater flow patterns, hydrocarbon plume composition and migration, and microbial activity at the site.

Based on site characterization activities, field studies, site conceptualization, as well as economic considerations, four remedial options from the RAP were selected for future evaluation in this research. These remedial options are:

- Groundwater extraction,
- Groundwater flushing via horizontal infiltration wells,
- Microbial fences, and
- Natural attenuation.

A brief description of these remedial options is provided below. A detailed review of pertinent literature detailing the various remedial technologies and how these technologies remediate hydrocarbon contaminated aquifers is presented in Chapter 2. Chapter 3 presents details of the site conditions and site conceptualization for the hydrocarbon contaminated aquifer utilized in this research. In addition, the development and calibration of the groundwater flow and transport models applied to this site are discussed. The application of the calibrated groundwater flow and transport models to evaluate the potential remedial technologies is presented in Chapter 4 as well as the selection of a remedial option for the site.

**Groundwater Extraction.** A commonly applied groundwater treatment technology is the pumping of contaminated groundwater from an aquifer and subsequent removal of the hydrocarbon constituents through an above ground treatment system, such as an air stripper or a granular activated carbon unit. This treatment technology is often referred to as “pump and treat.”

**Groundwater Flushing via Horizontal Wells.** This groundwater remediation technology involves the use of horizontal infiltration wells to enhance water movement through hydrocarbon contaminated aquifers. Artificial infiltration of clean water increases the velocity and volume of groundwater, which subsequently increases the dilution of groundwater concentrations and the dissolution rate of hydrocarbon constituents from residual NAPL. When applied in conjunction with groundwater extraction, hydrocarbon mass may be removed more rapidly than by pumping alone. This remedial option will be referred to as groundwater flushing.

**Microbial Fences.** Microbial fences are a method of remediating dissolved groundwater contamination by stimulating biodegradation processes in selected zones. Microbial fences are engineered zones of high biodecay. The microbial fence remedial option involves construction of

gravel trenches containing air sparging wells, which supply oxygen to promote microbial growth and aerobic biodegradation within the trenches.

**Natural Attenuation.** Natural attenuation is the term applied to the reduction of hydrocarbon constituents from an aquifer by natural processes of in situ biodegradation, volatilization, sorption, and dilution. Since biodegradation is usually the process most frequently associated with natural attenuation, other terms such as intrinsic biodegradation and passive biodegradation are often used synonymously with natural attenuation. Evaluation of natural attenuation provides a baseline for comparison of the engineered remedial technologies.

## 2. Literature Review

In order to assess remedial technologies associated with hydrocarbon contamination, a thorough understanding of petroleum hydrocarbons and how they behave in the environment is required. As the name implies, petroleum hydrocarbons are generally compounds of hydrogen and carbon atoms. These compounds are characterized by chemical composition and structure. Hydrocarbons are typically classified into four major structural forms: (1) alkanes, (2) cycloalkanes, (3) alkenes, and (4) aromatics. The carbon atoms in alkanes are joined by single bonds. These compounds are also commonly referred to as saturated hydrocarbons or paraffins. Alkanes have a general formula of  $C_nH_{2n+2}$ . If alkanes have a cyclical structure, they are referred to as cycloalkanes or cycloparaffins. These compounds are also called naphthenes and have a formula of  $C_nH_{2n}$ . Alkenes are characterized by a carbon-carbon double bond and are also referred to as unsaturated hydrocarbons or olefins. They have a general formula of  $C_nH_{2n}$ . Aromatic hydrocarbons are characterized as containing at least one 6-carbon benzene ring. These compounds are unsaturated and resemble benzene in chemical behavior.

Aromatic compounds are important with respect to environmental concerns as they are relatively soluble in water, and therefore, have a high potential mobility within groundwater systems. In addition, many aromatic compounds are carcinogens and can pose health risks when dissolved in drinking water aquifers. At many UST sites benzene, a known carcinogen, is the primary constituent of concern by the regulatory agency.

Refined petroleum products contained within USTs are typically gasolines, middle distillates (e.g., diesel fuel, kerosene, jet fuel), and heavy fuel oils. Each petroleum product has different composition and properties that influence its fate and transport in the subsurface. Gasolines contain high percentages of aromatic hydrocarbons, with most hydrocarbon compounds having between 4 and 10 carbon atoms per molecule. The majority of hydrocarbon constituents in middle distillates contain between 9 and 20 carbon atoms, which makes middle distillates less mobile, volatile, and soluble than gasolines. Heavy fuel oils are relatively viscous and insoluble with hydrocarbon compounds of more than 14 carbon atoms (U.S. EPA, 1996).

When petroleum hydrocarbon have been released into the subsurface, they can partition into one or more of the following phases:

- Mobile Liquid – the mobile free product is maintained at the water table and capillary fringe or perched above a low permeability layer in the unsaturated zone;
- Residual Liquid – the liquid hydrocarbon is trapped within the soil matrix both above and below the water table, depending on water table movement;
- Aqueous – the soluble hydrocarbon components dissolve in the groundwater and soil moisture; and
- Sorbed – the soluble hydrocarbon is adsorbed to soil particles
- Vapor – the volatile hydrocarbon components enter a gaseous state, which occurs primarily in the unsaturated zone.

All phases are generally present when a sufficient volume of NAPL has been released into the subsurface (U.S. EPA, 1996). Since free and residual phase liquid hydrocarbons are distinguished by the volume of oil and its ability to move within the formation, not by physical or chemical differences between the phases, they are both often referred to as NAPL or phase separate hydrocarbon (PSH).

## 2.1 Processes

Various physical, chemical and biological processes affect the fate and transport of petroleum hydrocarbons in the subsurface. Some of these processes are described in greater detail below.

**Dissolution.** Dissolution is the transfer of soluble hydrocarbon constituents from free phase or residual NAPL into the aquifer and is the primary physical property that controls the extent of a contaminant plume (Rifai et al., 1995). Surface area contact between NAPL and water as well as contact time affect dissolution (Testa and Winegardner, 1991). The rate of dissolution depends on the effective solubility of the hydrocarbon constituents in the aquifer and the amount and type of NAPL in the subsurface (Bedient et al., 1994). For multi-component NAPLs, the effective solubility for an individual hydrocarbon constituent, such as benzene, can be estimated from Raoult's law as the product of the constituent's mole fraction in the NAPL and its pure-phase solubility. The rate of dissolution for individual constituents will decline over time as the mole fraction of soluble components in the NAPL decreases.

**Advection.** Advection is the process by which solutes (dissolved hydrocarbons) are transported in flowing ground water (Fetter, 1994). High advection can cause increased spreading and dilution of dissolved contaminants.

**Hydrodynamic Dispersion.** Hydrodynamic dispersion is the termed applied to the combined effects of mechanical dispersion and molecular diffusion in causing a contaminant plume to spread within a groundwater system. Mechanical dispersion is the mixing of the solute with uncontaminated water, thus reducing the concentration of the contaminant. Variations in pore size, flow path, and pore friction cause dispersion. Longitudinal dispersion occurs in the direction of advective groundwater flow while transverse dispersion occurs perpendicular to groundwater flow. Diffusion is the movement of dissolved molecular species in response to concentration gradients and is governed by Fick's Second Law. Molecular diffusion occurs even in the absence of groundwater flow. Under normal advective flow systems, mechanical dispersion predominates (ASTM, 1998).

**Adsorption.** The term adsorption describes the partitioning of organic contaminants from the soluble or gaseous phase on to a solid phase, usually the soil matrix. Since most petroleum constituents are nonionic, they adsorb more readily to organic carbon rather than mineral particles in soil (Testa and Winegardner, 1991). Therefore, adsorption is a more important process in aquifers with high organic carbon content. In addition, adsorption reactions between NAPL constituents and organic particles are usually chemical in nature, and therefore, are reversible equilibrium reactions (Testa and Winegardner, 1991). In general, adsorption retards the movement of contaminants in aquifers. Various adsorption isotherms have been developed to describe the equilibrium relationship between sorbed and dissolved phases for an individual

hydrocarbon constituent. According to ASTM (1998) the most common method used to represent the equilibrium relationship is the distribution coefficient,  $K_d$ , which is defined as

$$K_d = \frac{C_s}{C_w}$$

where  $C_s$  is the adsorbed concentration of the hydrocarbon constituent and  $C_w$  is the aqueous concentration of the hydrocarbon constituent.  $K_d$  can also be estimated as the product of the fraction of organic carbon ( $f_{oc}$ ) in the soil and the organic carbon partition coefficient ( $K_{oc}$ ) of the hydrocarbon constituent.

**Volatilization.** The transfer of a chemical from the aqueous or liquid phase to the gas phase is termed volatilization. The rate of volatilization is controlled by molecular weight, solubility, and vapor pressure of the liquid as well as the gas-liquid interface (U.S. EPA, 1995). Volatilization can result in mass loss from the subsurface into the atmosphere. While this process accounts for mass loss, especially in shallow water table environments, this mechanism may not be significant compared to other processes and diminishes in importance over time as volatile organics are depleted from the subsurface. McAllister and Chang (1994) state that at a typical site about 5 to 10 percent of benzene mass loss is due to volatilization while biodegradation accounts for the remaining mass loss. The anticipated mass loss due to volatilization is even lower for less volatile hydrocarbon constituents.

**Biodegradation.** Biodegradation is a process by which hydrocarbons are consumed by microorganisms through a series of enzyme-catalyzed oxidative-reduction reactions. When oxygen is the electron acceptor, aerobic bacteria convert hydrocarbon contaminants to carbon dioxide and water by transferring electrons from the hydrocarbon to oxygen, thus reducing it to water. Approximately three units of oxygen are required to convert one unit of hydrocarbon to carbon dioxide and water (Wong et al., 1997; ASTM, 1998). Under anaerobic conditions, alternate electron acceptors are utilized by the microorganisms. Alternate electron acceptors, in order of preference, include nitrate, manganese, ferric iron, sulfate and carbon dioxide (ASTM, 1998).

The capability of petroleum hydrocarbons to biodegrade depends on composition and chemical structure. Lighter, more soluble hydrocarbons are typically more biodegradable than heavier, less soluble hydrocarbons. Hydrocarbons with simple chemical structures are more biodegradable than complex hydrocarbons. For example, straight-chain hydrocarbons degrade faster than branched structures and monoaromatic compounds, such as benzene, are more easily degraded than polycyclic aromatic compounds, such as naphthalene (Chapelle, 1993).

In the past 15 years, microbial degradation of petroleum hydrocarbons has been widely studied in the laboratory and in the field (Barker et al., 1987; Hadley and Armstrong, 1991; Chapelle, 1993). The presence of microbial populations capable of oxidizing petroleum hydrocarbons has been demonstrated in numerous locations and for diverse hydrologic conditions. Biodegradation has been shown in numerous studies to be the primary mechanism for attenuation of petroleum hydrocarbons in the subsurface (Chiang et al., 1989; Buscheck et al., 1993; Salanitro, 1993; McAllister and Chiang, 1994; and Maresco et al., 1995).

## 2.2 Remedial Technologies

Once aquifer contamination from petroleum products has been characterized, the focus then is how to effectively mitigate the contamination and restore the aquifer to acceptable levels. A variety of conventional and emerging technologies exist to remediate aquifer contamination. The following review discusses the four remedial options selected from the RAP and utilized in the research analyses. The review encompasses an evaluation of how the technologies work, current status of each technology within the industry, and previous applications at hydrocarbon contaminated sites. The use and previous application of computer modeling is also addressed. A general overview of modeling is provided below while the application of computer models to evaluate specific remedial technologies is discussed within each relevant subsection.

Groundwater models are applied to predict future conditions and to evaluate alternative remedial scenarios (U.S. EPA, 1994a). The modeling process also enhances understanding of the natural system and development of site conceptual models. The common use of groundwater models to characterize contaminant plumes and to evaluate remedial schemes is evident by the development of guidance documents by the U.S. EPA (1994a, 1994b) and standards by the American Society for Testing and Materials (ASTM, 1996). These documents provide a framework for regulators to understand, assess, and review modeling efforts. The *Ground-Water Modeling Compendium* (U.S. EPA, 1994b) provides summaries of six model applications for site characterization and remedial system design. The Committee on Ground Water Quality of the American Society of Civil Engineers (ASCE) has also prepared guidelines for the selection and application of frequently used groundwater models. The committee summarized findings from several surveys conducted within the industry and determined that as of 1994 more than 300 models were in use (ASCE, 1996). The document provides information on the capabilities and limitations of frequently used commercially and publicly available computer models.

### 2.2.1 Natural Attenuation

Natural attenuation is a passive technique that relies predominately on the ambient levels of nutrients and electron acceptors for microbial growth and reproduction associated with biodegradation. Natural attenuation is defined by ASTM (1998) as “reduction in mass or concentration of a compound in ground water over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes.” The physical processes include hydrodynamic dispersion, dilution from recharge, and volatilization. Chemical processes affecting hydrocarbons include adsorption and abiotic reactions. Although the physical processes and chemical adsorption reduce hydrocarbon mobility and dissolved hydrocarbon concentrations, these processes do not produce a reduction in hydrocarbon mass. Biodegradation results in the reduction of hydrocarbon mass, and is therefore commonly referred to as the most important process of natural attenuation (ASTM, 1998).

In aquifers without containment/remediation systems, the shape and extent of a contaminant plume is controlled by the source mass loading rate relative to the rate of natural attenuation processes (ASTM, 1998). The contaminant plume will continue to expand until natural attenuation processes compensate for additional mass loading and the system reaches a steady-state condition. The plume will remain stabilized at this steady-state condition until the rate of

natural attenuation exceeds source mass inputs, causing the plume to shrink. The time required for plume stabilization and subsequent reduction is dependent on specific site conditions.

Numerous studies have demonstrated decreases in concentrations of dissolved hydrocarbons due to natural attenuation (Piontek et al., 1994; McAllister and Chiang, 1994; Testa and Colligan, 1994; Brown et al., 1995; Maresco et al., 1995; Wiedemeier et al., 1995 and 1996). In a report to the California State Water Resources Control Board, the Lawrence Livermore National Laboratory recommends the use of passive bioremediation as a remedial alternative whenever possible (Rice et al., 1995). The report also states that reviews of more than 1,000 leaking UST sites indicated that dissolved hydrocarbon plumes tend to stabilize at relatively short distances from the sites.

To demonstrate the use of natural attenuation as a remedial alternative for petroleum contamination in groundwater, the Mobil Oil Corporation has developed a three-tiered approach (Novick et al., 1995). Tier I assessment includes categorizing whether the contaminant plume is stable, expanding or shrinking and then calculating natural attenuation rates based on Darcy flow. Tier II assessment requires the collection of monitoring data to indicate natural attenuation, such as dissolved oxygen and other electron acceptors. In a Tier III assessment, detailed groundwater modeling and microcosm studies are performed.

The Air Force Center for Environmental Excellence (AFCEE) has developed a technical protocol for implementing intrinsic bioremediation. Wiedemeier et al. (1994) provides an overview of the AFCEE technical protocol and presents an example from the Hill Air Force Base. The protocol stresses performing adequate site characterization to support intrinsic bioremediation, conducting numerical fate and transport modeling that incorporates biodegradation, and performing long-term monitoring. According to Wiedemeier et al., modeling of intrinsic remediation has "three primary objectives: (1) to estimate the future extent and concentration of a dissolved phase contaminant plume by modeling the combined effects of advection, dispersion, sorption, and biodegradation; (2) to assess the possible risk to potential downgradient receptors; and (3) to provide technical support for the natural attenuation remedial option at post-modeling regulatory negotiations." The example presented for Hill Air Force Base includes a modeling effort utilizing BIOPLUME II. The model assumes an instantaneous reaction between dissolved oxygen and the BTEX (benzene, toluene, ethylbenzene, and xylene) constituents. In addition, a first-order decay constant accounts for any additional degradation mechanisms, including anaerobic biodegradation.

In response to the increased awareness and understanding of natural attenuation, the U.S. EPA (1999) has recently issued a directive on the use of monitored natural attenuation (MNA) for the remediation of soil and groundwater. The directive states that MNA is not to be considered a "default" remedy, but needs to be evaluated with other applicable remedies. The directive further states that "due to the uncertainty associated with the potential effectiveness of MNA to meet remediation objectives that are protective of human health and the environment, EPA expects that source control and long-term performance monitoring will be fundamental components of any MNA remedy." Therefore, MNA maybe most appropriate when applied in conjunction with other remediation measures or as a follow-up to other active remediation. Another factor in the decision making process is that long-term monitoring costs associated with MNA may be greater than costs associated with other, more aggressive remedial alternatives. Although the rate of

natural attenuation at some sites may not be sufficient to allow natural attenuation as a remedial solution, estimating this rate can provide a baseline for comparison of other remedial options (Brubaker et al., 1993).

According to Rifai et al. (1995), numerical models can be used to determine contaminant distributions over time as a function of natural attenuation. Simulating natural attenuation requires calibrating the model to existing site hydraulics and contamination conditions. Fate and transport modeling of natural attenuation processes for BTEX constituents have been previously conducted. Chiang et al. (1989) used BIOPLUME II to evaluate a first-order biodegradation approach for BTX contamination at a gas plant facility in Michigan. The model achieved a reasonable match to observed data for BTX but not for the dissolved oxygen. In addition, the predicted biodegradation rate closely matched the rate measured in the field. Caldwell et al. (1992) evaluated the impact of biodegradation on BTEX components at a UST site in Florida. BIOPLUME II was calibrated to site data and the model was then utilized to predict future plume extents. The modeling effort demonstrated that the predicted plume extent without the application of biodegradation far exceeded the observed plume extent.

Increased interest in natural attenuation and biodegradation has propelled the enhancement of existing computer models to accommodate multispecies reactive transport. BIOPLUME III is an update of BIOPLUME II that is designed to evaluate natural attenuation and has enhancements to accommodate a variety of electron acceptors (Rifai et al., 1997). The model allows for direct input of DO, nitrate, iron, sulfate, and methane data. Clement et al. (1998) present details of a set of reaction modules that were incorporated into RT3D to simulate multispecies reactive transport. Several examples of model application and verification are presented, and the model is shown to be a useful tool for assessing aquifer bioremediation systems.

In summary, continuing research of natural attenuation processes has lead to a greater understanding of how hydrocarbon mass migrates and degrades in the subsurface environment. The use of monitored natural attenuation as a remedial alternative for hydrocarbon contaminated sites has been increasing and gaining regulatory acceptance. The development and application of numerical modeling of natural attenuation processes has also been increasing.

### **2.2.2 Groundwater Extraction**

A commonly applied groundwater treatment technology is the pumping of contaminated groundwater from an aquifer and subsequent removal of the hydrocarbon constituents through an above ground treatment system, such as an air stripper or a granular activated carbon unit. If free phase hydrocarbon is also recovered, the product is removed prior to treatment. This remedial technology is often referred to as “pump and treat.”

According to Wong et al. (1997), there are three primary goals of a pump and treat system:

- Prevent or contain contaminant migration,
- Aquifer restoration via a reduction in dissolved contaminant concentrations, and
- Free phase hydrocarbon recovery.

Pump and treat systems are one of the most commonly utilized remedial technologies. At Superfund sites with Record of Decisions (RODs) between 1982 and 1990 that addressed groundwater remediation, approximately 72 percent designated pump and treat as the remediation method (U.S. EPA, 1994c). However, the ability of pump and treat systems to achieve cleanup goals has been questioned. The U.S. EPA (1989) evaluated the performance of groundwater extraction remedies at 19 sites and determined that this technology was not as effective as originally predicted for most situations. The Committee on Ground Water Cleanup Alternatives of the National Research Council (NRC) performed a review of 77 contaminated sites utilizing pump and treat technologies and determined that only 8 sites had achieved the cleanup goals (NRC, 1994). Although pump and treat systems achieve hydraulic containment at most sites, aquifer restoration can be hindered due to contaminant dissolution, aquifer heterogeneities, and other factors (U.S. EPA, 1994c). In addition, dissolved contaminant reduction via pump and treat systems often becomes asymptotic prior to achieving desired cleanup levels (U.S. EPA, 1995). Recent concerns over the time required to meet cleanup goals and the volume of water that must be recovered to remove dissolved contamination have led to increased implementation of other remedial technologies (Wong et al., 1997).

Due to the complexity of calculations associated with multiple extraction well systems and the increased availability of desktop computers, modeling of groundwater extraction systems is routinely conducted to design the placement and number of recovery wells (Wong et al., 1997). In addition, Gorelick et al. (1993) states that quantitative evaluation of alternative capture system designs are frequently completed through the use of groundwater models. Previous modeling efforts to design pump and treat systems include Satkin and Bedient (1988), U.S. EPA (1994b), Rundell et al. (1992), and Wang et al. (1998).

Rundell et al. (1992) utilized a transient, numerical groundwater flow model to optimize the redesign of an existing groundwater and hydrocarbon recovery system. The model was calibrated to site conditions and then utilized to evaluate multiple remediation scenarios. The model was successfully applied to redesign the groundwater extraction system to reduce the overall volume of water recovered while still maintaining hydraulic control where free phase and dissolved hydrocarbons were present.

Wang et al. (1998) present results of a modeling study of the Engelse Werk wellfield. The wellfield provides domestic and industrial water supplies to the town of Zwolle in the Netherlands. High chloride and organic contaminants, including benzene, have been detected in the production wells. The study objectives included assessment of the capture area (and potential contaminants sources) of the well field and development of groundwater flow and transport models to aid with evaluation of a remediation strategy. MODFLOW, MODPATH and MT3D were calibrated to the site conditions. The calibrated benzene transport model was then utilized to test a remediation strategy for the aquifer that involved two rows of extraction wells. The modeling results indicate that benzene concentrations could be reduced to permissible levels within 5 years.

In summary, pump and treat remedial systems have been commonly used to contain and remediate hydrocarbon contamination in aquifers, and numerical modeling has often been applied in the design and placement of system components. However, recent concerns over the

time required to meet cleanup goals and the volume of water that must be recovered to remove dissolved contamination have led to increased implementation of other remedial technologies

### **2.2.3 Groundwater Flushing via Horizontal Wells**

Groundwater flushing, as defined for this research project, is a subset of another groundwater remediation technology, in situ flushing. In situ flushing is the injection or infiltration of a flushing solution (e.g., plain water, surfactants, cosolvents) into contaminated soil and/or groundwater in conjunction with a downgradient extraction system. According to Roote (1997), in situ flushing has been selected as part of the remedy scheme at 18 Superfund sites as of May 1997, and the flushing solution at these sites is treated groundwater with no additives. Containment of the flushing solution and any contaminants is critical to the success of an in situ flushing system. The extracted groundwater and elutriate (flushing solution mixed with contaminants) is treated above ground and either discharged or re-injected into the aquifer (Roote, 1997). By increasing the flushing rate and the contaminant removal capabilities of each pore volume, in situ flushing enhances conventional pump and treat technology and accelerates the remediation process. In situ flushing can also accelerate groundwater remediation by enhancing biodegradation. In situ flushing can be achieved through a variety of means, including injection wells, infiltration galleries, horizontal wells, trenches, and extraction wells (Roote, 1997).

Horizontal wells for groundwater remediation are an emerging technology. Although directionally drilled horizontal wells for groundwater remediation began in 1988, it has only received wide-spread application since 1995 (Wilson, 1999). Therefore, information regarding horizontal well implementation and effectiveness is limited. Parmentier and Klemovich (1996) describe the advancements and advantages of using horizontal wells for soil and groundwater remediation. Horizontal wells can access a greater extent of contaminated area with less surface disruption, and although horizontal wells cost more per drilled foot than vertical wells, a single horizontal well can replace up to 10 vertical wells. Horizontal wells are being utilized for both groundwater extraction and infiltration. In groundwater extraction systems, horizontal wells replace a series of vertical wells and can potentially achieve greater plume containment. As a mechanism for groundwater infiltration, horizontal wells provide a hydraulic barrier and promote groundwater flushing. Artificial infiltration of clean water increases the velocity and volume of groundwater, which subsequently increases the dilution of groundwater concentrations and the dissolution rate of hydrocarbon constituents from residual NAPL.

In addition to impacting the dissolution and dilution of hydrocarbon constituents, groundwater flushing has the potential to promote in situ bioremediation since the infiltrating water will contain dissolved oxygen. In situ bioremediation via a closed loop injection/recovery system was studied by Chiang et al. (1993). Two downgradient recovery wells provided plume capture and were utilized as the source for water injection. The purged groundwater was amended with DO and directly reinjected via two upgradient bi-level injection wells. The biodegradation of BTEX was determined by both material balance analyses and groundwater modeling. The researchers found that the injection system effectively delivered oxygen into the aquifer and they observed a consistent decline in BTEX concentrations at all monitoring locations. Brubaker et al. (1993) defined four issues relating to the design of injection/recovery systems for in situ bioremediation:

(1) groundwater flow rate and transport time, (2) hydraulic containment of the hydrocarbon plume, (3) distribution of injected oxygen and/or nutrients, and (4) cost.

As the use of horizontal wells for groundwater remediation increases, implementation of horizontal wells in groundwater models is also increasing. Lieuallen-Dulam and Sawyer (1997) present modifications to the U.S. Geological Survey finite difference flow model, MODFLOW, to improve the simulation of horizontal extraction wells.

In summary, groundwater flushing is a remedial technology that relies on the injection/infiltration of a flushing solution to promote contaminant removal from the aquifer. The use of horizontal wells for groundwater flushing is an emerging technology, and therefore limited reviews exist in the literature that describe implementation or modeling of horizontal wells.

## **2.2.4 Microbial Fences**

Another method of mitigating dissolved groundwater contamination involves stimulating biodegradation processes. Microbial fences are engineered zones of high biodecay that remediate dissolved constituents and prevent plume migration. The microbial fence remedial option involves construction of gravel trenches containing air sparging wells, which supply oxygen and promote microbial growth within the trenches.

Air sparging technology involves the injection of air under pressure into saturated soils. As the injected air displaces water, it provides a means to remove dissolved and adsorbed contaminants and transfers oxygen into the groundwater, which can promote microbial growth and hydrocarbon degradation. Numerous studies in recent years have demonstrated that air sparging can reduce dissolved concentrations and accelerate site remediation (Felten et al., 1992; Leonard and Brown, 1992; Marley et al., 1992; Bass and Brown, 1995). Bass and Brown (1995) performed a review of 21 case studies that evaluated the effectiveness of in situ air sparging on achieving a permanent reduction in groundwater contaminant concentrations. They concluded that in situ air sparging could achieve a permanent reduction in groundwater concentrations for both petroleum hydrocarbons and chlorinated solvents, but was not as effective at sites with NAPL present. In addition, when rebound of dissolved concentrations occurred, Bass and Brown found that a high density of closely spaced sparge wells with high flow rates minimized the rebound impacts. During evaluation of site remediation using an air sparging/soil vapor extraction system, Felten et al. (1992) observed increases of dissolved oxygen in the groundwater from 2 mg/L prior to system operation to as high as 10 mg/L during system operation. Felten et al. also observed an increase between 10- and 420-fold of indigenous hydrocarbon-degrading bacteria in four out of the five wells sampled.

Since the effectiveness of in situ air sparging depends on the mixing of air and water, this technology is generally more effective in aquifers with hydraulic conductivity values of a least  $10^{-3}$  cm/sec (Brubaker, 1993). When in situ air sparging is limited by the aquifer formation, aquifer aeration can still be achieved by placing the air sparging wells within an engineered trench filled with gravel. This approach is sometimes referred to as a "microbial fence" (Brubaker, 1993). While air sparging technology relies on the exchange of dissolved contaminants from the groundwater into the air channels, microbial fence technology relies on

the transfer of oxygen from the injected air into the groundwater to promote microbial growth and increased biodegradation.

Similar to air sparging, biosparging utilizes air and nutrients (if needed) injected into the saturated zone. The objective of biosparging, however, is to promote biodegradation of constituents rather than volatilization, and therefore, biosparging is performed with lower air injection rates (U.S. EPA, 1995). Since lighter petroleum products, such as gasoline, tend to volatilize, biosparging is frequently applied at sites with middle distillates (e.g., diesel fuel, jet fuel).

The use of "microbial fences" or sparging trench systems has been documented. Marley et al. (1994) describe the design of a low cost, low maintenance in situ sparging trench to control the migration of a dissolved gasoline plume. The trench design was approved by the state regulatory agency as the corrective action plan.

Pankow et al. (1993) present the theory and advantages of performing air sparging in a well/trench system, which they referred to as WTS, for control and remediation of dissolved hydrocarbon plumes. The authors argue that WTS is better suited for treating large contaminant plumes than in situ air sparging. WTS is also more efficient than pump and treat methods since contaminated water is treated as it flows through the trench system and does not require above ground treatment or disposal. In addition, unlike pump and treat systems, WTS does not mix uncontaminated and contaminated water.

Brubaker et al. (1998) presents an overview of design options available for microbial fences and provides examples of microbial fence implementation. Design options include continuous trench construction and funnel-and-gate construction. A continuous trench microbial fence is constructed with a homogeneous, highly permeable material, such as gravel. The funnel-and-gate approach combines a physical barrier with the microbial barrier. A slurry wall or sheet piling is constructed along 60 to 80 percent of leading plume edge to channel the flow into the "gate," which is biologically active. Use of funnel-and-gate barrier systems and well/trench sparging systems is also presented in Bedient et al. (1994).

References detailing modeling analyses of microbial fence systems were not discovered during this literature review.

## **3. Model Development**

The approach applied in this research involved the development of numerical flow and transport models to simulate the aquifer conditions in the study area and then to utilize these site models as tools to assess how the remedial options may effect contaminant reduction within the aquifer. This chapter provides detailed descriptions of the research site and the development and calibration of the groundwater models.

A report detailing a preliminary calibration of the groundwater flow model for this site was submitted to the U.S. EPA in 1994 (ES&T, 1994b). This research refines the preliminary calibration of the groundwater flow model and also includes both hydrocarbon flow modeling and dissolved phase fate and transport modeling. The groundwater flow model served as the foundation for both the hydrocarbon flow model and the transport model. In addition, the initial groundwater flow model was modified to incorporate the results of recent site characterization activities and field studies.

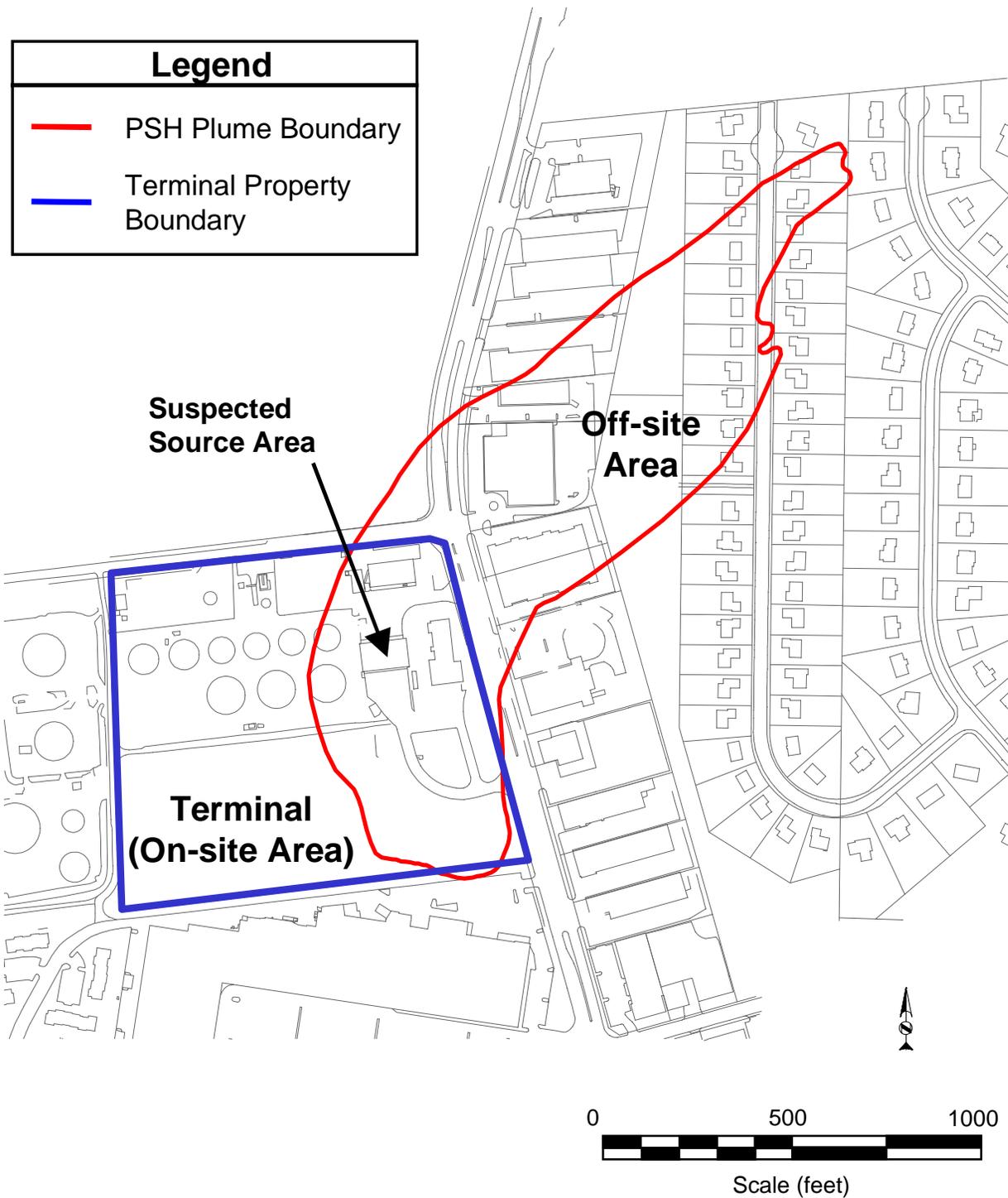
### **3.1 Site Description and History**

#### **3.1.1 Background**

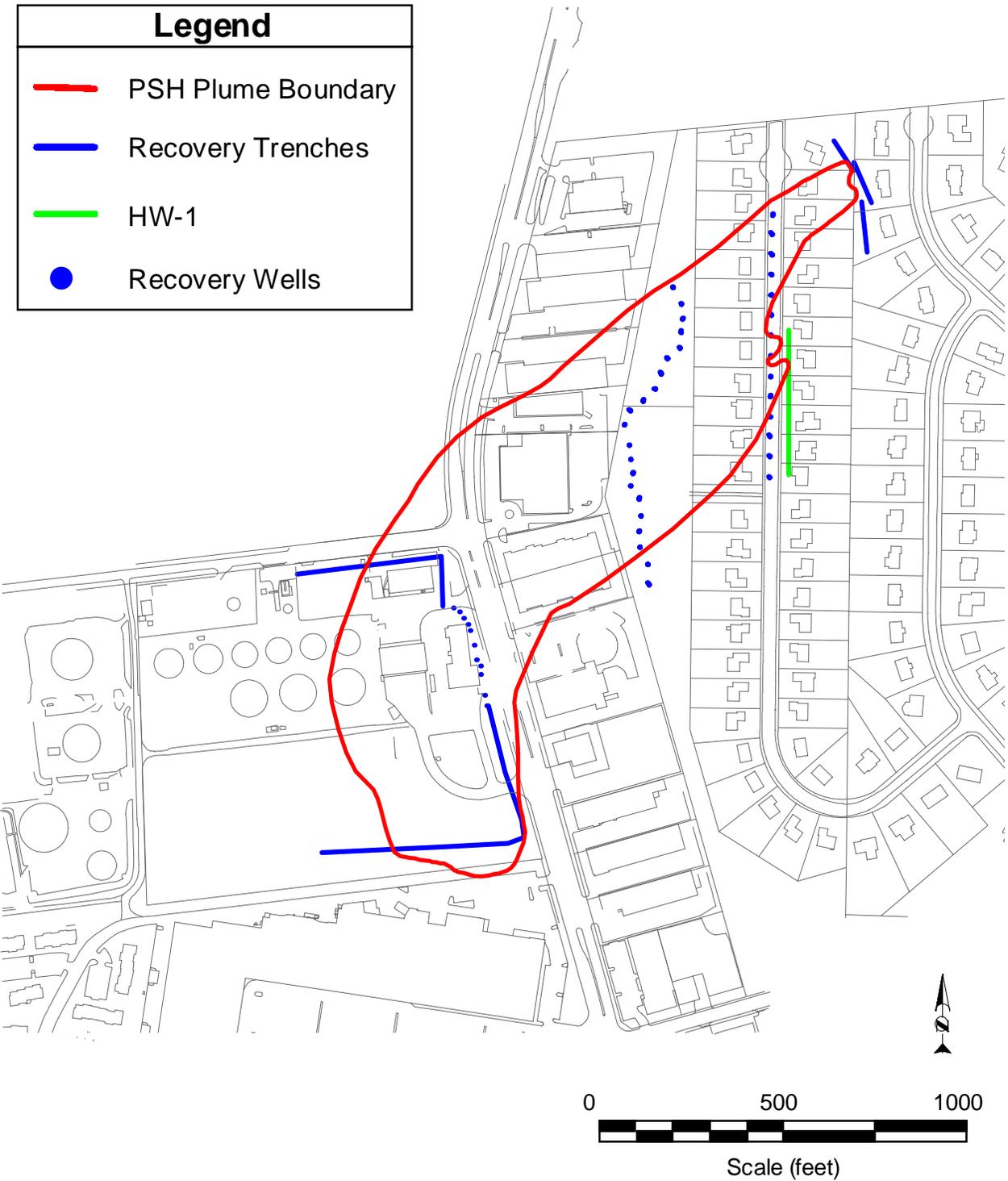
The research site is a fuel distribution terminal in the eastern United States. The terminal is bounded to the north and west by other fuel distribution terminals, to the east by a commercial zone, and to the south by a shopping center. In the fall of 1990, phase separated hydrocarbon (PSH) was discovered in the subsurface near the terminal. Subsequent site characterization activities determined that an elongated PSH plume had migrated across the terminal property boundary, approximately 1800 feet to the northeast into a residential area (Figure 3.1). The total area impacted by PSH is approximately 23 acres. The PSH impacted area that primarily occurs in the eastern portion of the terminal is approximately 7.5 acres and is termed the “on-site” area. The PSH impacted area that extends east of the terminal is approximately 15.5 acres and is termed the “off-site” area. In addition to the PSH plume, a dissolved phase hydrocarbon (DPH) plume is also present on the terminal property as well as the off-site area. Measured groundwater samples indicate that the DPH plume extends approximately 50 to 100 feet in front of the PSH plume.

In response to discovery of the PSH and DPH plumes, an interim containment system was installed. The containment system is currently comprised of 5 recovery trenches and more than 50 recovery wells. In addition, a horizontal infiltration well (HW-1) was installed in September 1994 along a portion of the eastern edge of the PSH plume to ensure hydraulic containment of the plume (Figure 3.2). A monitoring well network was installed throughout and around the perimeter of the PSH and DPH plumes. Fluid elevations and water quality samples are routinely obtained from the monitoring well network and submitted to the U.S. EPA in progress reports.

The source of the hydrocarbon release is not known. Based on soil contamination, the suspected source area is the loading rack area, which is located west of the main terminal building (Figure 3.1). A long-term, slow release of hydrocarbons is suspected.



**Figure 3.1. Study area and site features.**



**Figure 3.2. Interim containment system.**

### **3.1.2 Topography**

Figure 3.3 illustrates the current topography across the study area. The terminal is located at approximately 410 feet above mean sea level (MSL). South of the terminal, the topographic relief is toward the former creek channel, in which 20 to 30 feet of fill material was placed (ESE, 1993). A northeast trending topographic divide extends northward from the terminal. East of the topographic divide, the surface slopes to the east and south towards the creek. The topographic relief across the study area ranges from approximately 410 to 320 feet MSL.

### **3.1.3 Geology**

The research site is underlain by saprolite and bedrock. The saprolite consists primarily of silt and clay with minor amounts of sand. Across the area, the saprolite varies from tens of feet to over 100 feet in thickness and is derived from weathering of the underlying bedrock. Two types of bedrock underlie the site, phyllite and metasilstone. The inferred contact between the units crosses the site in a northeast direction from the southern terminal boundary to the central portion of the off-site area (ESE, 1997). The phyllite occurs north of the contact and underlies the majority of the area (Figure 3.4). It is highly fractured and is generally less competent than the less fractured metasilstone. Because the saprolite is weathered in situ, it retains many of the structural features of the parent bedrock. This results in the saprolite containing relict structures such as foliation, joints, and quartz veins from the bedrock. For example, relict foliation retained from the underlying phyllite is observable in the saprolite. The foliation trends northeast with a strike ranging from N12°E to N40°E and a northwest dip of 80 to 90 degrees (ESE, 1993).

### **3.1.4 Precipitation and Recharge**

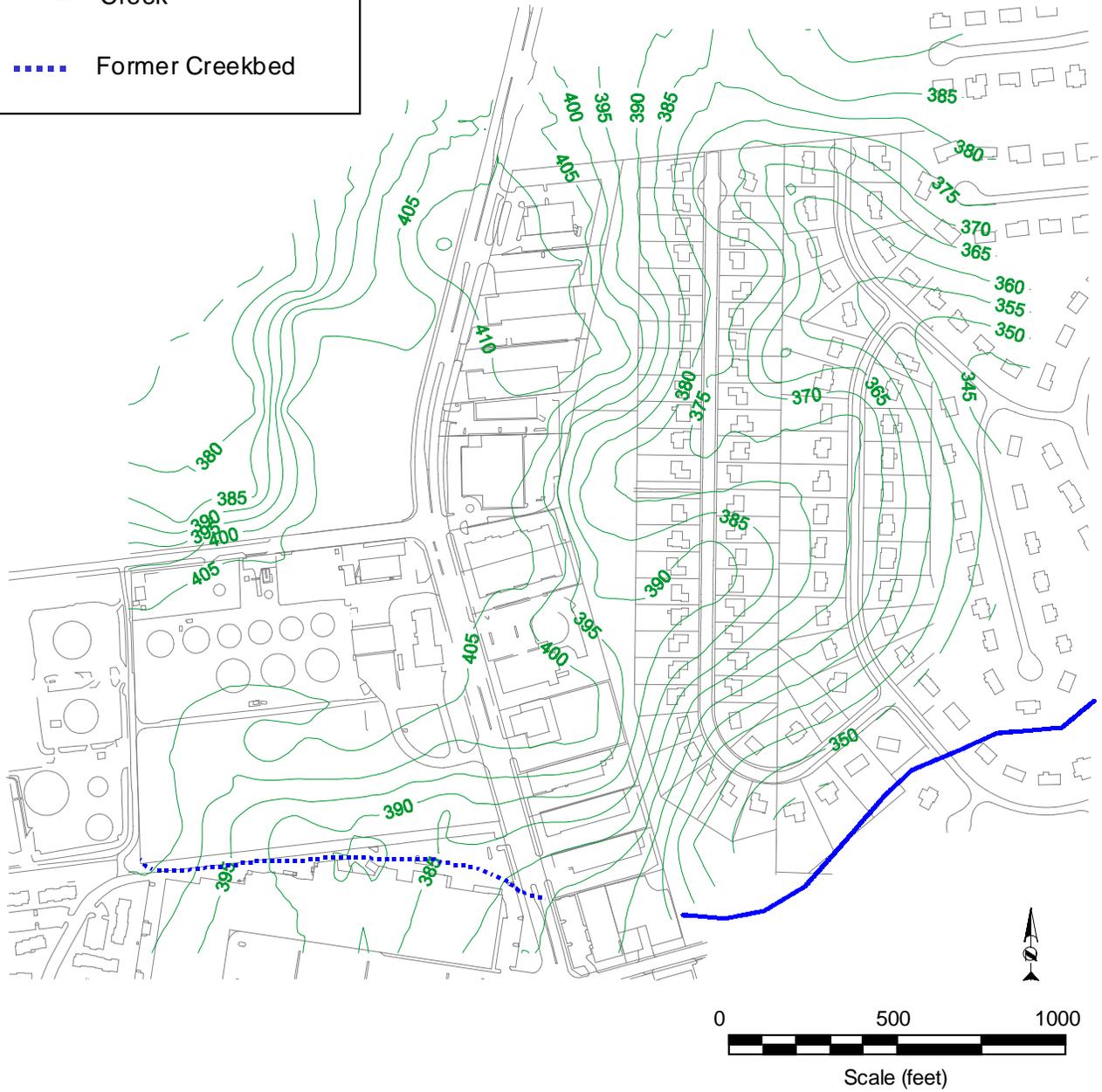
The climate of the study area is characterized by four seasons and is considered to be temperate. The average annual precipitation is approximately 41 inches (RETEC, 1997). Recharge to the aquifer occurs predominately through infiltration. Although precipitation occurs throughout the year, recharge to the aquifer is less during the summer due to increased evapotranspiration (RETEC, 1997).

### **3.1.5 Groundwater**

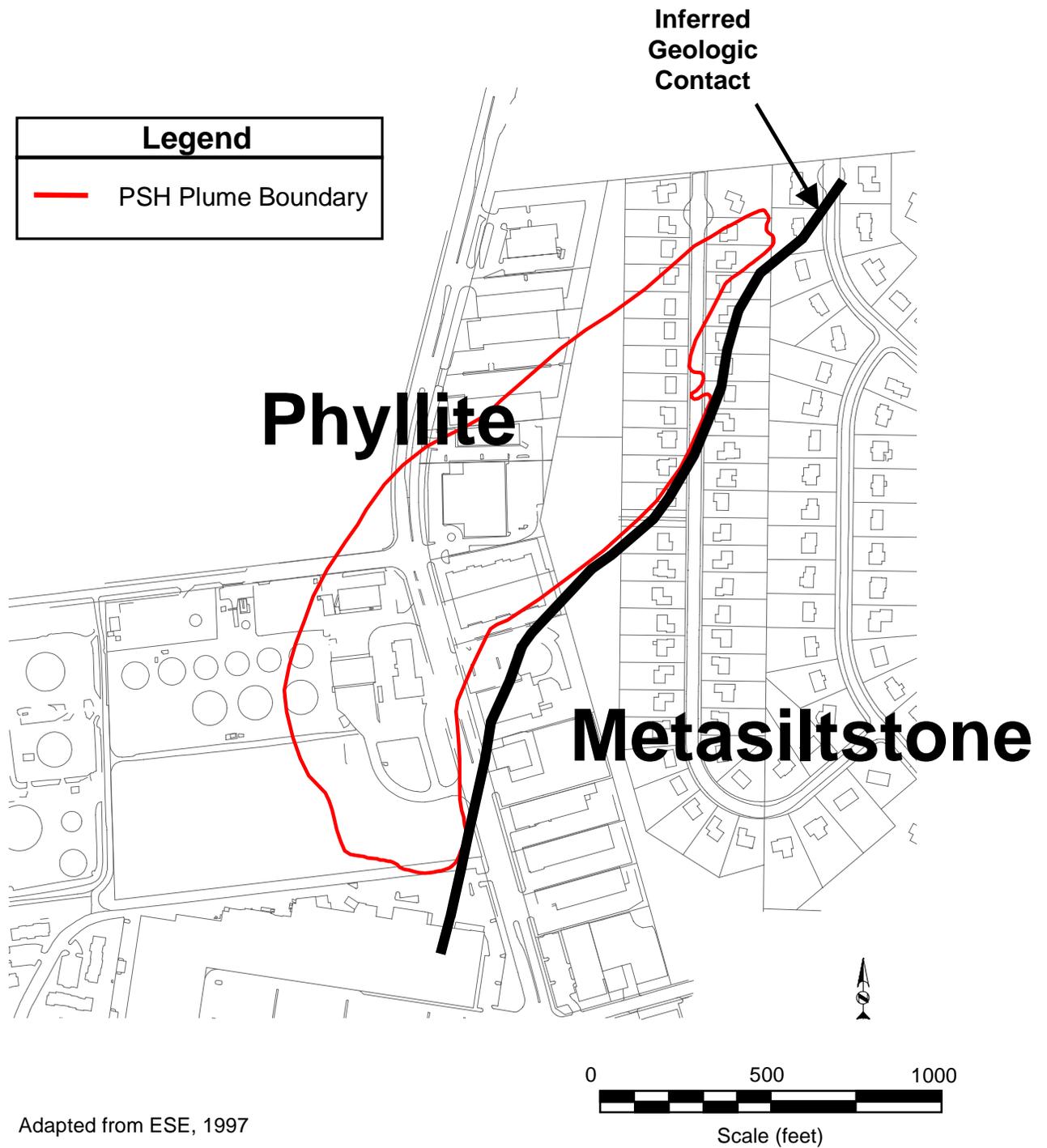
The groundwater table underlying the area occurs at a depth of 5 to 40 feet below ground surface. The water table gradient ranges from 0.01 to 0.06 and slopes predominately east and south from a groundwater divide that trends northeast from the terminal (ESE, 1993). Figure 3.5 illustrates a piezometric surface prior to installation of the interim containment system. Operation of the interim containment system has affected groundwater elevations within the study area. Recovery operations have resulted generally in a lowering of the water table and have created localized drawdown areas (Figure 3.6).

Soil moisture analyses indicate that the formation retains its moisture and that the effective porosity is approximately 2.5 percent (Daniel B. Stephens and Assoc., 1991; ESE, 1993). Measurements of aquifer specific yield confirm the low effective porosity and range from 0.001 to 0.05 (ESE, 1993). Due to the small specific yield, the aquifer is sensitive to both recharge and recovery operations causing water table elevations to fluctuate. These fluctuations typically range from 5 to 9 feet across the site as illustrated for selected monitoring wells in Figure 3.7.

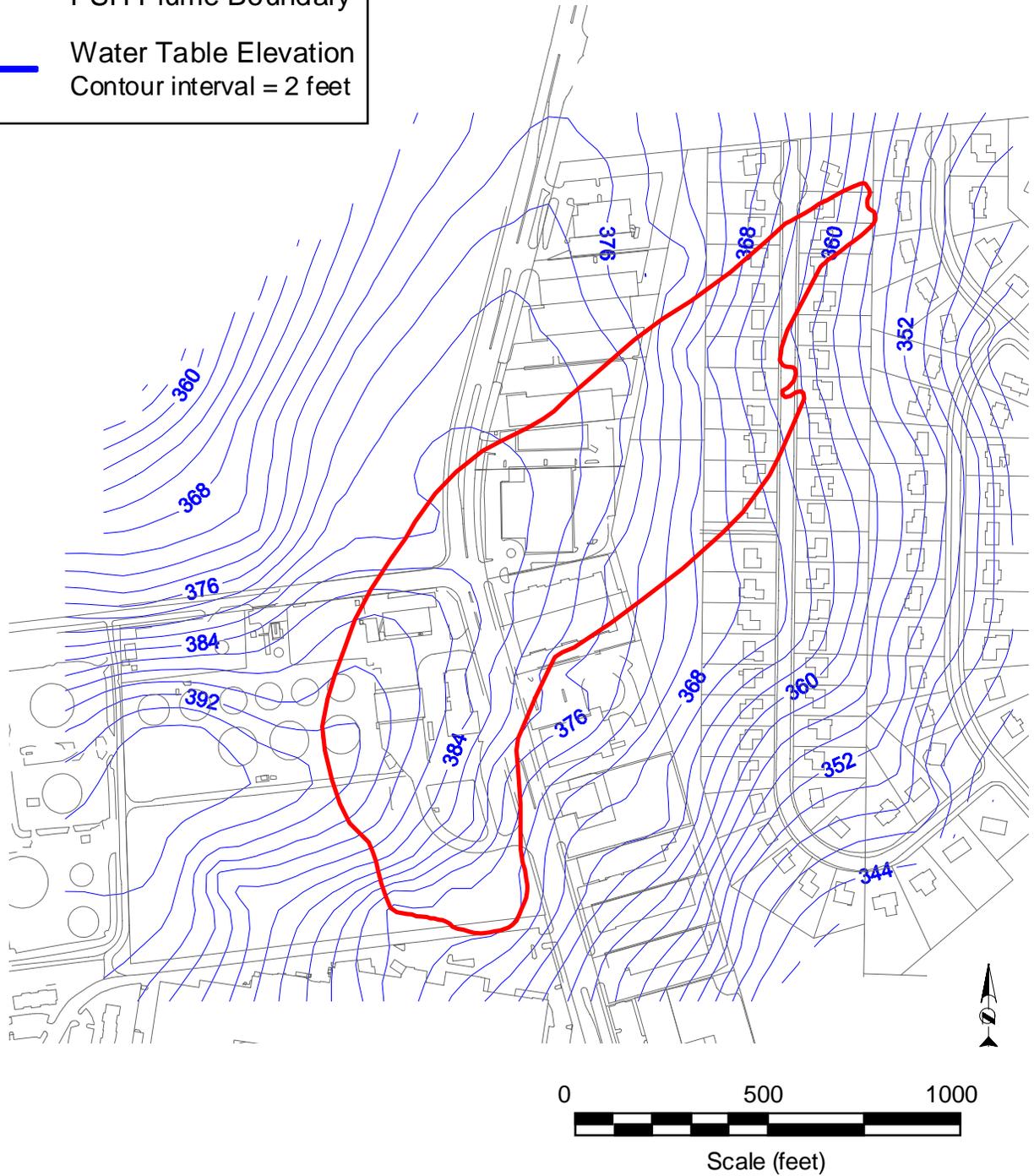
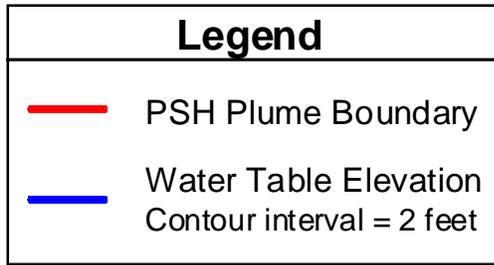
Legend	
	Ground Surface Elevation (ft MSL)
	Creek
	Former Creekbed



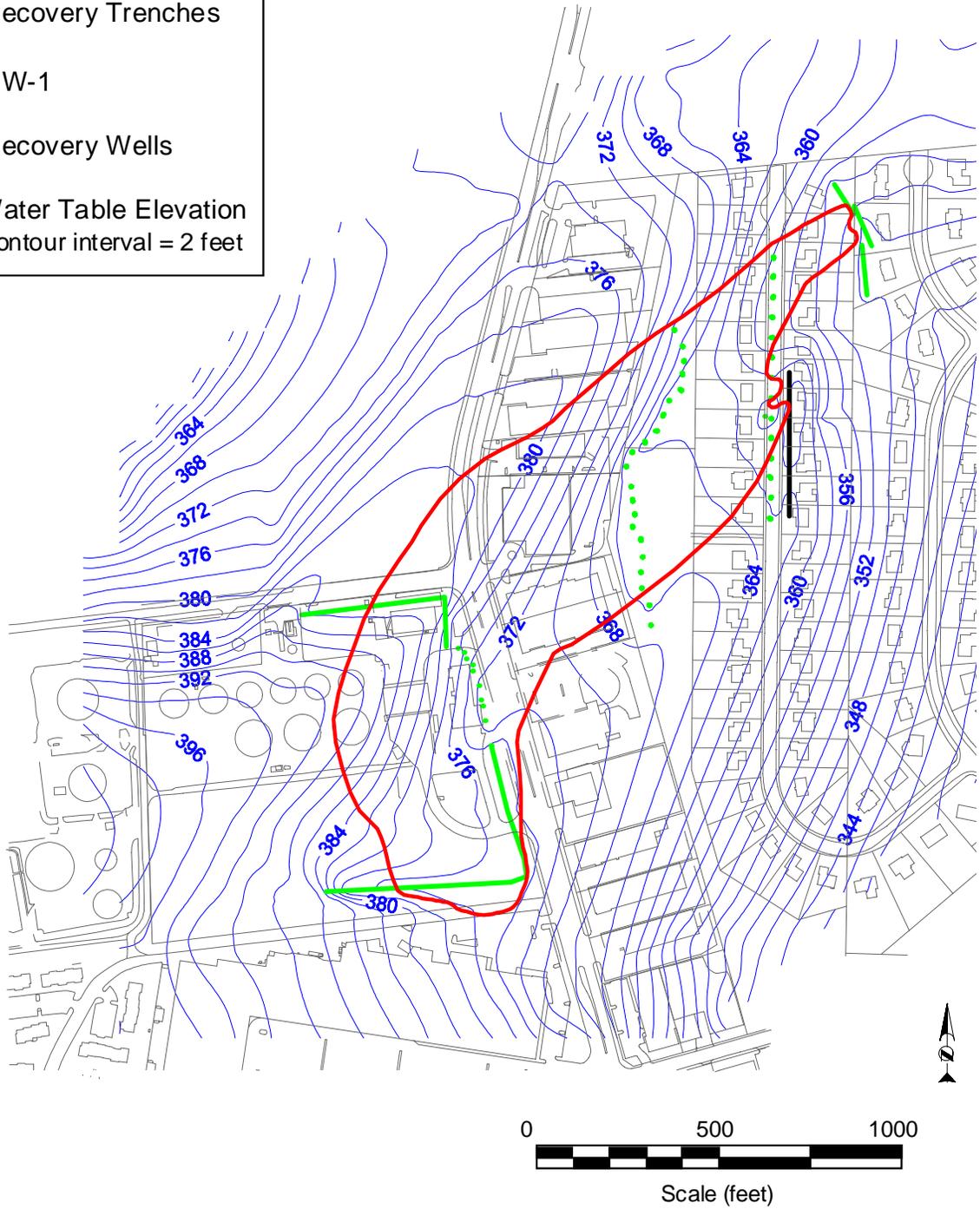
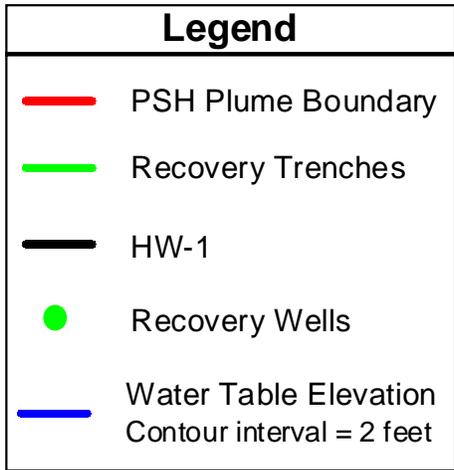
**Figure 3.3. Site topography.**



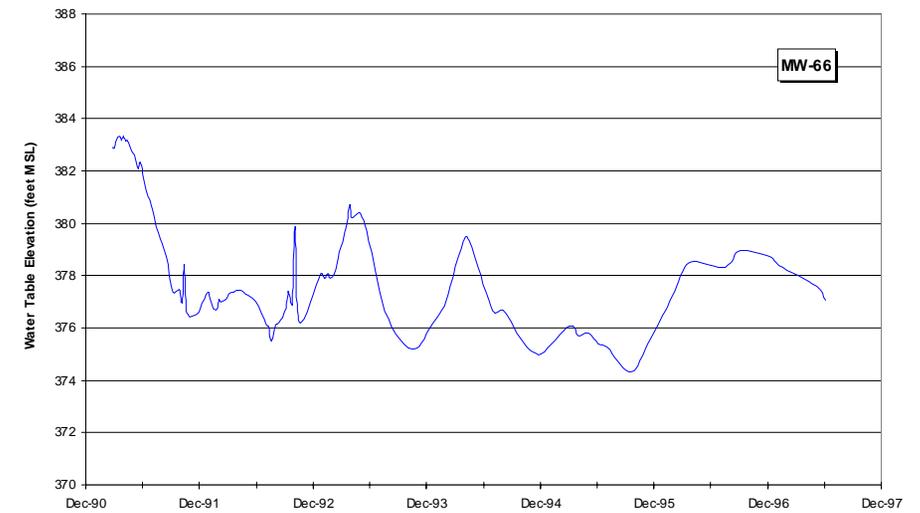
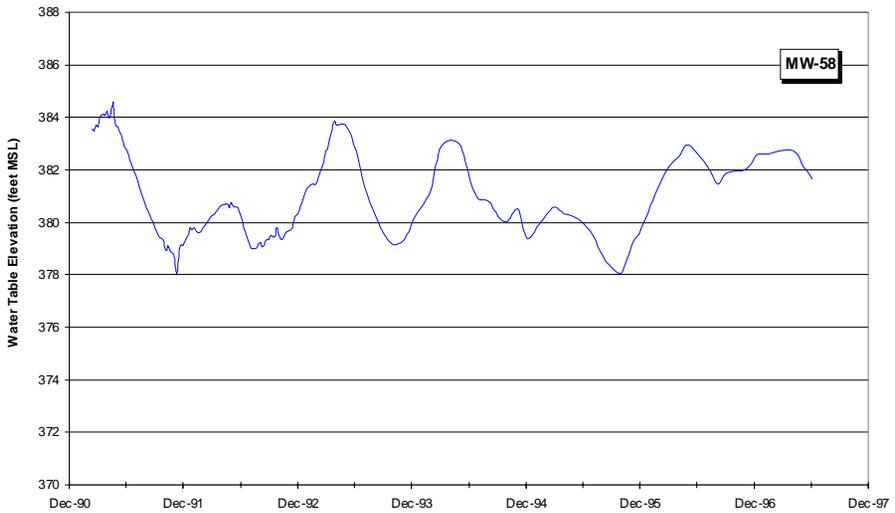
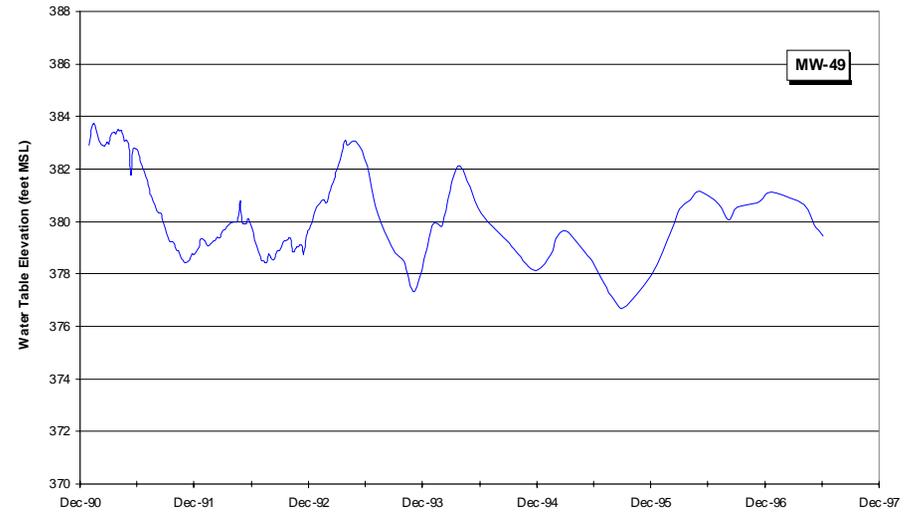
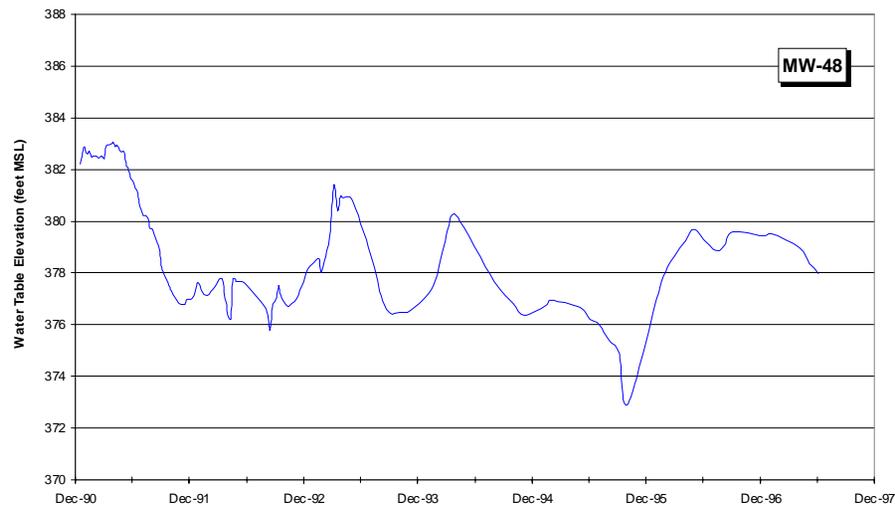
**Figure 3.4. Approximate location of geologic contact.**



**Figure 3.5. Water table elevations prior to installation of the interim containment system.**



**Figure 3.6. Average water table elevations after installation of the interim containment system.**



**Figure 3.7. Examples of water table fluctuations within the aquifer.**

Groundwater flow is predominantly horizontal, as small vertical head gradients occur within the aquifer (ESE, 1993). Because the aquifer consists primarily of foliated and jointed saprolite to a depth ranging from near surface to 70 to 140 feet, the relict northeast (N12°E - N40°E) striking foliation and joints in the saprolite cause the aquifer hydraulic conductivity to be highly anisotropic. In particular, hydraulic conductivities sub-parallel to the foliation are 1.5 to 7.5 times greater than conductivities perpendicular to the foliation (ESE, 1993). These conditions cause groundwater to flow in a northeast direction across most of the site. Field measurements of hydraulic conductivity range from 0.3 to 14.0 feet per day based on pump and slug tests and from 0.4 to 4.3 feet per day based on exfiltration tests (ESE, 1993).

### **3.1.6 Phase Separated Hydrocarbon**

Data characterizing the nature, volume, and distribution of phase separated hydrocarbon has been collected since 1990. The data consists of product thickness measurements at monitoring wells, soil analyses for total petroleum hydrocarbons (TPH), hydrocarbon composition analyses, and recovered hydrocarbon volume measurements from containment systems and well bailing. Phase separated hydrocarbon occurs as a northeast trending, elongated plume that extends from the terminal. The plume is approximately 1,750 feet long and 500 feet wide. With active bailing and skimming, apparent hydrocarbon thicknesses within the plume are typically less than 1 foot. The distribution of hydrocarbon varies through time and localized zones with higher product thicknesses exist throughout the plume.

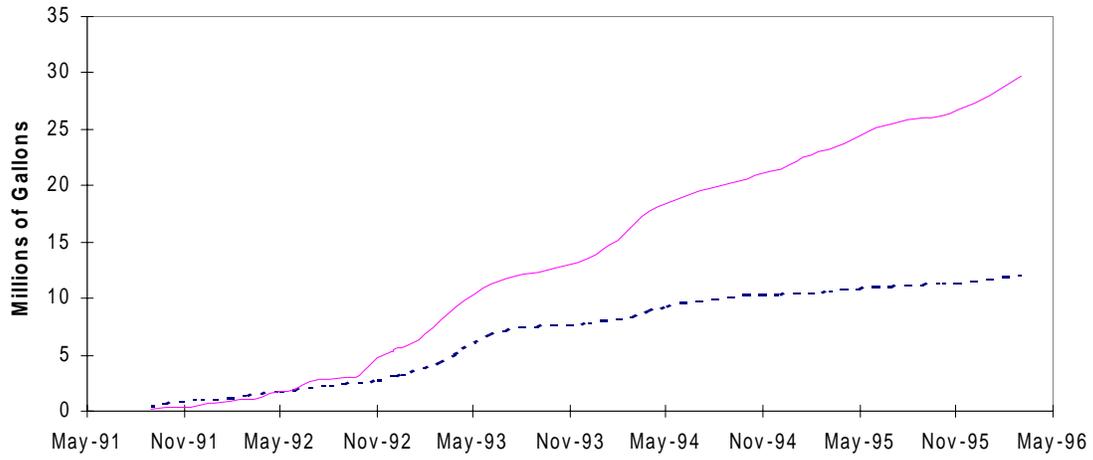
PSH composition was determined by laboratory analyses of samples collected from more than 40 monitoring wells. PSH samples were analyzed for gasoline, jet and diesel fuel, BTEX (benzene, toluene, ethylbenzene, and xylene), and MTBE (methyl-tert-butylether). The data indicate that the PSH consists mainly of a mixture of diesel (45%) and jet fuel (45%) with about 10 percent gasoline (Texaco, 1991). Of the BTEX species, xylenes typically exhibit the highest concentrations. MTBE has not been frequently detected nor at high concentrations.

Recovery of hydrocarbon has been performed since 1990. Product recovery operations include the interim containment system and bailing of monitoring wells. As of January 1996, these efforts resulted in the recovery of approximately 34,500 gallons of PSH and 40,000,000 gallons of co-produced water. Figure 3.8 illustrates the recovery trends through time for PSH and water. The recovery volume from off-site systems is approximately twice that obtained from on-site systems. Recovery of PSH was relatively rapid initially but has declined since 1994. The asymptotic product recovery is indicative of a reduction in mobile PSH at the site.

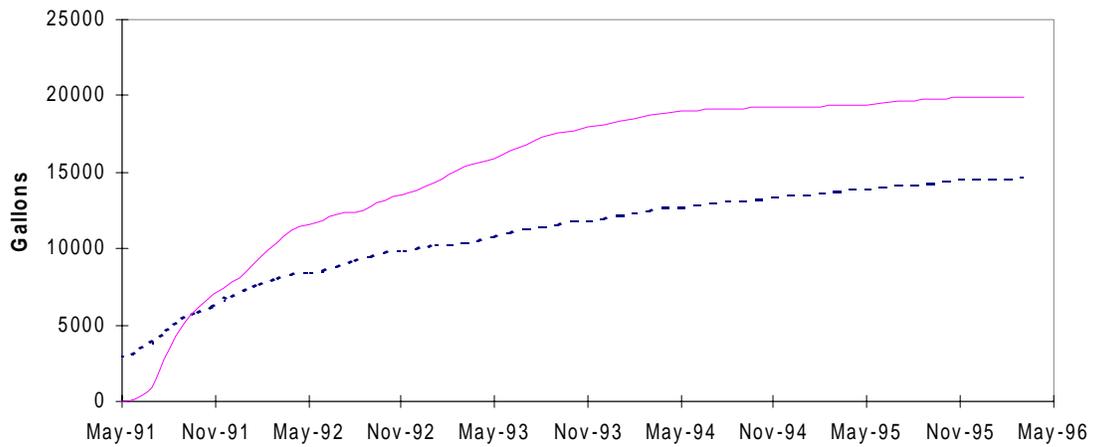
### **3.1.7 Dissolved Constituents**

In addition to fluid level measurements, groundwater has been regularly sampled for dissolved hydrocarbon constituents. Over 2,500 samples have been collected and analyzed from more than 300 monitoring wells. The sampling events have been limited to the perimeter of the dissolved plume, as it was difficult to obtain accurate measurements within the plume due to the presence of free phase hydrocarbon. Groundwater samples are usually analyzed for BTEX species and TPH as diesel, jet fuel, and gasoline. Within the perimeter of the main PSH plume, dissolved hydrocarbon concentrations vary both spatially and temporally. For example, average observed concentrations for various wells range from non-detect to 700 µg/L for benzene and from

### Measured Water Recovery



### Measured PSH Recovery



----- Total On-site

----- Total Off-site

**Figure 3.8. Measured water and PSH recovery.**

non-detect to 4,175 µg/L for TEX (a pseudo-species of toluene, ethylbenzene, and xylene). In addition, the average standard deviation in the concentration trend through time for wells within the perimeter of the plume is approximately 200 µg/L for benzene and 950 µg/L for TEX. Similar trends are observed in TPH concentrations. Concentrations of TPH as jet fuel range from non-detect to 930 mg/L with an average of 3 mg/L while concentrations of TPH as diesel range from non-detect to 2,000 mg/L with an average of 6 mg/L. Figure 3.9 illustrates monitoring locations with detections of dissolved hydrocarbon constituents.

Dissolved oxygen (DO) sampling for fourteen wells was conducted during November 1994 and March 1995. The sampling indicates that upgradient of the hydrocarbon plume the dissolved oxygen concentration in the aquifer is approximately 5 mg/L. DO concentrations within and near the plume perimeter decrease and generally range from 0.4 to 2.0 mg/L. This suggests active aerobic biodegradation of hydrocarbon within the aquifer.

### **3.1.8 Microbial Activity**

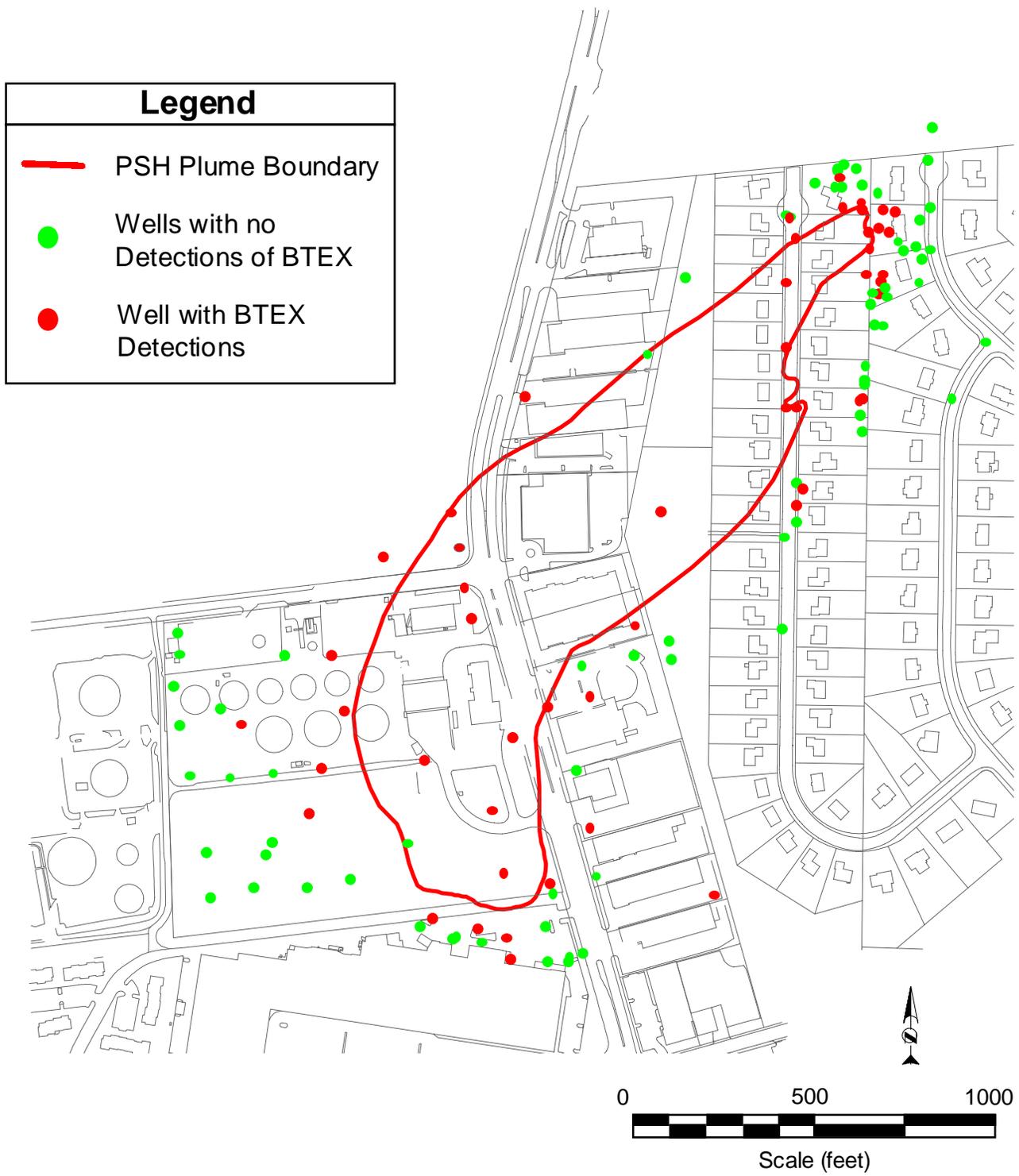
Site characterization activities included enumeration of total heterotrophic and toluene degrading bacteria. Eighteen soil and 22 groundwater samples were analyzed. Heterotrophic and toluene degrading bacteria were present at low to moderate densities across the site (RETEC, 1995a). In addition to microbial enumerations, a microbial stimulation study indicates that indigenous microbial population densities are related to the availability of oxygen (RETEC, 1995a).

### **3.1.9 Field Studies**

To better assess potential remedial alternatives at this site, small-scale field studies were conducted to evaluate the implementation and effectiveness of groundwater infiltration via horizontal wells and increased microbial decay through aquifer aeration in engineered trenches, termed microbial fences. Brief descriptions of the implementation and results of the two field studies are provided below. Detailed descriptions are available in RETEC and ESE (1995) and RETEC and ESE (1996).

**Groundwater Infiltration Field Study.** This field study was implemented to evaluate the use of artificial groundwater infiltration to improve hydraulic containment and to reduce BTEX concentrations. A horizontal infiltration well (HW-1) was installed in September 1994. Additional monitoring wells were installed upgradient and downgradient of HW-1 to assess changes in water table elevations and BTEX concentrations as a result of the artificial infiltration. The field study demonstrated that infiltration of clean water could be applied at this site to reduce BTEX concentrations. For example, dissolved benzene concentrations at one monitoring location decreased from nearly 700 µg/L to less than 5 µg/L after one and half years of infiltration (RETEC and ESE, 1995). The field study also helped delineate the geologic contact between the phyllite and the metasilstone due to the varying infiltration rates along the length of HW-1.

**Microbial Fence Field Study.** The objective of this field study was to create a zone of oxygen-enriched groundwater to enhance microbial degradation of dissolved phase hydrocarbons. A microbial fence was constructed perpendicular to the gradient near the leading, northeastern edge



**Figure 3.9. Observed dissolved phase distribution.**

of the plume and operated for 13 weeks. The microbial fence was constructed as a gravel trench containing a series of air sparging wells, which supplied oxygen to promote microbial growth in the trench. The microbial fence contained eight air sparging wells, two vapor extraction wells, and six monitoring wells. In addition, five monitoring wells were installed in the surrounding aquifer to assess changes in BTEX and DO concentrations. Results of the field study indicated an increase in microbial populations and a decrease in BTEX concentrations within the trench. In particular, after four weeks of continuous air sparging, approximately 70 percent of the BTEX samples collected within the trench were less than 5 µg/L compared to average BTEX concentrations of 160 µg/L in upgradient wells (RETEC and ESE, 1996).

## 3.2 Site Conceptualization

The flow of groundwater and hydrocarbon is conceptualized as occurring in a spatially heterogeneous and anisotropic aquifer. The heterogeneous and anisotropic conditions result from the foliated and jointed aquifer material and the variable surface and soil characteristics. Water and hydrocarbon are controlled by gradients induced by groundwater recovery and recharge. The flow of water and hydrocarbon is primarily horizontal in the aquifer. This is supported by minimal observed vertical gradients and vertical heterogeneity in the saturated aquifer. Vertical movement of water and oil occur primarily in the unsaturated zone. For example, vertical water flow results from rainfall infiltration, and downward vertical oil flow results from drainage of residual hydrocarbons above the water table. In addition, water table fluctuations due to the low specific yield of the aquifer, in conjunction with recovery operations and seasonal recharge, have caused vertical movement of hydrocarbon and the development of a hydrocarbon smear zone. Hydrocarbon migration could also be controlled in some areas by lithology, as the less fractured metasiltstone appears to act as a barrier to hydrocarbon flow (ESE, 1997). Figure 3.10 illustrates the conceptualization of groundwater and hydrocarbon flow within the aquifer.

The conceptual model of dissolved phase hydrocarbon fate and transport includes the dissolution, migration, retardation and degradation of dissolved hydrocarbons within the aquifer. Soluble species in the PSH dissolve into the aquifer via two mechanisms: (1) recharge infiltrating vertically through the unsaturated zone, and (2) horizontal groundwater flow. Once present in the dissolved phase, the constituents are transported by advection and dispersion. Other processes that may influence the transport include adsorption-desorption and biodecay. In particular, biodegradation is considered an aerobic process and is oxygen-limited.

## 3.3 Groundwater and Hydrocarbon Flow Model

Previous modeling efforts at this site utilized the numerical model ARMOS to simulate groundwater flow. Therefore, ARMOS was also utilized in this analysis to model groundwater and hydrocarbon flow. ARMOS is a two-dimensional, finite element computer model that is capable of simulating transient water and hydrocarbon flow in heterogeneous, anisotropic aquifers. ARMOS is a proprietary model developed by Environmental Systems & Technologies (ES&T) that is widely utilized and recognized by the U.S. EPA. ARMOS assumes vertical equilibrium pressure distributions of water and hydrocarbon and considers residual hydrocarbon in the saturated and unsaturated zones associated with changing water and oil tables. ARMOS can also perform the following:

- simulate complex patterns of recovery wells and trenches utilizing an irregular mesh,
- specify recovery well and trench pump intake control elevations,
- automatically disable recovery when water levels drop below pump control elevations, and
- simulate spatially and temporally variable recharge.

These capabilities allow ARMOS to accurately simulate the changing aquifer conditions associated with the research site. Detailed descriptions and verification of ARMOS are available in ES&T (1994a, 1996a).

### 3.3.1 Model Domain

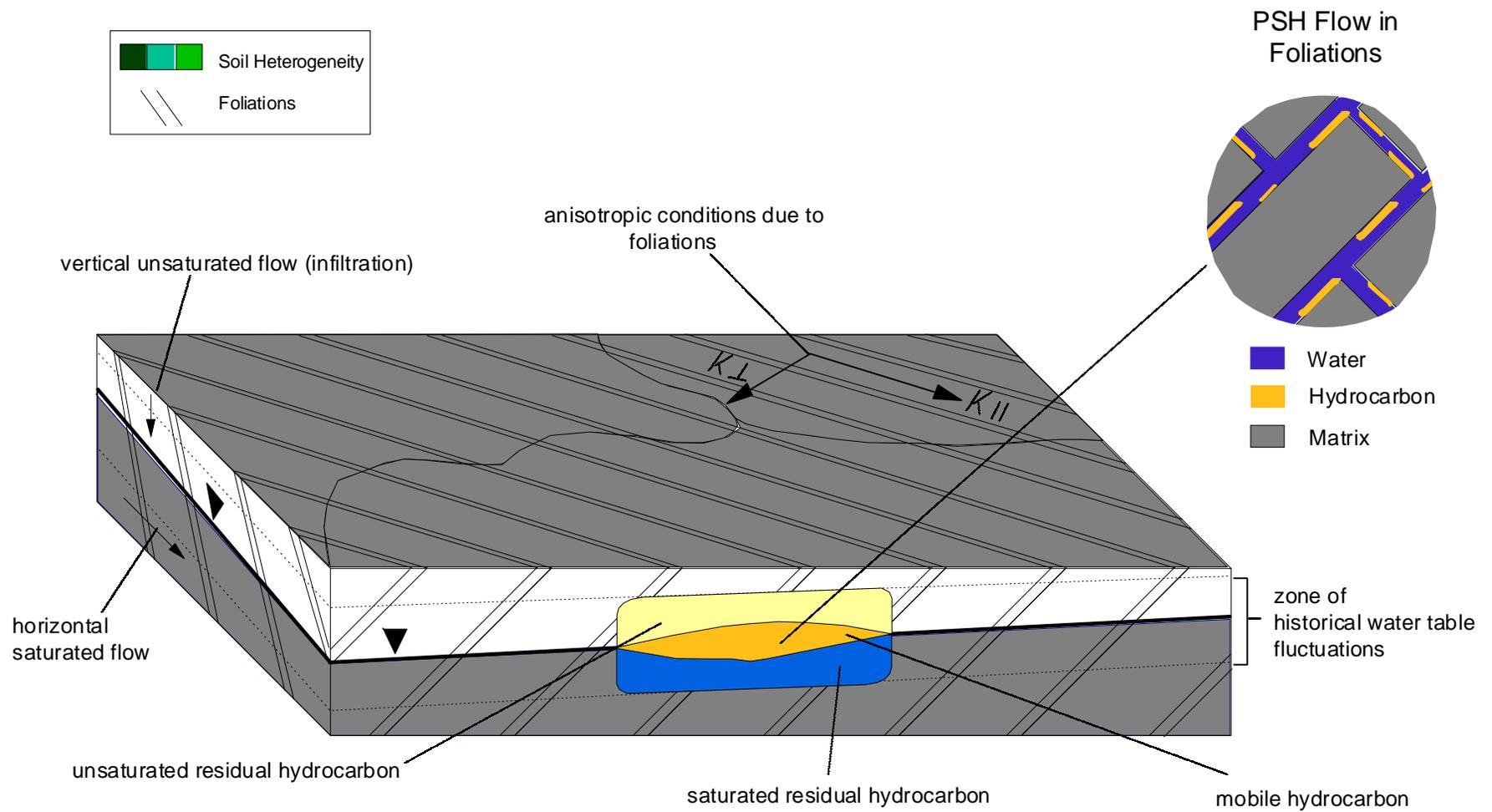
The finite element mesh utilized in the original modeling effort was maintained in this research. The model domain covers approximately 150 acres and incorporates both on- and off-site areas where reliable monitoring well fluid level data exist. The finite element mesh is constructed primarily of quadrilateral elements, with triangular elements in transition zones (Figure 3.11). The mesh consists of 9,527 nodes, with nodal spacing ranging from 6.25 feet (to accommodate water infiltration from HW-1) to 100 feet on the perimeter of the domain. Nodal spacing proximal to recovery wells and trenches is 12.5 feet. Nodal locations were specified to coincide with recovery well locations.

### 3.3.2 Model Parameters and Initial Conditions

Field and laboratory measurements were utilized whenever possible to directly define input parameters for the groundwater and hydrocarbon flow model. Selected parameters were then refined during the model calibration process.

**Recharge.** Recharge is a significant hydrologic component at this site due to the low specific yield of the aquifer. Transient recharge rates were estimated with the aid of the U.S. EPA's Hydrologic Evaluation of Landfill Performance (HELP) model. HELP is a quasi two-dimensional deterministic water budget model that uses daily climatological data to compute runoff, evapotranspiration, and vertical and lateral drainage (Schroeder et al., 1988). The HELP modeling utilized daily precipitation data collected from January 1991 to January 1996. Ten recharge zones were defined to simulate variable surface cover conditions observed at the site. For each recharge zone, the temporally transient recharge rate was scaled by a factor to compensate for surface coverage differences. Appendix A provides precipitation data, estimated recharge rates, and the spatial delineation of recharge zones applied to the site.

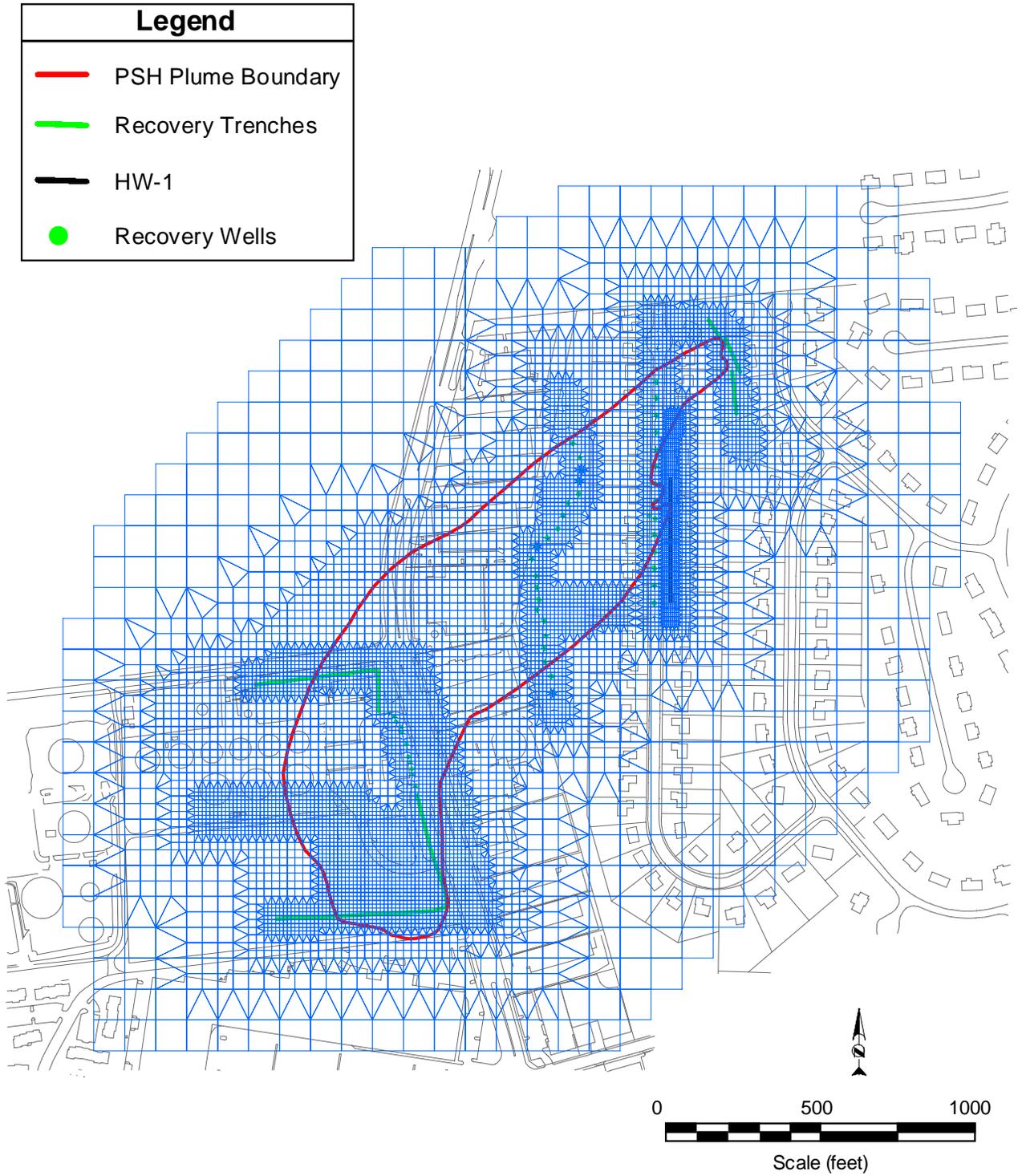
**Soil Properties.** Spatially heterogeneous soil properties can be simulated in ARMOS by delineating multiple soil zones. Sixteen soil zones were defined to reflect differences in hydraulic conductivity, anisotropy, or lithology. Delineation was based on results of site characterization and field activities. Soil zones that represent fill material were modeled as isotropic media. Soil zone delineation and soil parameters associated with each soil zone are provided in Appendix A.



### Site Conditions:

- Anisotropic flow conditions
- Horizontal water and PSH flow in aquifer
- Vertical water and PSH flow in the unsaturated zone
- Heterogeneous soil and infiltration conditions
- Hydrocarbon migration between mobile and residual phases due to water fluctuations

**Figure 3.10. Conceptualization of groundwater and hydrocarbon flow within the aquifer.**



**Figure 3.11. Model mesh.**

**Hydrocarbon Properties.** Hydrocarbon migration and recovery depend upon hydrocarbon properties and capillary pressure scaling factors. The properties and factors considered in the model are based on laboratory analyses of PSH samples. The analyses indicated that the hydrocarbon consists mainly of a mixture of diesel (45%) and jet fuel (45%) with a minor amount of gasoline (10%). Descriptions of the hydrocarbon parameters and their values applied in the model are available in Appendix A.

**Recovery Wells and Trenches.** Recovery operations have influenced groundwater flow patterns and elevations across the site. These flow conditions were considered in the model. Water recovery from wells and trenches was simulated by specifying a controlled water level. This water level represents the high probe elevation of the pumps in the wells or trenches. In the model, water recovery at a well occurred unless surrounding water levels decreased below the assigned high probe elevation, in which case a no-flow condition was imposed at the well. Unlike individual recovery wells, water may flow along a trench. Therefore, in the model sections of a trench were allowed to recharge provided net flow for the entire trench was positive. Pump elevations in some wells varied over time and are represented accordingly in the model. In addition, recovery wells and/or trenches were activated or deactivated over time and these system changes were also incorporated into the model.

Hydrocarbon recovery in wells and trenches was simulated in a manner similar to water recovery. In the model, hydrocarbon removal occurred at a recovery well unless product levels adjacent to the well fell below the high probe elevation in the well. In addition to product recovered by trenches and recovery wells, thousands of gallons of product have been removed by bailing of monitoring wells. To account for this product removal mechanism in the model, bailing wells were added. A bailing well simulated only oil pumping and was controlled by the presence of product in the well. Any monitoring well from which at least 100 gallons of product had been bailed by October 1993 was designated in the model as a bailing well.

**Initial and Boundary Conditions.** The initial water table elevations in the model represent fluid levels observed in monitoring wells in May 1991. These data were augmented by fluid levels collected from additional monitoring wells that were installed between May 1991 and August 1991 and from fluid levels collected from monitoring wells at the adjacent terminal in the time period around May 1991. For wells containing free product, water levels were corrected for the oil thickness.

The water table on the perimeter of the model domain was allowed to vary according to known historical water table fluctuations. This condition was implemented by applying a boundary water table fluctuation schedule to the perimeter nodes to simulate seasonal water table fluctuations. The boundary fluctuation schedule was generated by interpolating observed groundwater levels at different times to the boundary nodes. This approach allowed for the simulation of seasonal high and low water table conditions.

Since seasonal water table fluctuations were assumed to have produced a hydrocarbon smear zone, the initial hydrocarbon distribution in the model was composed of both mobile and residual PSH. The mobile PSH volume in the model was calculated using nodal values for the hydrocarbon thickness, the hydrocarbon fluid properties, and the soil capillary properties. The apparent hydrocarbon thickness is difficult to accurately define at a given time because manual

and automated recovery efforts have been routinely performed on the monitoring wells, and hence, hydrocarbon equilibrium conditions have not occurred during any monitoring event. Therefore, to estimate the mobile PSH volume, the maximum observed hydrocarbon thickness for all wells screened at the water table was assumed as the initial condition. These data points were interpolated to the nodes of the domain using a kriging algorithm. The estimated total mobile PSH volume was approximately 160,000 gallons. Based on estimated capillary parameter values and the average smear zone thickness, the total residual hydrocarbon volume was calculated to be approximately 37,000 gallons, of which 75 percent was assumed to be saturated residual. Therefore, the total initial hydrocarbon volume in the model was estimated to be approximately 197,000 gallons.

### **3.3.3 Calibration**

Calibration is the process by which site-specific model parameters are estimated from field data. Through model calibration, a set of parameters and boundary conditions is determined that is capable of reproducing measured field conditions to a specified level of accuracy. Model calibration may be performed by manual trial-and-error parameter adjustment or by automated parameter estimation (Anderson and Woessner, 1992). In this modeling, the trial-and-error calibration method was applied.

Calibration of the groundwater and PSH flow models was performed for a 1000-day time period, extending from May 1991 to February 1994. Although calibration for groundwater flow and hydrocarbon flow are discussed in separate sections and have differing calibration criteria, the model solves for groundwater and hydrocarbon flow simultaneously.

#### **3.3.3.1 Groundwater Flow**

Calibration of the groundwater flow model involved three criteria: (1) comparison of simulated and observed cumulative water recovery volumes, (2) statistical analysis of the difference between simulated and observed groundwater elevations, and (3) spatial and temporal comparison between simulated and observed groundwater elevations. More specifically, the model was considered calibrated when all of the following were achieved:

- the difference between simulated and observed cumulative water recovery volumes was less than 10 percent for both on-site and off-site systems,
- the root mean square error (RMSE) between simulated and observed water table elevations was less than 3 feet (5 percent of the average observed head difference within the model domain) for selected observation periods, and
- an average of 80 percent of the simulated water table elevations were within 3 feet of the observed water table elevations for selected observation periods.

Model calibration was conducted by adjusting the recharge factor of the recharge zones and the hydraulic conductivity, anisotropy ratio, anisotropy angle, and boundaries of the soil zones. Detailed descriptions of these modeling parameters and the final calibrated values are provided in Appendix A.

The results of the calibration indicated that the groundwater flow model reasonably simulated the observed conditions. In particular, the simulated cumulative trend in water recovery for both on-site and off-site systems agreed well with the observed trends (Figure 3.12). Simulated water recovery volumes were within the calibration criterion of 10 percent of the observed water recovery volumes for the calibration period.

Statistical analyses of the difference between simulated and observed water table elevations were performed for seven time periods between October 1991 and February 1994. The analyses indicated that the model reasonably simulated the water table elevations. Specifically, the RMSE ranged from 1.66 to 2.4 feet, with an average of 2.07 feet (Table 3.1). All RMSE values were less than the calibration criterion and the average RMSE value was approximately 1 foot less than the calibration criterion.

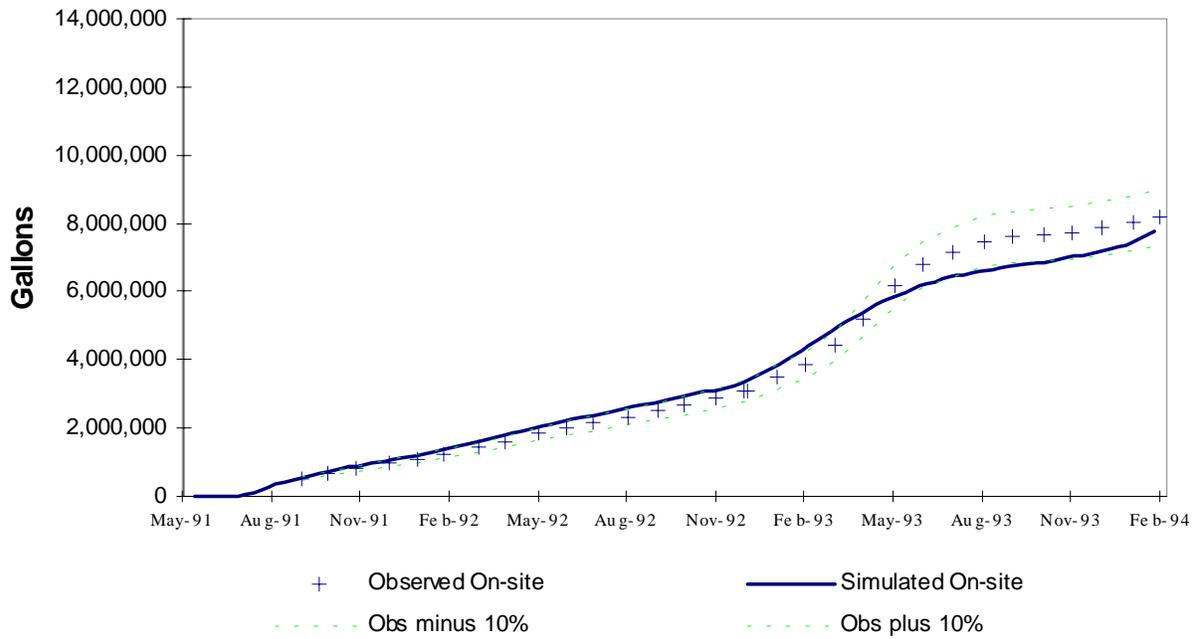
Plots of the difference in simulated and observed groundwater elevations were generated at different time periods to ascertain potential trends spatially and temporally within the calibration time period. Emphasis was placed on the later portion of the calibration period, when more observed data were available. Results of this analysis indicated that the model reliably simulated the observed water table elevations across the site. On average, 85 percent of the observed elevations were simulated within 3 feet by the model for the selected observation times (Table 3.1). As an example, Figure 3.13 illustrates the difference between the simulated and observed water table elevations for November 1993.

In summary, results of the calibration process were within the specified calibration criteria and indicated that the model reasonably simulated the spatial and temporal groundwater flow conditions.

**Table 3.1. Results of Calibrated Groundwater Flow Model.**

<b>Observation Time</b>	<b>Number of Wells Gauged</b>	<b>Percent of Simulated WT Elevations Within 3 Feet of Observed Elevations</b>	<b>Root Mean Square Error (feet)</b>
October 1991	164	80	2.32
March 1992	168	77	2.40
August 1992	216	84	2.00
January 1993	291	88	2.02
August 1993	287	89	1.94
November 1993	287	93	1.66
February 1994	290	85	2.14
<b>Average</b>	N/A	85	2.07

### On-site Water Recovery



### Off-site Water Recovery

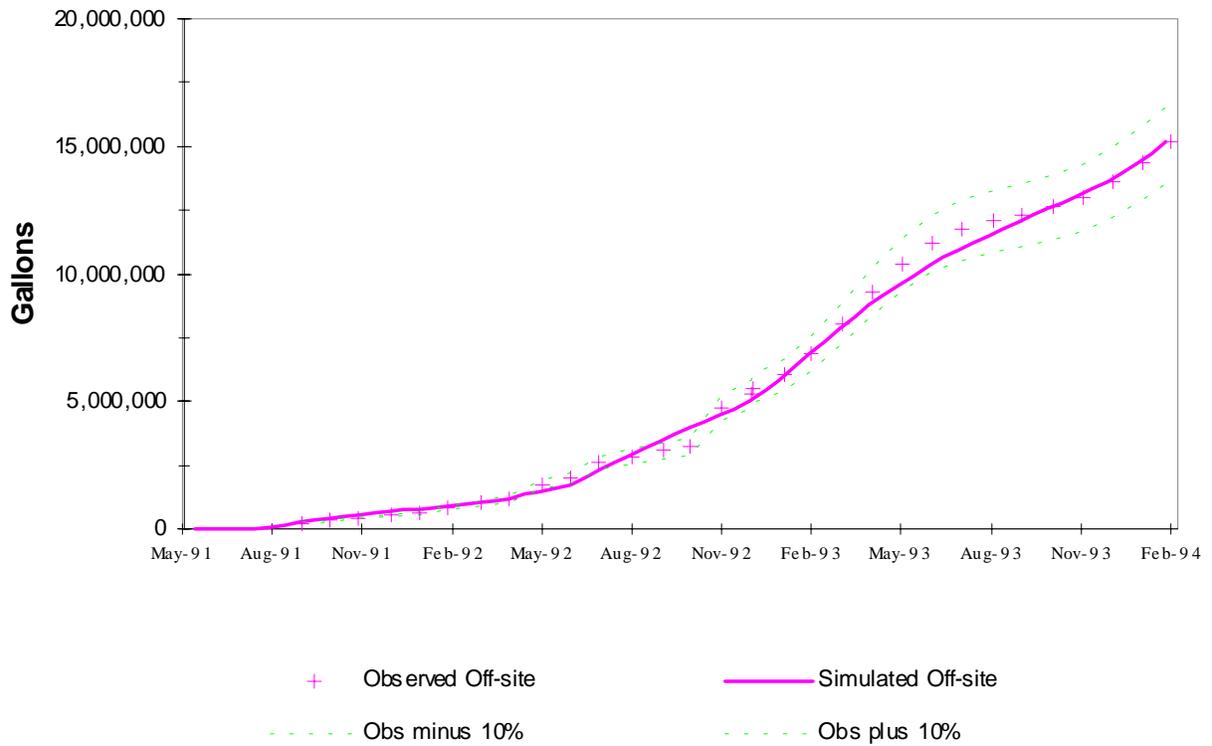
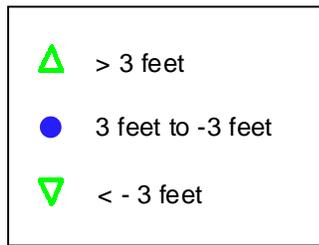
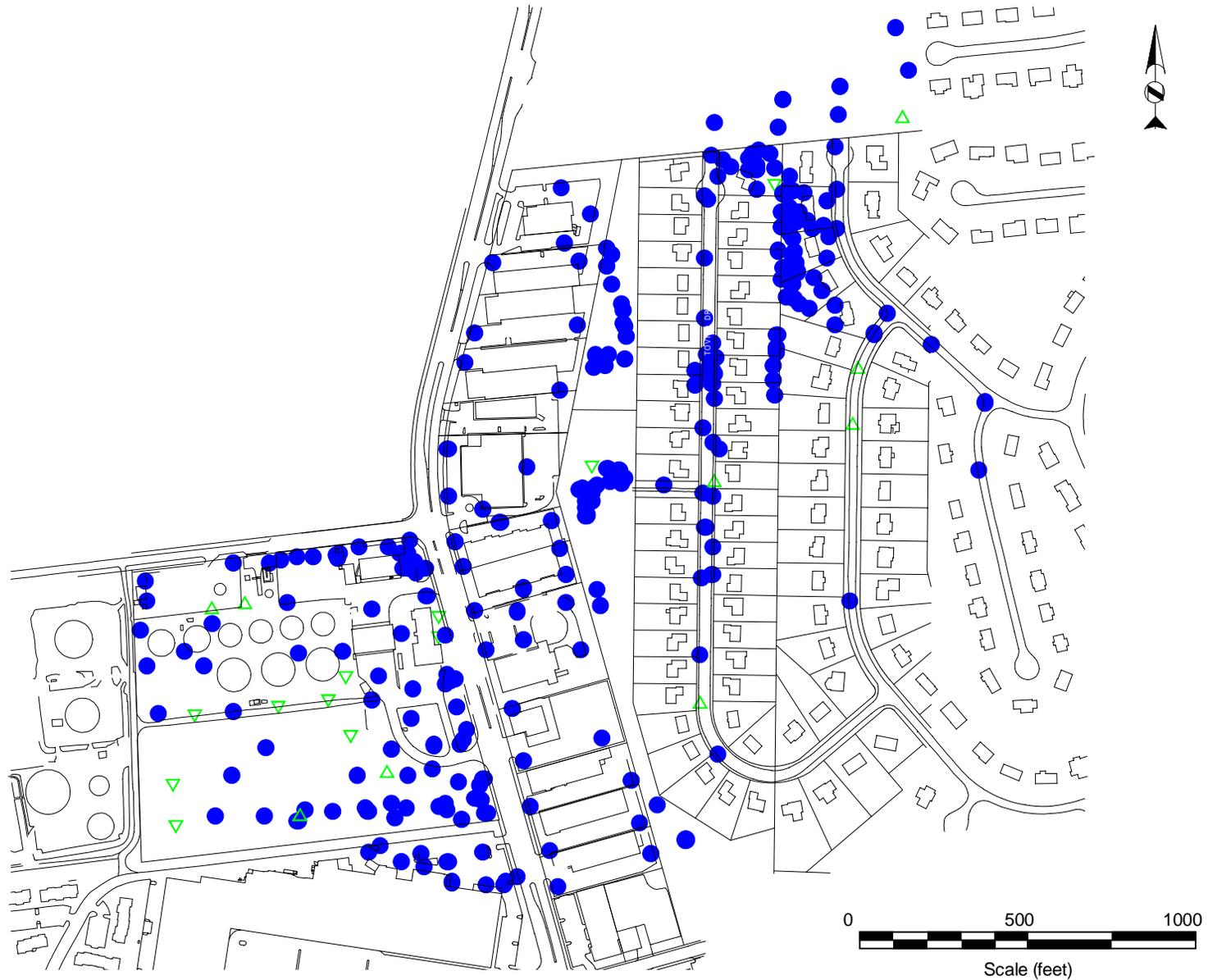


Figure 3.12. Predicted on-site and off-site water recovery during calibration period.



RMSE = 1.66

93% of predicted values  
within 3 feet of observed  
values



**Figure 3.13. Difference between simulated and observed water table elevations for November 1993.**

### **3.3.3.2 Hydrocarbon Flow**

Calibration of the hydrocarbon flow model involved comparison of simulated and observed cumulative hydrocarbon recovery. More specifically, the model was considered calibrated when all of the following were achieved:

- the difference between total simulated and observed cumulative hydrocarbon recovery volumes was less than 10 percent,
- the difference between simulated and observed cumulative hydrocarbon recovery volumes was less than 10 percent for both on-site and off-site systems, and
- the simulated rates of recovery reasonably matched the observed recovery rates as evidenced by similar slopes of the cumulative recovery curves.

Hydrocarbon thickness at monitoring well locations was not used as a calibration criteria because the monitoring wells are routinely bailed, and hence, do not achieve equilibrium.

Model calibration was conducted by adjusting the van Genuchten  $\alpha$  and  $n$  parameters and the maximum residual hydrocarbon content in the saturated and unsaturated zones. Detailed descriptions of these modeling parameters and the final calibrated values are provided in Appendix A.

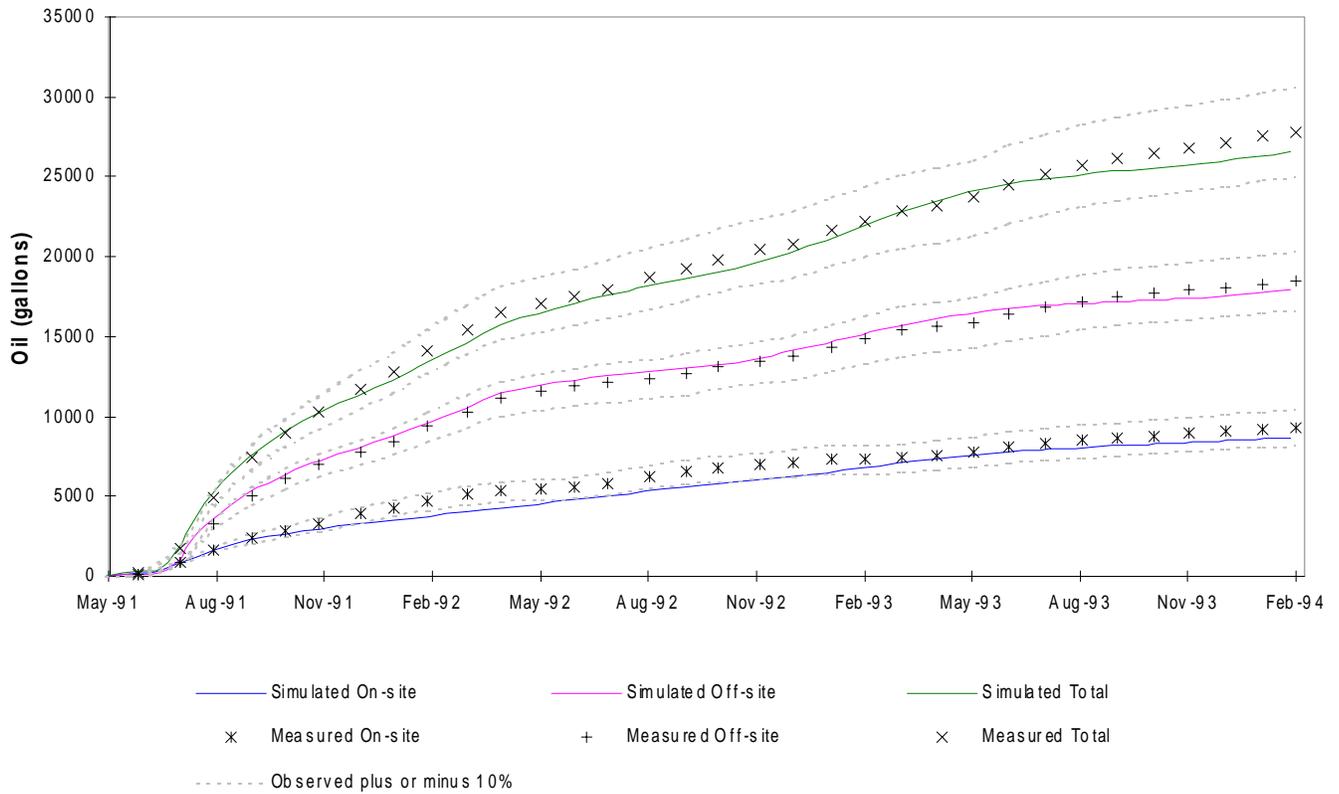
The results of the calibration indicated that the hydrocarbon flow model reasonably simulated the observed hydrocarbon recovery. In particular, the simulated trend in cumulative hydrocarbon recovery was within the calibration criteria and slopes of the recovery curve were matched. As shown in Figure 3.14, the model simulated observed conditions through the calibration time period. Deviations between simulated and observed recovery were generally less than 5 percent. Most importantly, the model simulated the varying hydrologic conditions during the calibration period, as exemplified by the good match in the slope of the cumulative curve through time.

Cumulative hydrocarbon recovery was simulated within 10 percent of the observed recovery volumes for both on-site and off-site systems. The model simulation of off-site recovery agreed closely with observed recovery trends through time. For the on-site system, the simulated hydrocarbon recovery volumes were less than the observed recovery volumes for most of the calibration period. However, the differences were generally less than 10 percent, and the simulated hydrocarbon recovery was generally within the calibration criterion. Therefore, the trends in hydrocarbon recovery were reliably matched.

### **3.3.4 Verification**

Model verification is the process whereby model assumptions and parameter values are tested by comparing model results with data that was not utilized for model calibration to establish the predictive capability of the model (ASTM, 1996). In general, the independent data set should be one that represents a unique hydrologic event, such as a pumping test, a major recharge event, or a drought. The resultant goal of the verification process is to test the model to determine “if its accuracy and predictive capability have been proven to lie within acceptable limits of error” (Konikow, 1978).

## Observed and Simulated PSH Recovery



**Figure 3.14. Predicted on-site and off-site hydrocarbon recovery during calibration period.**

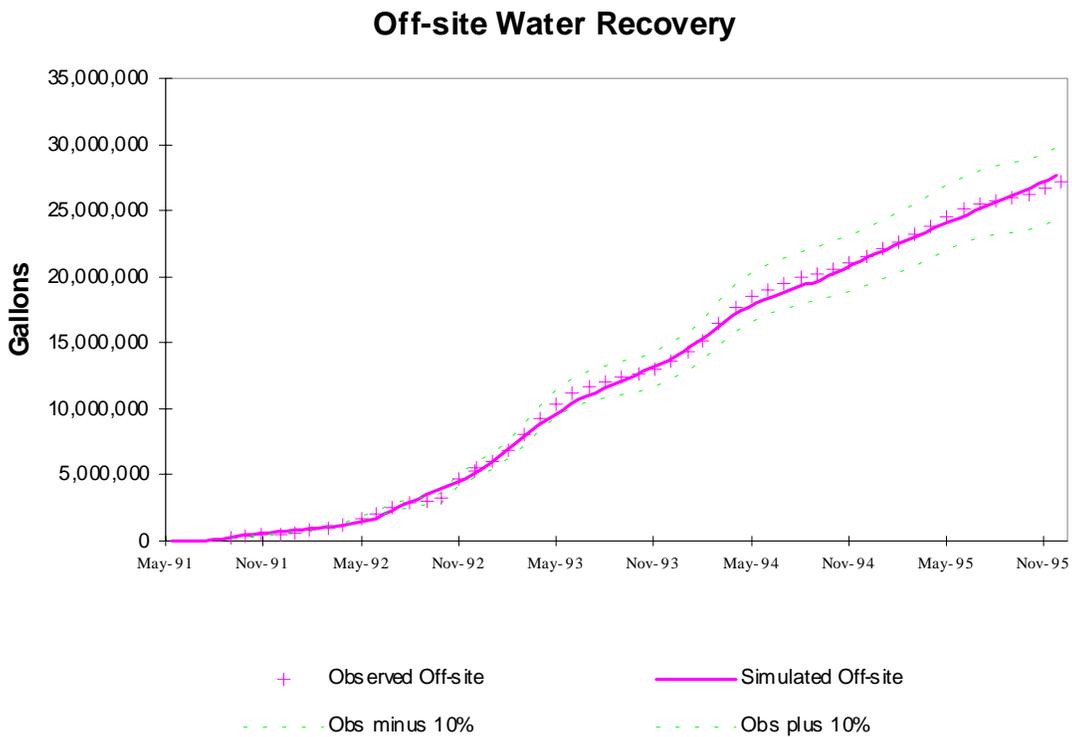
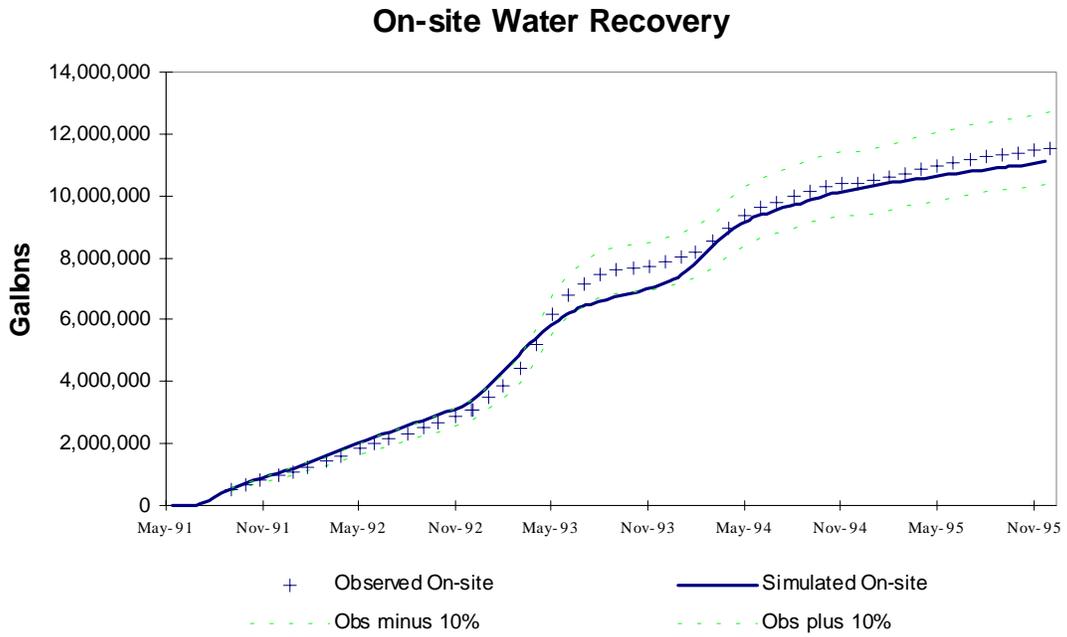
Verification of the groundwater and hydrocarbon flow model was conducted over a 675-day time period, extending from the end of the calibration period (February 1994) to December 1995. The verification period was characterized by different conditions than during the calibration period. In particular, significant precipitation occurred early in the verification period and was followed by a long period of relatively low precipitation. In addition, infiltration in the horizontal well HW-1 was initiated in September 1994. These conditions were unique to the verification period, and hence, provided insight into the reliability of the model. The criteria for verification were the same as those defined for the model calibration.

#### **3.3.4.1 Groundwater Flow**

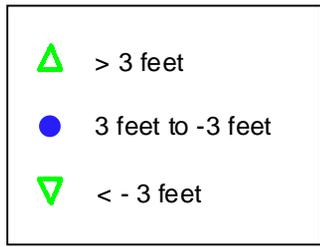
Results of the verification indicated that the model reliably simulated groundwater flow conditions at the site. In particular, the simulated cumulative trend in water recovery for both on-site and off-site systems agreed well with the observed trends (Figure 3.15). Simulated water recovery volumes were within the verification criterion of 10 percent of the observed water recovery volumes during the verification period.

Statistical analyses of the difference between observed and simulated water table elevations were performed for four time periods: July 1994, December 1994, July 1995, and October 1995. The analyses indicated that the model reliably predicted water table elevations. During the verification period, the RMSE ranged from 1.6 to 2.0 feet and averaged 1.8 feet (Table 3.2). The maximum RMSE was less than the verification criteria of 3 feet. In addition, the average RMSE value during the verification period was less than the average RMSE during the calibration period. Plots of the difference in simulated and observed water table elevations were generated at the four time periods to evaluate potential spatial and/or temporal trends in the model results. The plots indicated that the model reliably simulated observed water table elevations. On average, more than 90 percent of the observed elevations were simulated within 3 feet by the model for the selected observation times. Figure 3.16 illustrates the difference between observed and simulated water table elevations for October 1995.

In conclusion, the model reliably simulated the observed groundwater flow conditions across the site as indicated by the results of model verification. The model simulated the observed transient groundwater table conditions under various and changing states of recharge and pumping. In addition, the on-site and off-site water recovery volumes and trends were also well simulated by the model. These results indicated that reliable values have been determined for the various aquifer parameters and that the model can simulate groundwater flow conditions under different and unique conditions.



**Figure 3.15. Predicted on-site and off-site water recovery during verification period.**



RMSE = 1.56

94% of predicted values  
within 3 feet of observed  
values



**Figure 3.16. Difference between simulated and observed water table elevations for October 1995.**

**Table 3.2. Results for the Groundwater Flow Model during Verification Period.**

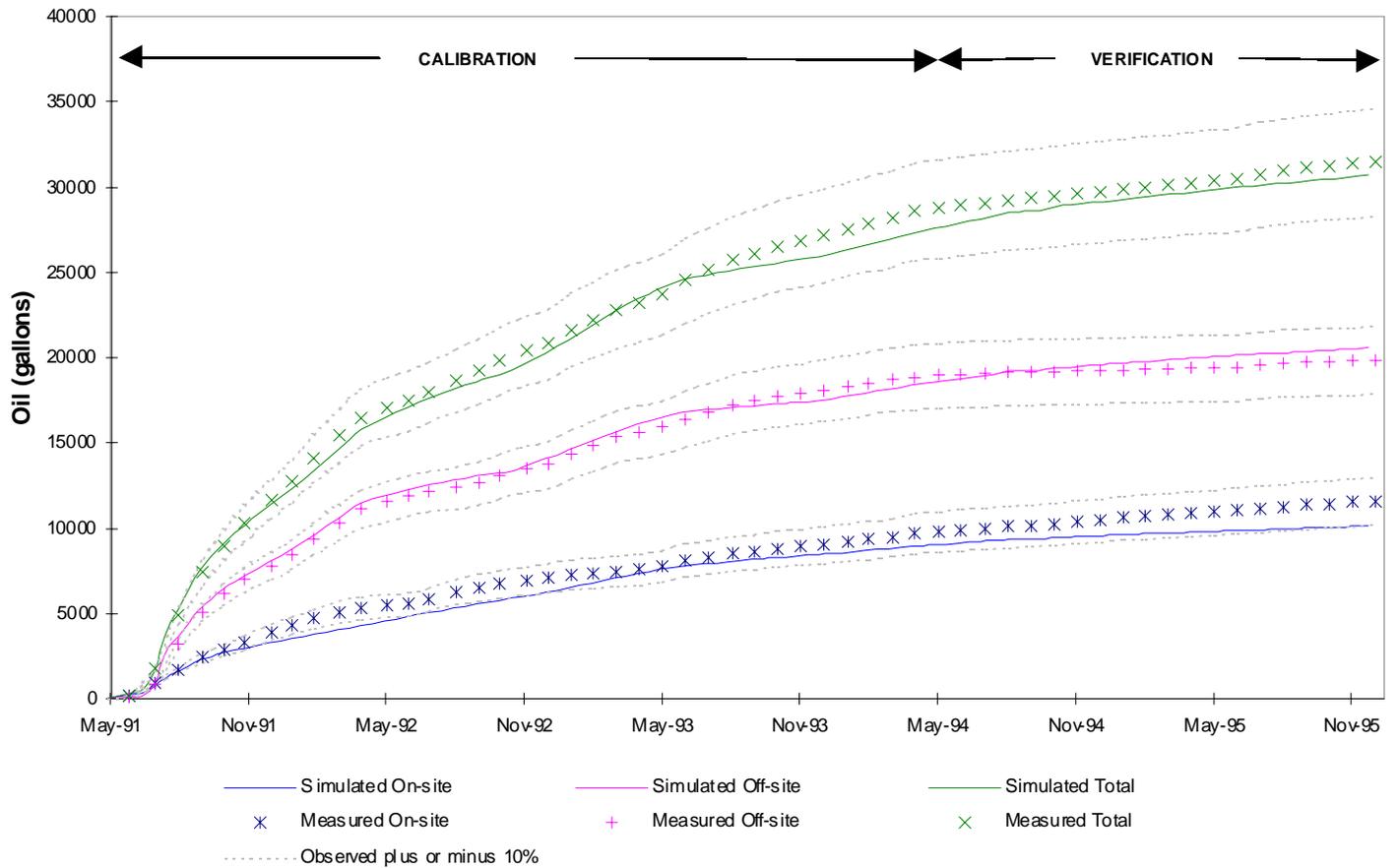
<b>Observation Time</b>	<b>Number of Wells Gauged</b>	<b>Percent of Simulated WT Elevations Within 3 Feet of Observed Elevations</b>	<b>Root Mean Square Error (feet)</b>
July 1994	294	85	1.96
December 1994	247	94	1.71
July 1995	250	90	1.95
October 1995	248	94	1.56
<b>Average</b>	N/A	91	1.80

#### **3.3.4.2 Hydrocarbon Flow**

Results of the verification analysis indicated the model reliably simulates hydrocarbon recovery at the site. The results of the model were within the verification criteria. Specifically, throughout the verification period total simulated cumulative hydrocarbon recovery was less than 10 percent of the total observed hydrocarbon recovery (Figure 3.17). In addition, the gradual asymptotic trend of the observed hydrocarbon recovery curve was matched by the model. Given the unique conditions characterizing the verification period, the model reliably simulated the observed hydrocarbon recovery.

Cumulative hydrocarbon recovery was simulated within 10 percent of the observed recovery values for both on-site and off-site systems during the verification period. Although within the verification criteria, simulated hydrocarbon recovery volumes by the off-site systems were generally greater than the observed volumes. The overprediction of off-site recovery by the model may result from the initial assumption of utilizing maximum observed well product thicknesses. Simulated on-site hydrocarbon recovery was slightly less than observed on-site recovery. However, the deviation was less than the verification criterion and the trend of the simulated hydrocarbon recovery reliably matched the observed recovery. Hence, based on the verification criteria, the hydrocarbon model reliably simulated hydrocarbon recovery across the site as well as within the on-site and off-site areas.

## Observed and Simulated PSH Recovery



**Figure 3.17. Predicted on-site and off-site hydrocarbon recovery during verification period.**

## 3.4 Contaminant Fate and Transport Model

Dissolved hydrocarbon fate and transport was simulated using the numerical model BIOTRANS, which is a companion code for the groundwater flow model ARMOS. BIOTRANS is a two-dimensional, finite element model that can simulate the fate and transport of multiple dissolved species in heterogeneous, anisotropic aquifers and can utilize flow fields and hydrocarbon distributions generated from the ARMOS model. The program considers convective-dispersive transport, adsorption, and oxygen-limited or first-order biodecay. In BIOTRANS, transport of dissolved species is simulated by solving the two-dimensional, vertically averaged convective-dispersive-reactive equation. The model utilizes steady-state velocity fields that represent average flow conditions. The model considers velocity changes due to recovery or infiltration activities through discrete changes in the flow field at specified times. For oxygen-limited biodecay, the model considers a maximum decay rate associated with limiting factors other than oxygen and assumes that oxygen consumption is essentially instantaneous relative to groundwater velocities. Decay of multiple species is considered and available oxygen is divided among each hydrocarbon species proportional to their aqueous phase concentrations. Detailed descriptions and verification of BIOTRANS are available in ES&T (1994a, 1996b).

### 3.4.1 Model Domain, Parameters, and Initial Conditions

The BIOTRANS model domain is identical to the groundwater and hydrocarbon flow model domain (Figure 3.11). Field and laboratory measurements obtained during site characterization and field studies were utilized to define input parameters for the transport model. Local-scale modeling of the field studies was utilized to refine selected model parameters. The following provides a brief description of model parameters utilized in BIOTRANS and the values defined for the site. A detailed description of the parameter values used in the transport model calibration is available in Appendix A.

**Phase Separated Hydrocarbon Source.** Conceptualization of the hydrocarbon source in the foliated aquifer and its interaction with the aqueous phase are important aspects of the transport modeling. Hydrocarbon was assumed to exist over the entire zone of water table fluctuations, potentially occurring as mobile PSH near the water table and as residual PSH in the unsaturated and saturated zones. Since BIOTRANS utilizes PSH as the source for dissolution of soluble hydrocarbon species, the PSH distribution was a critical component of the transport modeling. The PSH distribution generated from the calibrated ARMOS flow model was used as the hydrocarbon source in the transport modeling. Since BIOTRANS does not allow for a transient PSH source, mass removal due to product recovery operations cannot be modeled explicitly through time. Therefore, the initial PSH source mass utilized in the fate and transport modeling was reduced to reflect the current product recovery volume of approximately 35,000 gallons.

**Dissolved Hydrocarbon Species Parameters.** Many soluble hydrocarbon species exist in the PSH present at the research site. Since it is impractical to model every species explicitly, the PSH source in the model was conceptualized as a four-component mixture. The four hydrocarbon components considered in the model were benzene, the pseudo-species TEX (sum of toluene, ethylbenzene and xylenes), other relatively soluble hydrocarbons (referred to as TPH1) and insoluble hydrocarbons (referred to as TPH2). Because benzene is a known

carcinogen and is the hydrocarbon constituent of the greatest regulatory concern at the site, it was modeled as a discrete species.

PSH compositional analysis provided estimates for defining the pseudo-species TPH1 and TPH2. TPH1 was defined as all non-BTEX constituents with a solubility of at least 1 mg/L. Any constituent that had a solubility less than 1 mg/L was defined as insoluble and was considered TPH2. This analysis provided estimates for TPH1 mass fraction, solubility, and molecular weight (see Appendix B). Because TPH2 was defined as insoluble, and hence was not a dissolved constituent, no parameter values were assigned to TPH2 except for molecular weight, which was required to calculate species mole fractions.

**Initial Species Mass Fraction Distribution.** The spatial distributions of the initial benzene and TEX species mass fractions in the PSH plume were interpolated from BTEX measurements of PSH samples collected at the site. The initial mass fraction for TPH1 was estimated from PSH composition analyses to be 0.3 (Appendix B).

**Initial Species Concentrations.** The first groundwater sampling event to provide complete spatial coverage of the site occurred in September 1992, and hence, benzene and TEX measurements from this sampling event were utilized as the initial concentrations near the perimeter of the PSH plume. Since most of the monitoring wells within the PSH plume contained free product, dissolved benzene and TEX measurements were not available. Therefore, the initial species concentrations were assumed to be at effective solubility values since the PSH plume is contained and has been in contact with the groundwater for an extended length of time.

**Dissolved Oxygen Initial and Boundary Conditions.** The initial dissolved oxygen concentration was defined as 5 mg/L outside of the PSH plume and 1 mg/L beneath the PSH plume based on measured values. The DO concentration available in groundwater entering the site (boundary inflow) and by infiltration from precipitation (recharge) was assumed to be 5 mg/L.

### 3.4.2 Calibration

Calibration of the dissolved phase transport model was performed over a simulation time period extending from September 1992 through December 1995. The starting time for the transport simulation was selected as September 1992 because this was the first groundwater sampling event to provide a sufficient number of data points to define the initial conditions.

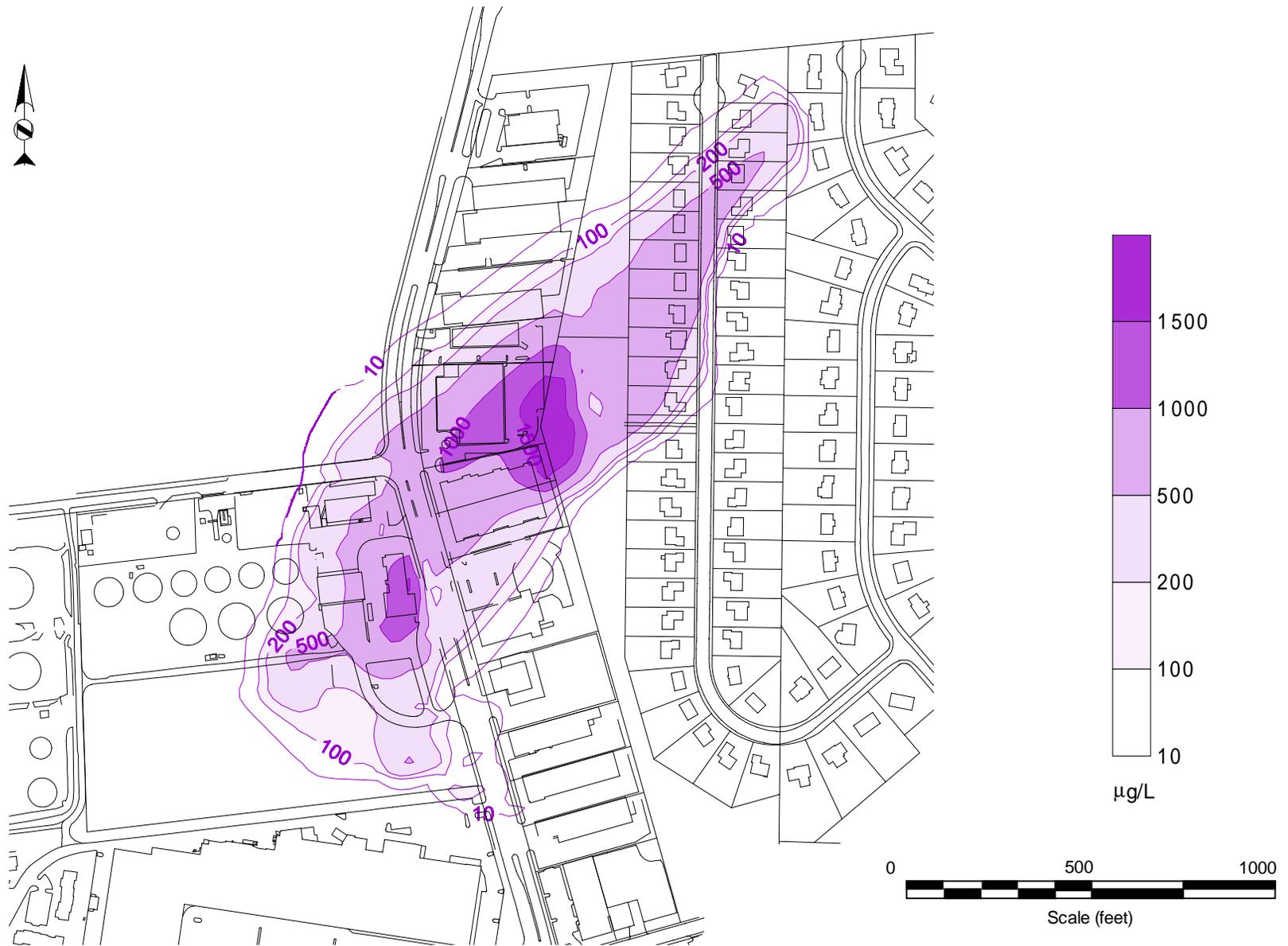
The groundwater flow conditions utilized in the calibration of the transport model were based on the ARMOS groundwater flow model. The transport model calibration involved simulating two separate groundwater flow conditions. The first time period was from September 1992 to September 1994 and represented the current recovery system prior to activation of HW-1. In September 1994, infiltration from HW-1 was initiated. Because operation of HW-1 altered the flow regime, an updated steady-state flow field was simulated to represent groundwater conditions after September 1994. Therefore, the second time period ranges from September 1994 to the end of the calibration period.

The dissolved phase model was considered calibrated when the following were achieved:

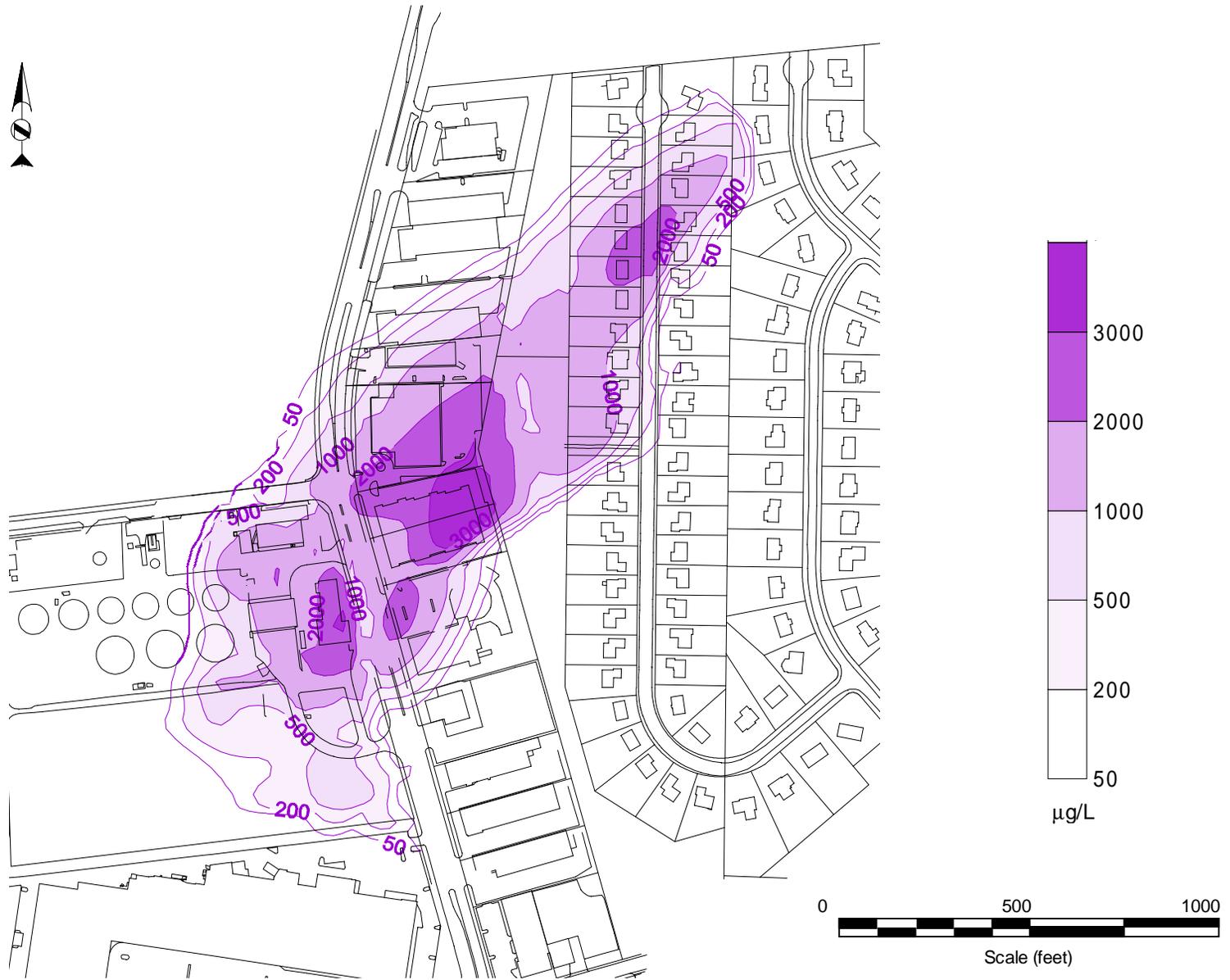
- the model simulations reasonably delineated the DPH plume boundary, and
- 80 percent of the simulated concentrations matched the average observed concentrations within 10 µg/L for benzene and 50 µg/L for TEX or were within one standard deviation of the average concentrations measured from 1993 to 1995.

To reflect the objective of the groundwater sampling program, the calibration focused on delineating the perimeter of the dissolved plume and simulating the concentrations outside the PSH plume. Dissolved benzene and TEX measurements collected from more than 100 wells were utilized in the calibration.

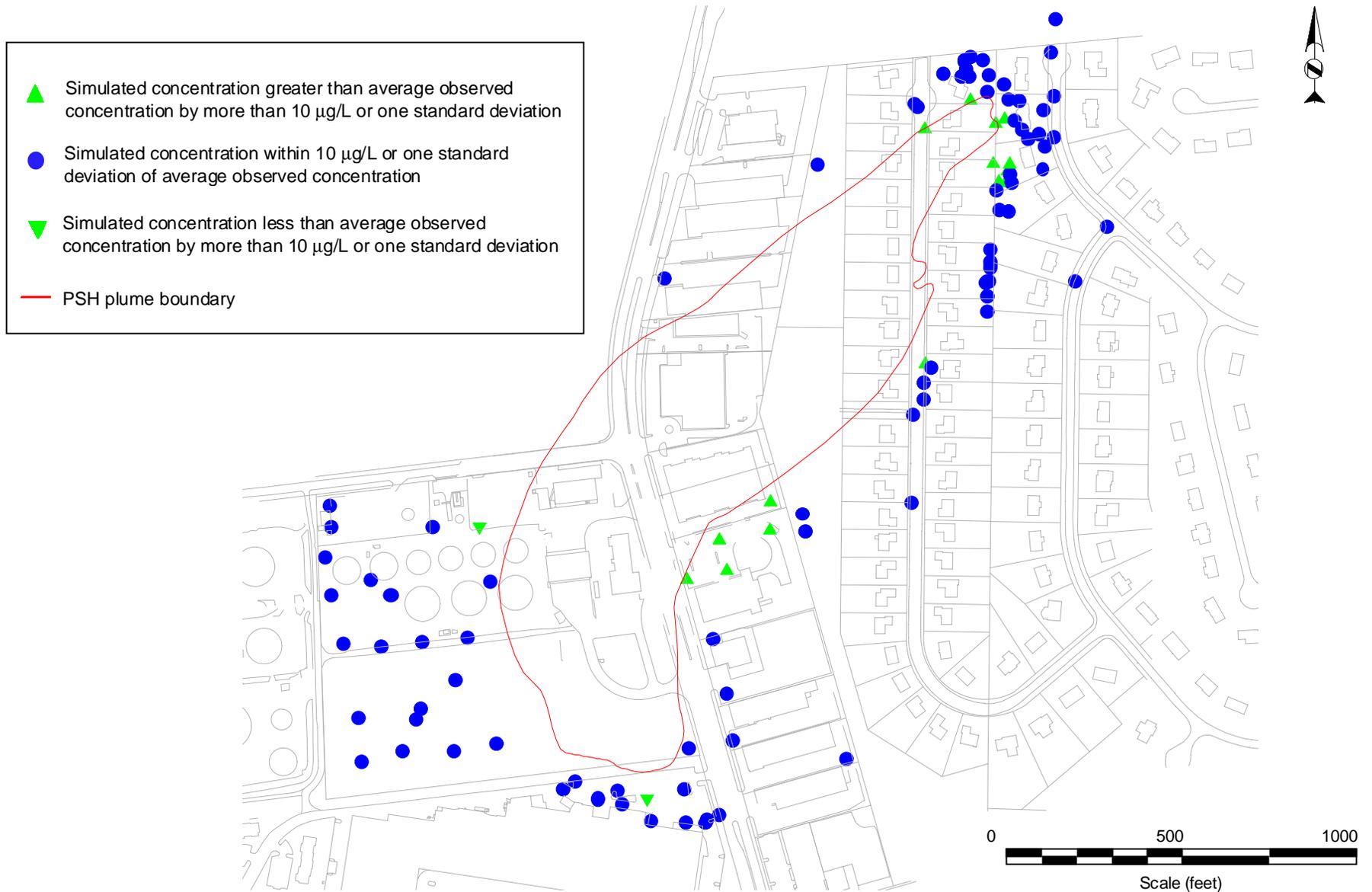
The results of the calibration indicated that the transport model reasonably delineated the shape of the observed DPH plume (Figures 3.18 and 3.19). The simulated plume perimeter for both benzene and TEX was typically within 50 feet of the field observations. The simulated concentrations of benzene and TEX generally agreed with average observed measurements. Specifically, the model was within the calibration criteria for 80 percent of the wells (Figures 3.20 and 3.21). Based on these results, the model reliably reflected the distribution and concentration magnitude of dissolved benzene and TEX.



**Figure 3.18. Simulated benzene concentrations at the end of the calibration period (December 1995).**

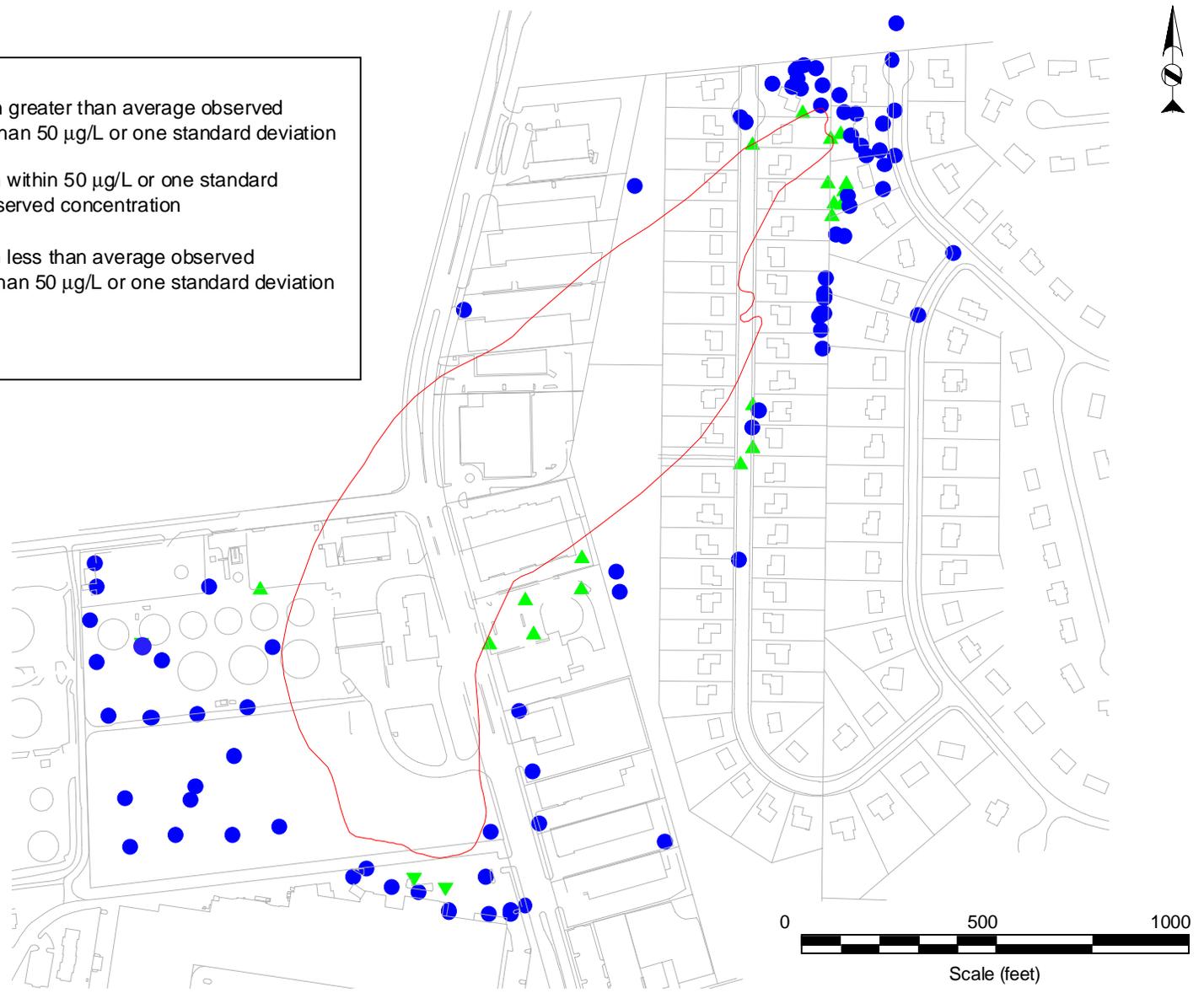


**Figure 3.19. Simulated TEX concentrations at the end of the calibration period (December 1995).**



**Figure 3.20. Comparison of simulated and average observed benzene concentrations.**

- ▲ Simulated concentration greater than average observed concentration by more than 50  $\mu\text{g/L}$  or one standard deviation
- Simulated concentration within 50  $\mu\text{g/L}$  or one standard deviation of average observed concentration
- ▼ Simulated concentration less than average observed concentration by more than 50  $\mu\text{g/L}$  or one standard deviation
- PSH plume boundary



**Figure 3.21. Comparison of simulated and average observed TEX concentrations.**

## 4. Application of Models to Assess Remedial Technologies

The final stage of this research is to utilize the calibrated flow and transport models to evaluate the potential effectiveness of the various remedial options: groundwater extraction, groundwater flushing, microbial fences, and natural attenuation. The potential effectiveness of each remedial option is evaluated based on a reduction of both aquifer concentrations and residual source mass. The evaluation of effectiveness focuses on the benzene and TEX constituents. The modeling activities associated with this research are aimed at assisting with the selection of the most effective technology to reduce dissolved hydrocarbon concentrations in the off-site portion of the research site. Remediation of the off-site area is the primary consideration due to political and litigation concerns.

### 4.1 Modeling Approach

The calibrated flow and transport models served as the foundation and starting point to simulate the four remedial options. The model parameters utilized in the calibration process were maintained in the predictive simulations unless otherwise denoted. The aquifer concentrations and residual source mass present in the model at the end of the calibration period (January 1996) were assumed as the initial conditions for all the predictive simulations. Figure 4.1 illustrates the aquifer concentrations of benzene and TEX at the end of the calibration period (year 0 for the predictive simulations). The mass of benzene and TEX in the residual PSH source was 115 and 2,600 kg, respectively. Since water table fluctuations occur within the hydrocarbon smear zone, residual PSH can occur as either saturated or unsaturated. An analysis of water table movement within the smear zone indicated that on average 60 percent of the smear zone is saturated. Therefore, the residual mass in the model was assumed to be distributed as 40 percent in the unsaturated zone and 60 percent in the saturated zone.

Due to regulatory, legal, and political considerations, containment on the leading, northeastern edge of the plume must be maintained. Therefore, simulation of all remedial options includes continued operation of the recovery trenches, some recovery wells and HW-1. These systems are denoted on Figure 4.2.

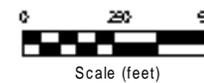
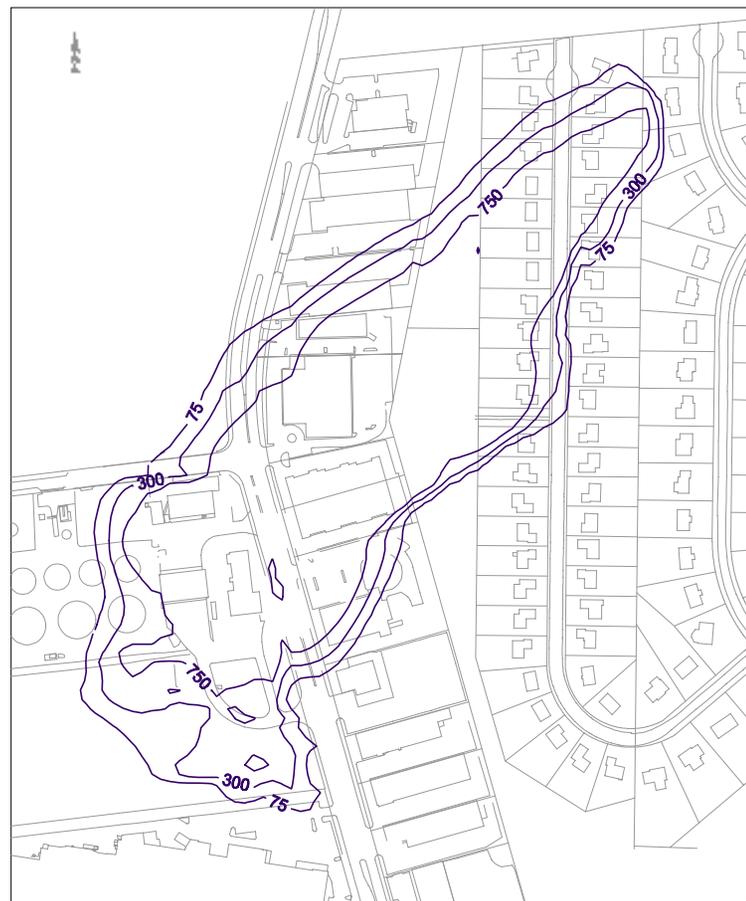
To perform a comprehensive evaluation of each remedial option, predictive simulations were conducted for a 20-year period. Changes in source mass and aquifer concentrations were evaluated in four year increments.

To perform the predictive simulations for the remedial options, some modifications to the calibrated flow and transport models were required. Details of these modifications as well as how each remedial option was implemented are discussed in the following subsections.

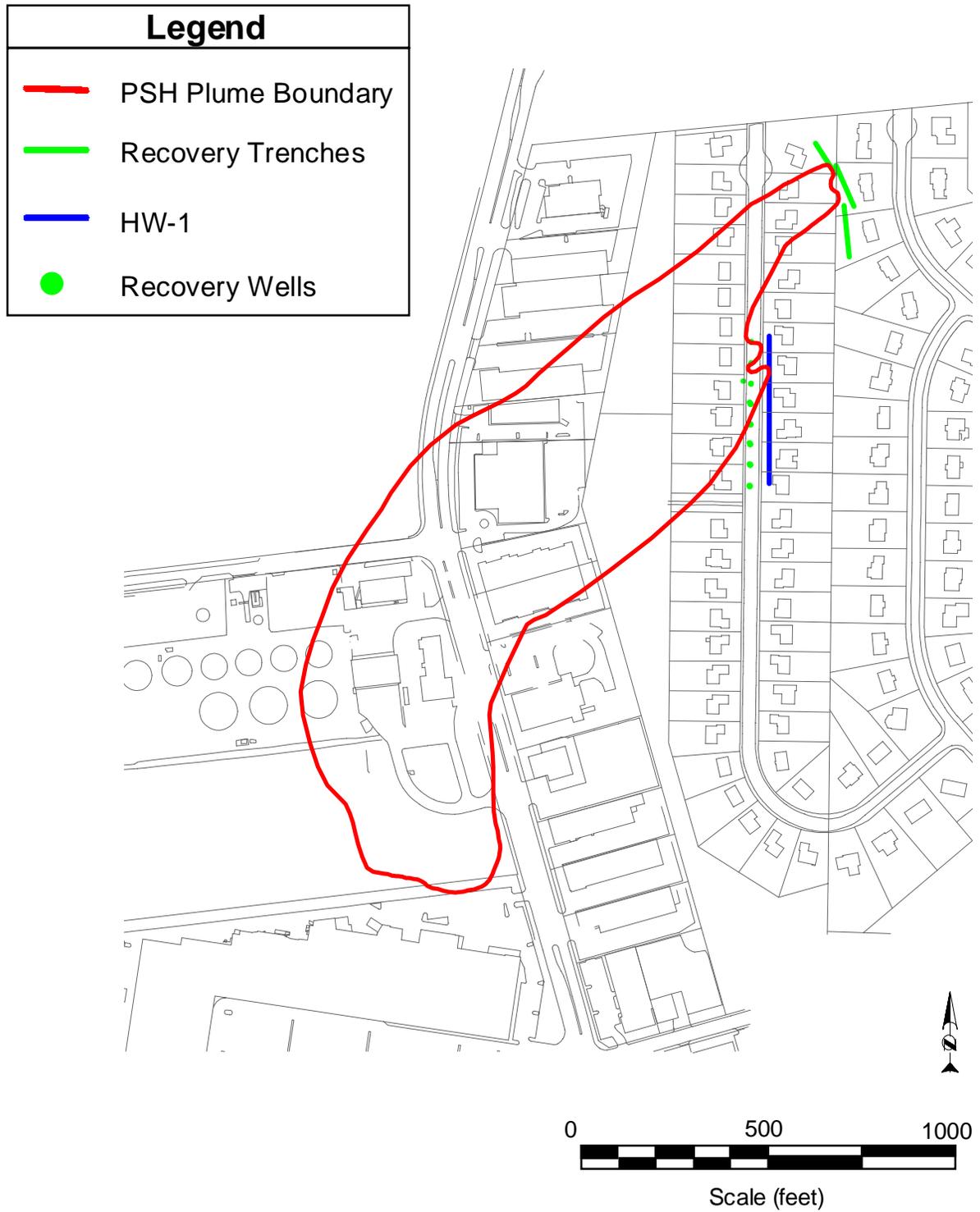
### Benzene



### TEX



**Figure 4.1. Dissolved benzene and TEX concentrations at the beginning of the predictive simulations.**



**Figure 4.2. Containment system components operating during predictive simulations.**

### **4.1.1 Natural Attenuation**

The natural attenuation remedial option assumes that no engineered systems are operating. Therefore, the current groundwater recovery system would be deactivated, except for the systems along the leading edge of the plume as previously discussed. This requires an adjustment to the groundwater flow model. All pertinent recovery systems were removed from the flow model and a new steady-state flow field was generated. No modification to the transport model was required to simulate natural attenuation processes.

### **4.1.2 Groundwater Extraction**

The groundwater extraction remedial option assumes continued operation of the existing recovery and containment system. Since the calibrated flow and transport models already incorporate the current groundwater extraction system, no modifications to the models were required for this simulation.

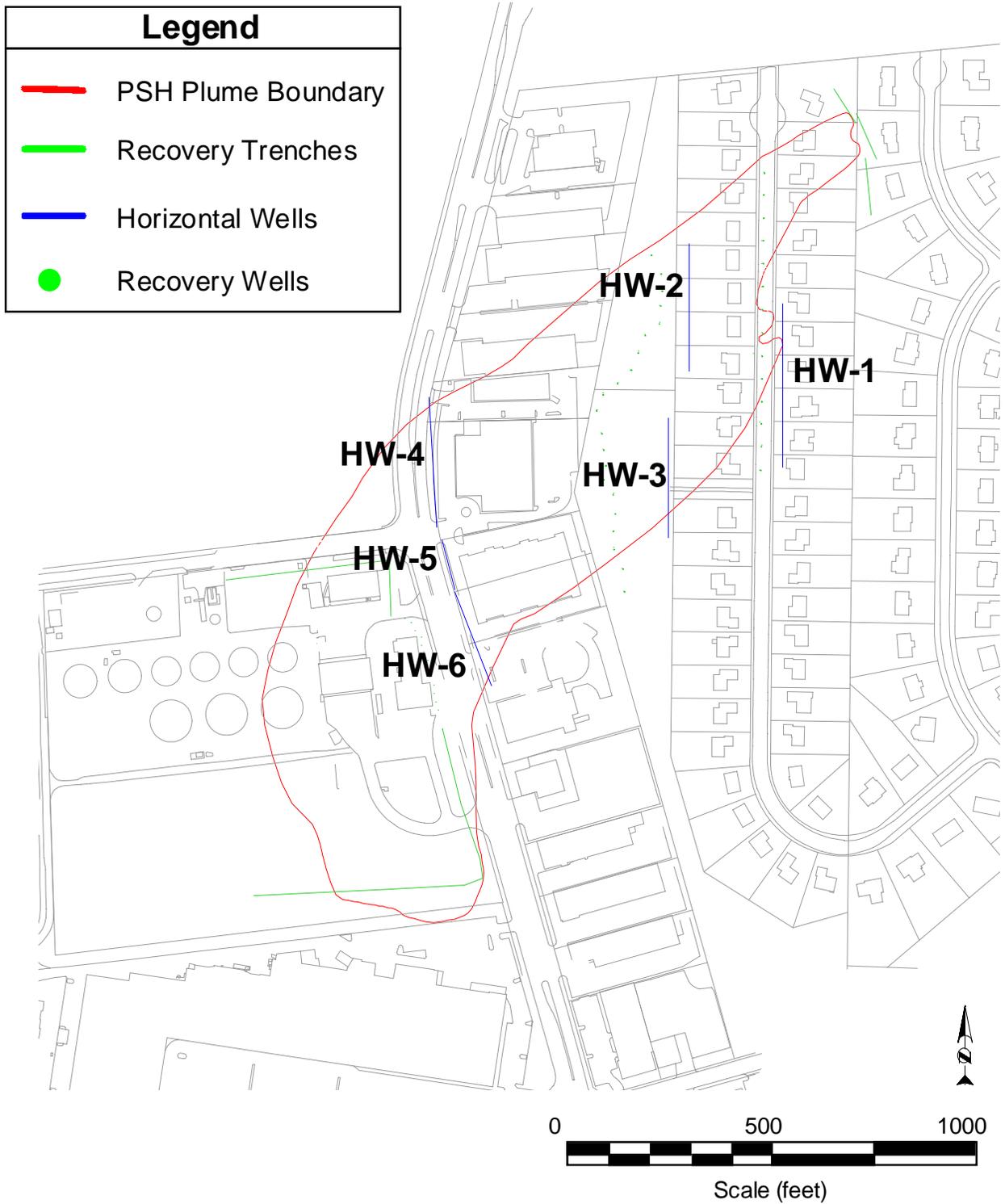
### **4.1.3 Groundwater Flushing**

Implementation of the groundwater flushing remedial option assumes installation of a series of horizontal infiltration wells working in conjunction with the existing groundwater recovery system. Applying infiltration in conjunction with the current recovery system maximizes flow through the system, prevents uncontrolled increases in the water table, and allows recovered groundwater to be treated and returned to the aquifer through the horizontal infiltration wells. For this remedial option, installation of five horizontal wells (HW-2 through HW-6) was assumed. The locations of the horizontal wells are depicted on Figure 4.3 along with the existing recovery system components.

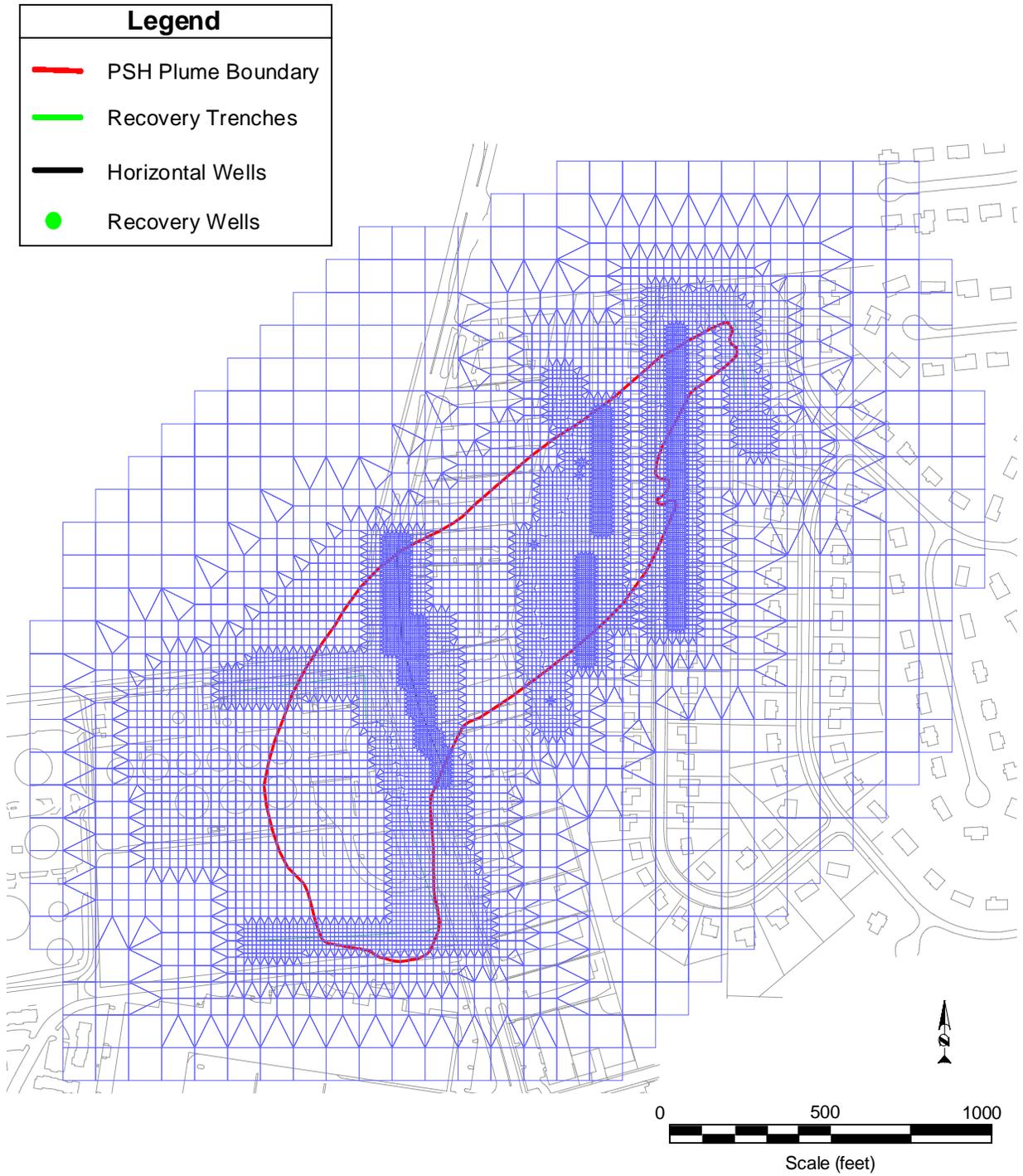
The flow model required a variety of modifications to simulate infiltration from the series of horizontal wells. First, the model mesh needed to be refined in the areas of infiltration to simulate the water fluxes from the horizontal wells. The model mesh was refined to a nodal spacing of 6.25 feet for approximately 50 feet on each side of the horizontal infiltration wells (Figure 4.4). To ensure that the additional mesh refinement would not impact the model solution, the new mesh was utilized to simulate the calibration period and the results were compared with the original calibration results. No discernible differences were identified between the two model simulations for water table elevations, groundwater velocities, aquifer concentrations or residual source mass.

Next, the horizontal infiltration wells were added to the model and simulated as fixed head nodes. The simulated water elevation for each infiltration well was defined as 10 feet above the average water table elevation along the length of the well. These elevations are denoted below:

- HW-2 at 378.0 feet MSL
- HW-3 at 375.0 feet MSL
- HW-4 at 391.5 feet MSL
- HW-5 at 386.5 feet MSL
- HW-6 at 382.5 feet MSL



**Figure 4.3. Location of horizontal infiltration wells.**



**Figure 4.4. Model mesh with additional refinement to accommodate infiltration from horizontal wells.**

In the fate and transport model, each horizontal well was assumed to be infiltrating clean, oxygenated water. Therefore, dissolved oxygen was simulated at 6 mg/L along each horizontal well. The total oxygen mass input at each node in the transport model corresponded to the water flux generated at that node in the flow model.

#### **4.1.4 Microbial Fences**

This remedial option assumes the installation of a series of engineered trenches to produce zones of increased biodegradation. The microbial fences were simulated at the same locations as the horizontal infiltration wells in the groundwater flushing remedial option to allow for a reasonable comparison of the two technologies (Figure 4.5). Simulation of the microbial fence system also utilized the same model mesh as the groundwater flushing remedial option.

To provide the greatest groundwater flow through the off-site area and to maximize the efficiency of the microbial fence system, the groundwater recovery and containment system was assumed to be deactivated, except along the leading edge of the plume as previously mentioned. The flow model was adjusted to reflect these modifications, and a new steady-state flow field was generated.

Since installation of the microbial fences requires trench construction, and hence excavation of aquifer material, the initial PSH source mass in the transport model was adjusted to account for removal during excavation activities. The microbial fences were simulated in the transport model as a single row nodes and assumed an input of 10 mg/L of dissolved oxygen along the entire length of each microbial fence. Therefore, the mass loading of dissolved oxygen varied depending on the water flux at the microbial fence locations.

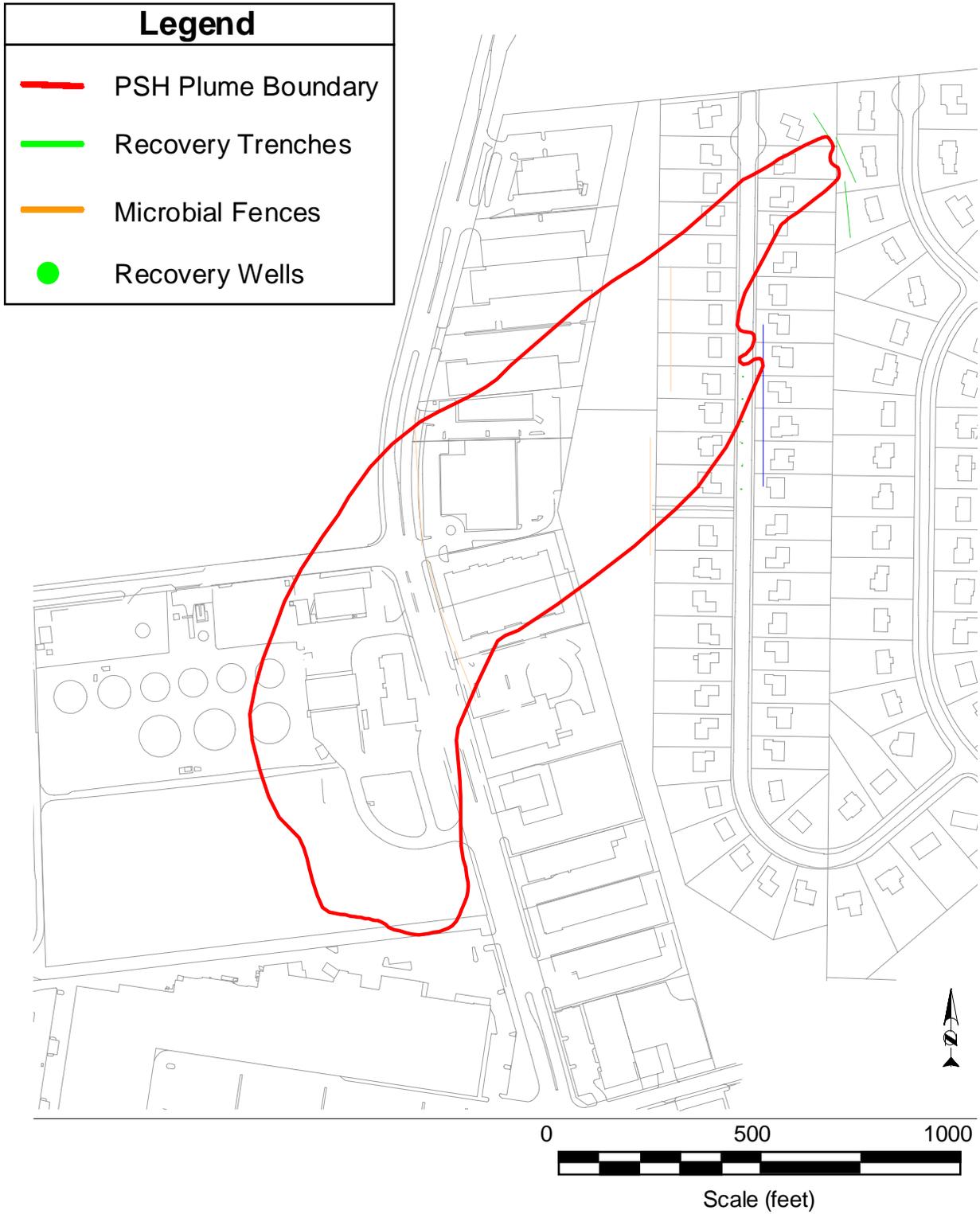
## **4.2 Modeling Results**

The effect of each remedial option was evaluated by assessing: (1) the predicted benzene and TEX removal from the PSH source mass and (2) the predicted reduction of dissolved benzene and TEX concentrations in the aquifer. Reduction of benzene and TEX constituents from the PSH source mass was evaluated for residual PSH in both the unsaturated and saturated zones. Changes in dissolved aquifer concentrations were evaluated after 4, 8, 12 and 20 years of remediation.

### **4.2.1 Natural Attenuation**

Simulation of natural attenuation provides a mechanism to evaluate the natural rate of reduction of PSH source mass and DPH concentrations. This analysis provides a baseline for comparison of engineered remedial technologies.

Table 4.1 summarizes the predicted reduction in the benzene and TEX source mass as a result of natural attenuation processes. In the unsaturated zone, approximately 60 percent of the benzene mass and 16 percent of the TEX mass are expected to be removed from the PSH source in 20 years. A reduction of approximately 45 percent of the benzene mass and 16 percent of the TEX mass is predicted for the saturated zone in 20 years. The total predicted mass removal from the PSH source in 20 years is 58 kg for benzene and 420 kg for TEX.



**Figure 4.5. Location of microbial fences.**

**Table 4.3. Predicted Reduction of Benzene and TEX Source Mass for Natural Attenuation.**

Constituent	Estimated Source Mass (kg)					
	Initial	Year 4	Year 8	Year 12	Year 16	Year 20
Benzene						
Unsaturated Zone	45.9	34.9	28.4	23.9	20.7	18.2
Saturated Zone	68.8	62.6	56.5	50.3	44.4	38.9
Total	114.7	97.5	84.9	74.2	65.1	57.1
TEX						
Unsaturated Zone	1,040	999	963	932	903	876
Saturated Zone	1,559	1,494	1,441	1,392	1,347	1,304
Total	2,599	2,493	2,404	2,323	2,249	2,180

A comparison of dissolved benzene and TEX concentration contours predicted for natural attenuation over a 20-year period indicates that the dissolved hydrocarbon plume will expand from its current extents and that the interior concentrations in the off-site area will remain above 500 µg/L for benzene and 750 µg/L for TEX (Figures 4.6 and 4.7). Predicted benzene concentrations near the recovery trenches at the leading edge of the plume decrease from 500 µg/L to approximately 200 µg/L in 20 years while predicted TEX concentrations in the same area decrease from 750 µg/L to approximately 300 µg/L.

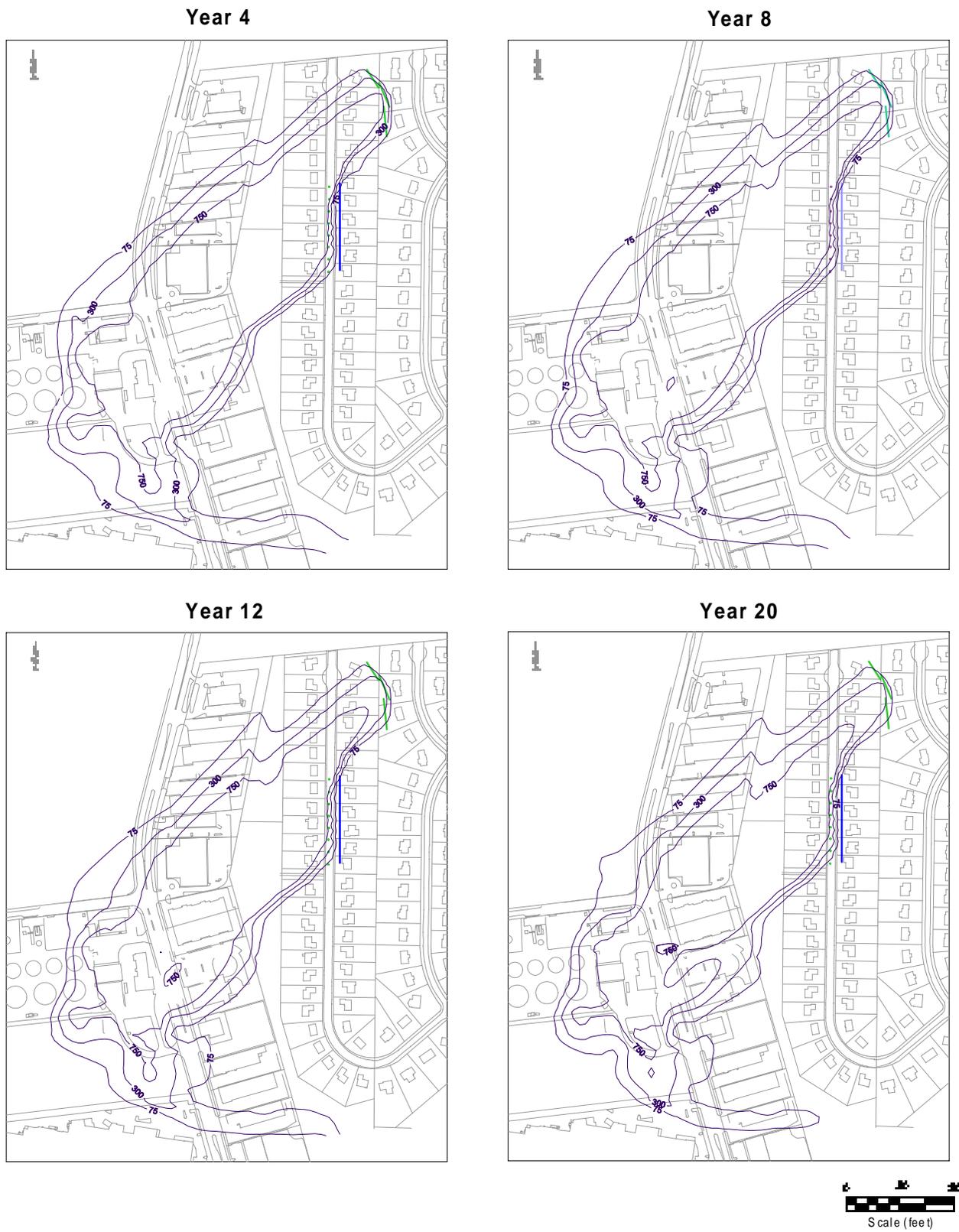
#### 4.2.2 Groundwater Extraction

Simulation of the current groundwater extraction system provides an estimate of the benzene and TEX removal that will occur if no additional remedial action is taken but continued PSH and water recovery occurs. The predicted benzene and TEX source mass during 20 years of groundwater extraction is summarized in Table 4.2. Since the groundwater extraction system impacts the saturated zone, predicted unsaturated zone mass removal is the same as natural attenuation. Over a 20-year period, groundwater extraction is predicted to remove approximately 38 kg of benzene and 286 kg of TEX from the residual PSH in the saturated zone. This equates to a reduction of approximately 55 percent for benzene and 18 percent for TEX.

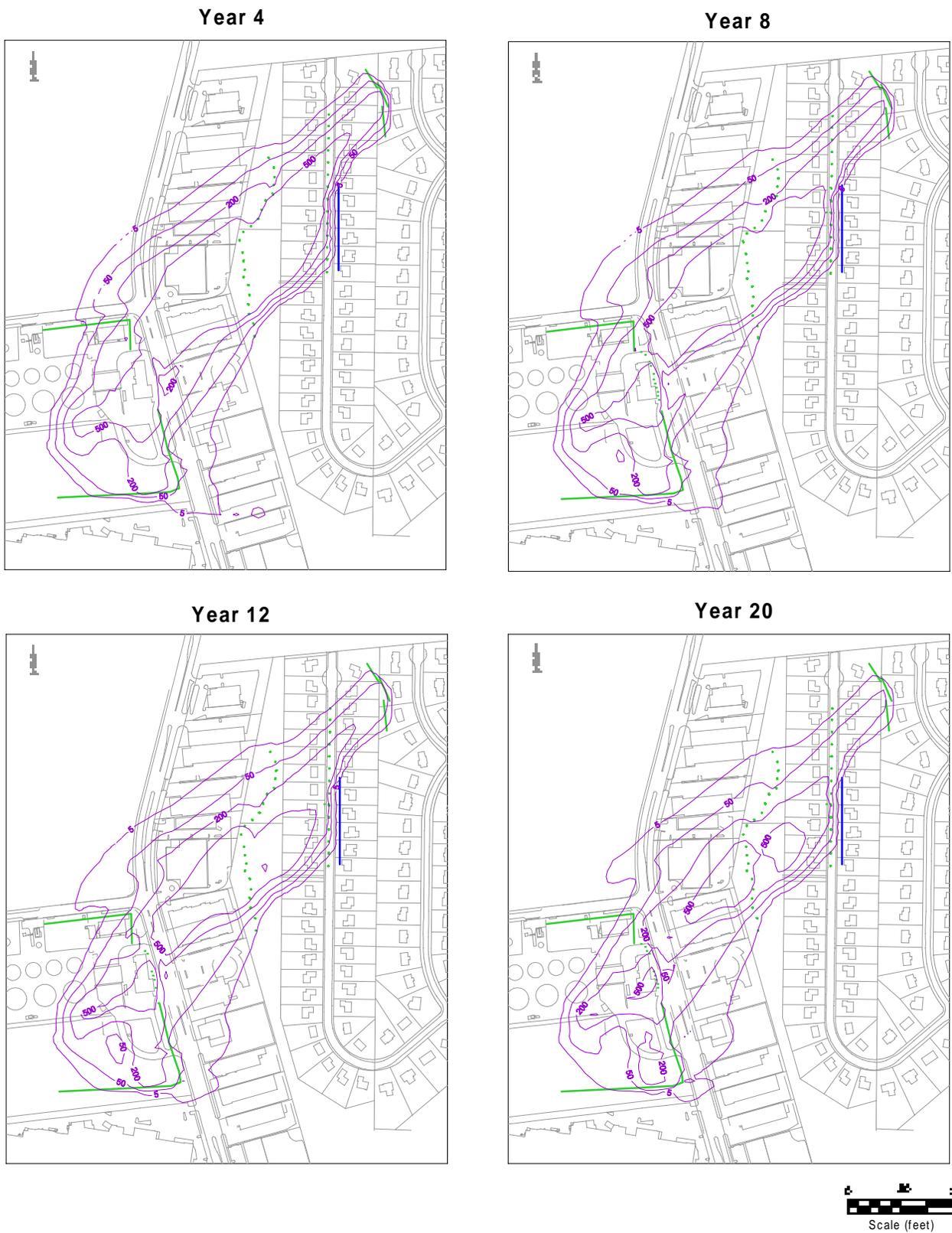
Figures 4.8 and 4.9 illustrate the predicted aquifer concentrations of benzene and TEX, respectively, after 20 years of operating the current groundwater extraction system. Concentrations of both benzene and TEX decrease over time. Predicted benzene concentrations near the recovery trenches at the leading edge of the plume decrease from 500 µg/L to approximately 50 µg/L in 20 years while predicted TEX concentrations in the same area decrease from 750 µg/L to less than 300 µg/L. Operation of the groundwater extraction system also generates a reduction in the lateral extent of the dissolved phase plume. Predicted concentrations in the off-site interior portion of the plume remain greater than 500 µg/L for benzene and greater than 750 µg/L for TEX after 20 years of operation.



**Figure 4.6. Predicted dissolved benzene concentrations after 4, 8, 12, and 20 years of natural attenuation.**



**Figure 4.7. Predicted dissolved TEX concentrations after 4, 8, 12, and 20 years of natural attenuation.**



**Figure 4.8. Predicted dissolved benzene concentrations after 4, 8, 12, and 20 years of groundwater extraction.**



**Figure 4.9. Predicted dissolved TEX concentrations after 4, 8, 12, and 20 years of groundwater extraction.**

**Table 4.4. Predicted Reduction of Benzene and TEX Source Mass for Groundwater Extraction.**

Constituent	Estimated Source Mass (kg)					
	Initial	Year 4	Year 8	Year 12	Year 16	Year 20
Benzene						
Unsaturated Zone	45.9	34.9	28.4	23.9	20.7	18.2
Saturated Zone	68.8	58.5	49.5	42.0	35.8	30.6
Total	114.7	93.4	77.9	65.9	56.4	48.8
TEX						
Unsaturated Zone	1,040	999	963	932	903	876
Saturated Zone	1,559	1,487	1,426	1,371	1,320	1,273
Total	2,599	2,486	2,389	2,302	2,223	2,149

### 4.2.3 Groundwater Flushing

The predicted benzene and TEX mass remaining in the PSH source after 20 years of performing groundwater flushing are provided in Table 4.3. Since the groundwater flushing system impacts the saturated zone, predicted unsaturated zone mass removal is the same as natural attenuation. The predicted source mass reduction in the saturated zone after 20 years of groundwater flushing is approximately 85 percent for benzene and 33 percent for TEX. The rate of mass removal is faster in the first several years and then decreases over time. For example, in the first 4 years of the simulation, the predicted benzene mass reduction is almost 42 percent. However, 16 more years are required to achieve another 42 percent reduction.

**Table 4.5. Predicted Reduction of Benzene and TEX Source Mass for Groundwater Flushing.**

Constituent	Estimated Source Mass (kg)					
	Initial	Year 4	Year 8	Year 12	Year 16	Year 20
Benzene						
Unsaturated Zone	45.9	34.9	28.4	23.9	20.7	18.2
Saturated Zone	68.8	40.1	25.9	18.1	13.6	10.9
Total	114.7	75.0	54.3	42.0	34.3	29.1
TEX						
Unsaturated Zone	1,040	999	963	932	903	876
Saturated Zone	1,559	1,410	1,296	1,201	1,118	1,045
Total	2,599	2,408	2,259	2,132	2,021	1,921

The dissolved concentrations of benzene and TEX are predicted to decrease throughout the off-site area due to groundwater flushing. Figure 4.10 illustrates the predicted benzene concentrations after 4, 8, 12, and 20 years of groundwater flushing. After 4 years of system operation, zones of reduced concentration levels are apparent around the horizontal well locations. After 12 years of flushing, predicted benzene concentrations east of HW-2 are predominately less than 5 µg/L and interior concentrations are less 500 µg/L. At the end of the simulation, the maximum predicted benzene concentrations are less than 200 µg/L in the interior portion of the off-site plume and less than 5 µg/L near the recovery trenches that contain the leading edge of the DPH plume. Changes in predicted dissolved TEX concentrations follow patterns similar to changes in dissolved benzene concentrations, however the remaining TEX concentration levels are greater than the benzene levels (Figure 4.11). After 20 years of groundwater flushing, the predicted TEX concentrations near the leading edge of the plume are less than 300 µg/L, but are still greater than 750 µg/L in the interior of the plume.

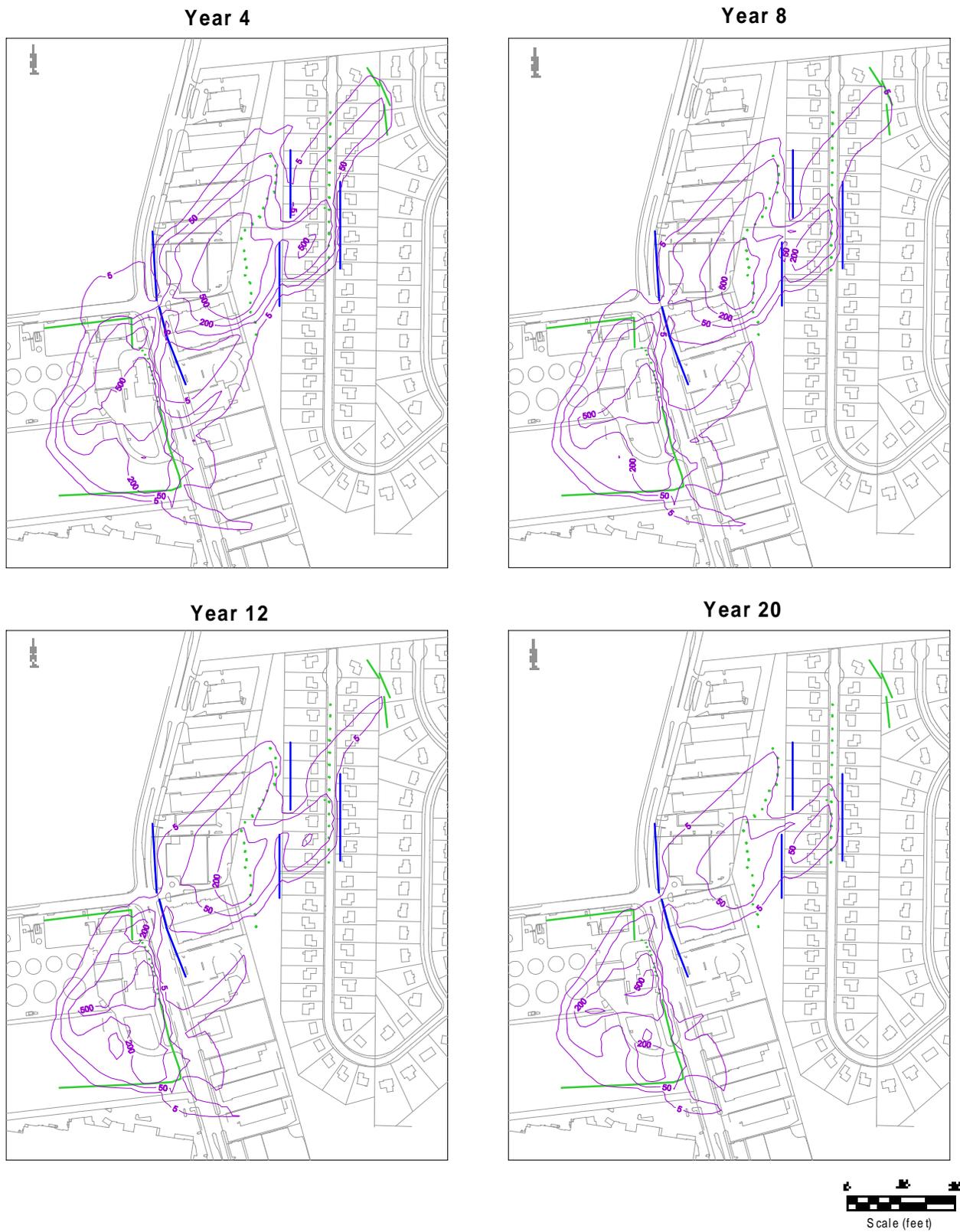
#### 4.2.4 Microbial Fences

The predicted changes in benzene and TEX source mass during 20 years of microbial fence operation are summarized in Table 4.4. Since the microbial fences supply oxygen to the saturated zone, mass reductions in the unsaturated zone are a result of natural attenuation processes. After 20 years of operation, benzene source mass in the saturated zone is predicted to decrease by almost 39 kg or 57 percent. The predicted reduction of TEX source mass in the saturated zone after 20 years of operation is approximately 300 kg or 20 percent.

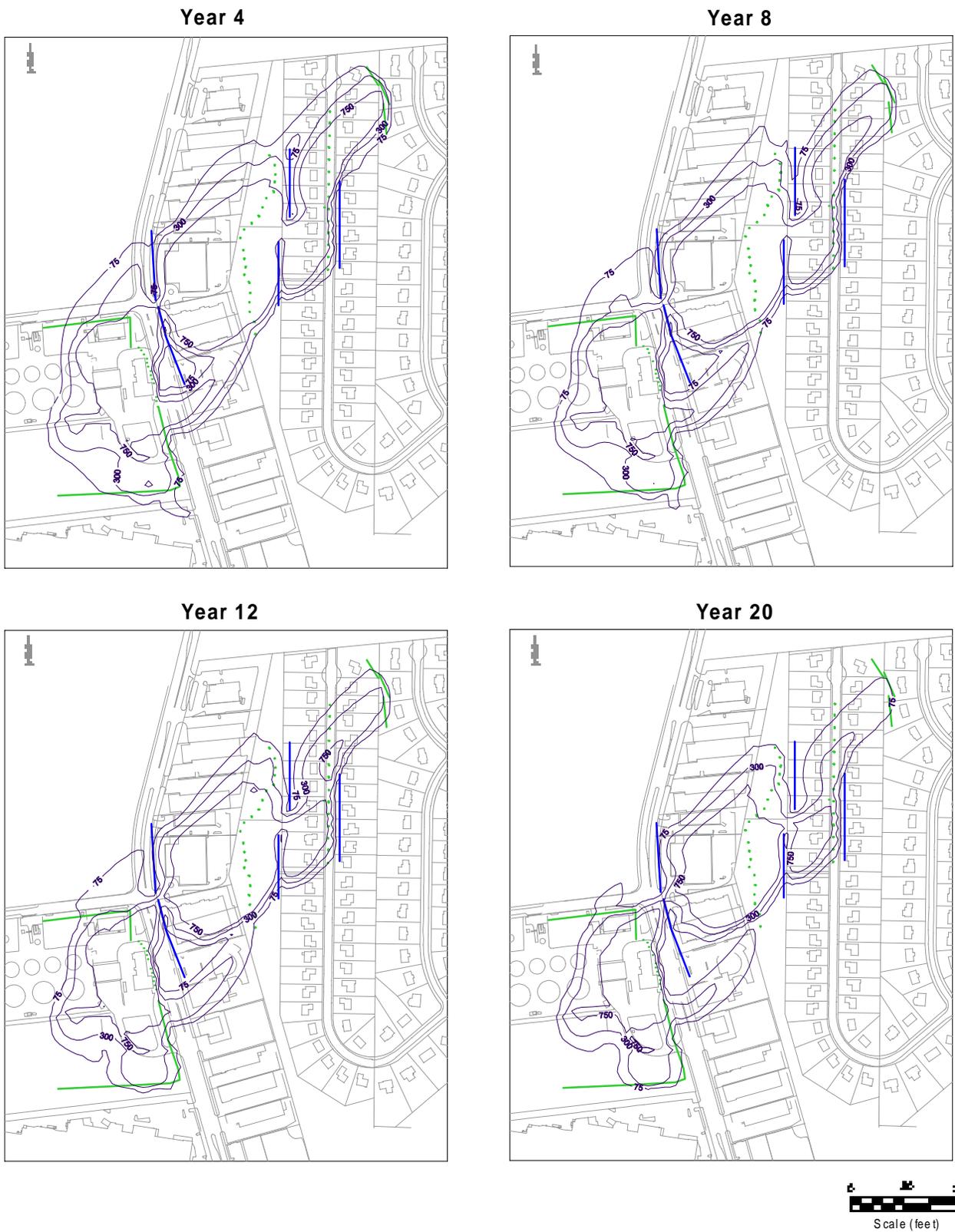
An evaluation of dissolved benzene and TEX concentration contours predicted for the microbial fence system over a 20-year period indicates that the dissolved hydrocarbon plume will expand from its current extents and that the interior concentrations in the off-site area will remain above 500 µg/L for benzene and 750 µg/L for TEX (Figures 4.12 and 4.13). A reduction in predicted aquifer concentrations occurs near the microbial fences and is evident by the 4<sup>th</sup> year. Predicted benzene concentrations near the recovery trenches at the leading edge of the plume decrease from 500 µg/L to approximately 50 µg/L in 20 years while predicted TEX concentrations in the same area decrease from 750 µg/L to less than 300 µg/L.

**Table 4.6. Predicted Reduction of Benzene and TEX Source Mass for Microbial Fences.**

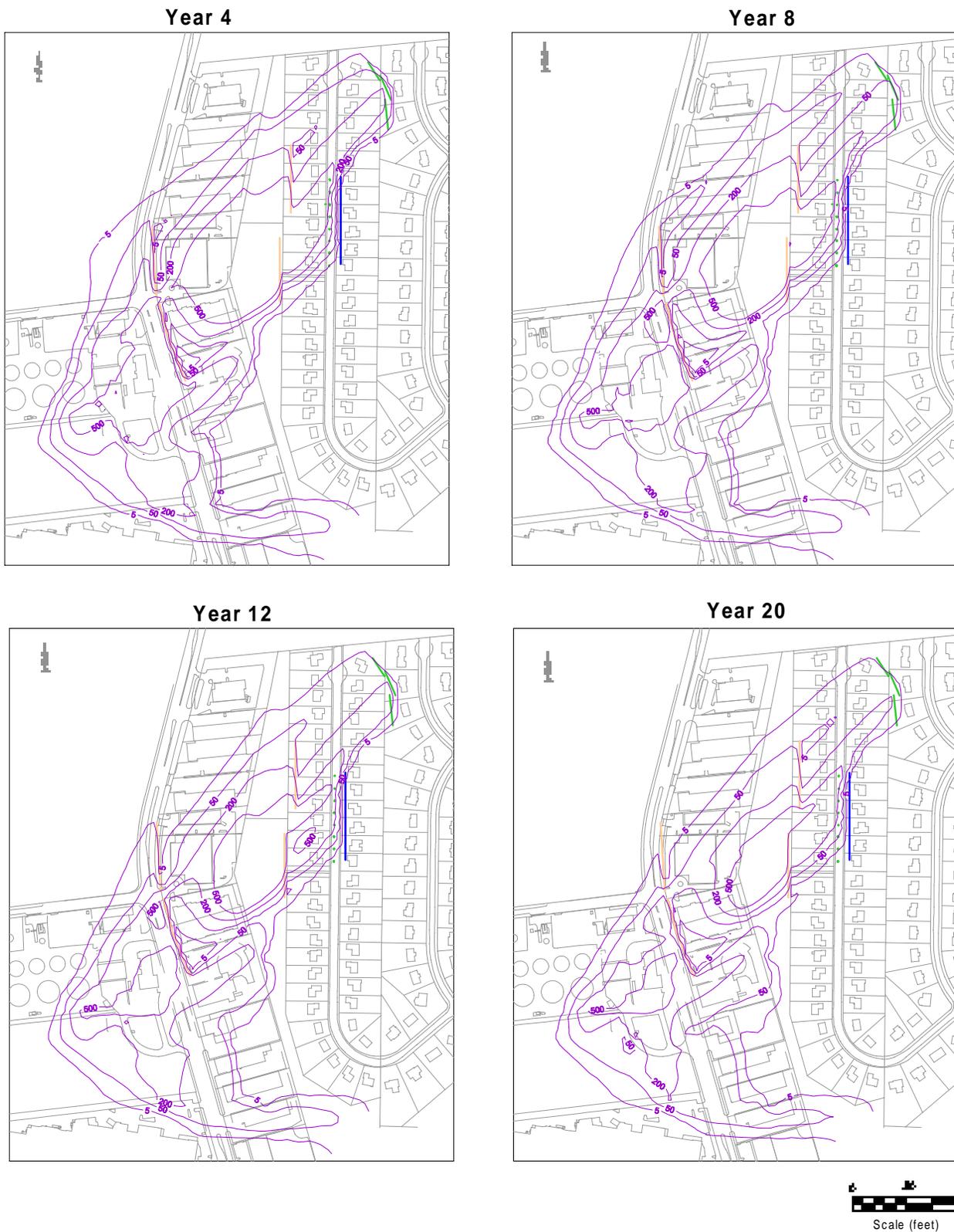
Constituent	Estimated Source Mass (kg)					
	Initial	Year 4	Year 8	Year 12	Year 16	Year 20
Benzene						
Unsaturated Zone	45.6	34.6	28.2	23.7	20.5	18.0
Saturated Zone	68.4	58.2	49.8	42.2	35.3	29.6
Total	114.0	92.8	78.0	65.9	55.8	47.6
TEX						
Unsaturated Zone	1,033	992	957	925	896	869
Saturated Zone	1,549	1,469	1,404	1,347	1,293	1,245
Total	2,582	2,461	2,361	2,272	2,189	2,114



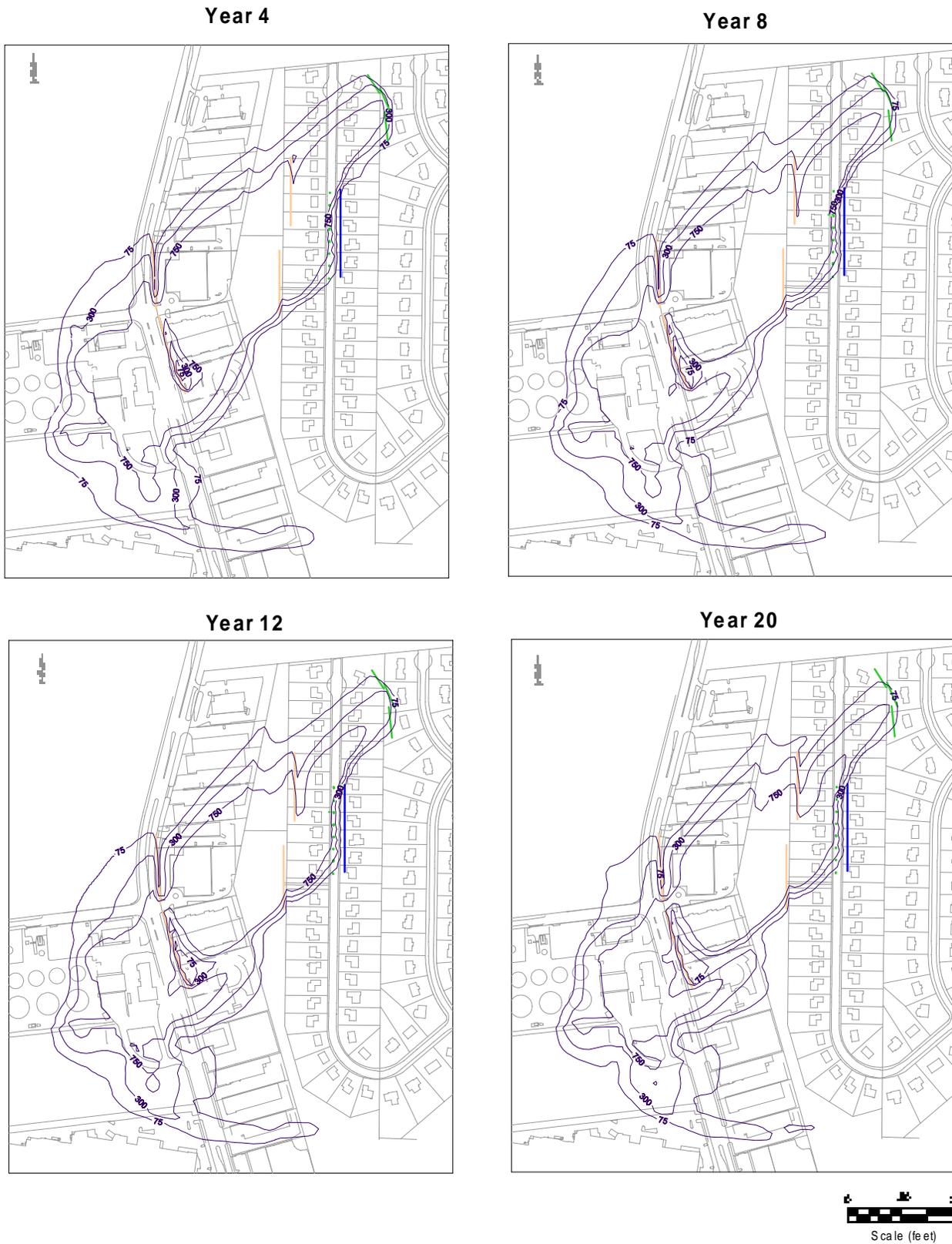
**Figure 4.10. Predicted dissolved benzene concentrations after 4, 8, 12, and 20 years of groundwater flushing.**



**Figure 4.11. Predicted dissolved TEX concentrations after 4, 8, 12, and 20 years of groundwater flushing.**



**Figure 4.12. Predicted dissolved benzene concentrations after 4, 8, 12, and 20 years of groundwater remediation using microbial fences.**



**Figure 4.13. Predicted dissolved TEX concentrations after 4, 8, 12, and 20 years of groundwater remediation using microbial fences.**

### 4.3 Discussion

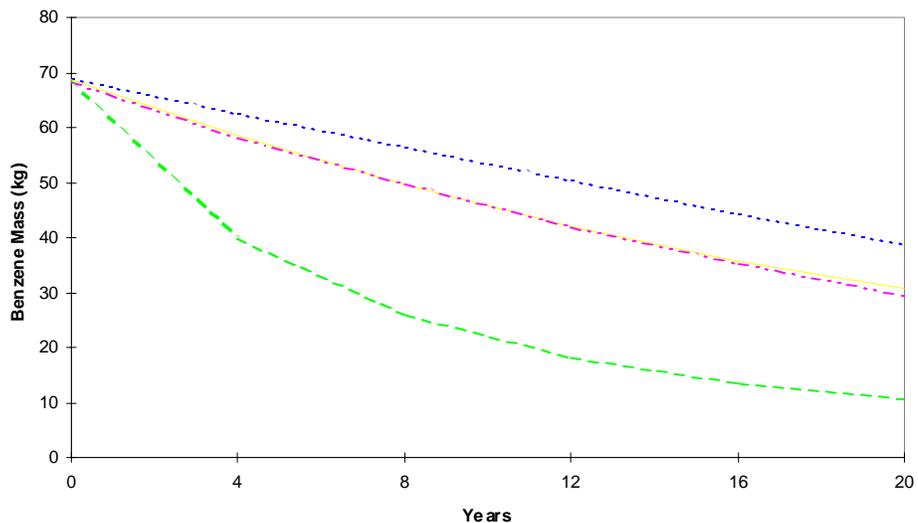
The results of the predictive simulations were compared to select the most effective remedial option. Figure 4.14 illustrates the predicted removal of benzene and TEX mass from residual PSH in the saturated zone for each of the remedial options. The groundwater flushing option removes more benzene and TEX mass than the other remedial options. The graphs also demonstrate the decline in mass removal over time for each of the remedial options. This decrease in the rate of mass removal is further quantified in Table 4.5, which provides a summary of the predicted average rate of benzene mass removal for each of the remedial options. The predicted rate of removal is greatest in the first four years of the simulation for all of the remedial options and then declines over time. The groundwater flushing remedial option has the greatest rate of benzene mass removal at an average rate of 9.9 kg per year during the first four years. Natural attenuation, which serves as the baseline, had an average benzene mass removal rate of 4.3 kg per year. Therefore, groundwater flushing supplied an additional 5.6 kg of benzene removal per year. Results from the groundwater extraction and microbial fence remedial options were similar and only slightly greater than natural attenuation. The decline in benzene mass removal rates is most likely due to the decrease in the benzene mole fraction within the saturated zone PSH and the subsequent decrease in effective solubility. The asymptotic aspect of mass removal is also a function of residual PSH in the unsaturated zone and in the terminal area that is not mitigated by the engineered remedial options as implemented.

Figures 4.15 and 4.16 provide a comparison of the predicted dissolved benzene and TEX concentrations, respectively, for each of the remedial options after 20 years of implementation. The aquifer concentrations after 20 years of groundwater flushing are clearly less than the aquifer concentrations after implementation of the other remedial options. Groundwater flushing is the only remedial option that reduces benzene concentrations to less than 200 µg/L in the off-site area and less than 5 µg/L near the recovery trenches that contain the leading edge of the DPH plume.

**Table 4.7. Comparison of Benzene Source Mass Removal for the Remedial Options.**

<b>Remedial Option</b>	<b>Average Predicted Benzene Source Mass Removal (kg per year)</b>				
	<b>Years 1 to 4</b>	<b>Years 5 to 8</b>	<b>Years 9 to 12</b>	<b>Years 13 to 16</b>	<b>Years 17 to 20</b>
Natural Attenuation	4.3	3.2	2.7	2.3	2.0
Groundwater Extraction	5.3	3.9	3.0	2.4	1.9
Groundwater Flushing	9.9	5.2	3.1	1.9	1.3
Microbial Fences	5.3	3.7	3.0	2.5	2.1

### Predicted Benzene Mass Removal from PSH in the Saturated Zone



### Predicted TEX Mass Removal from PSH in the Saturated Zone

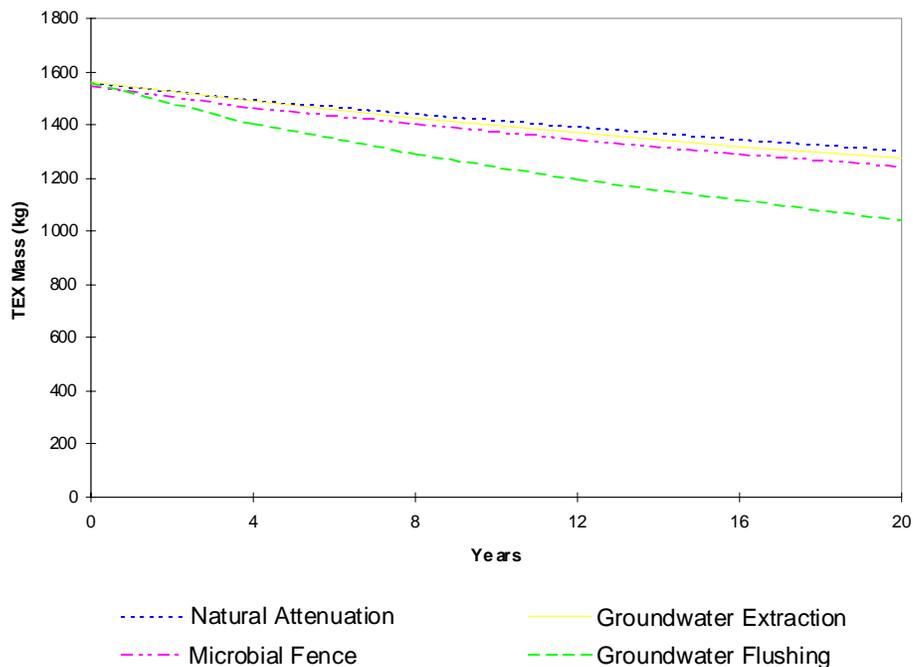
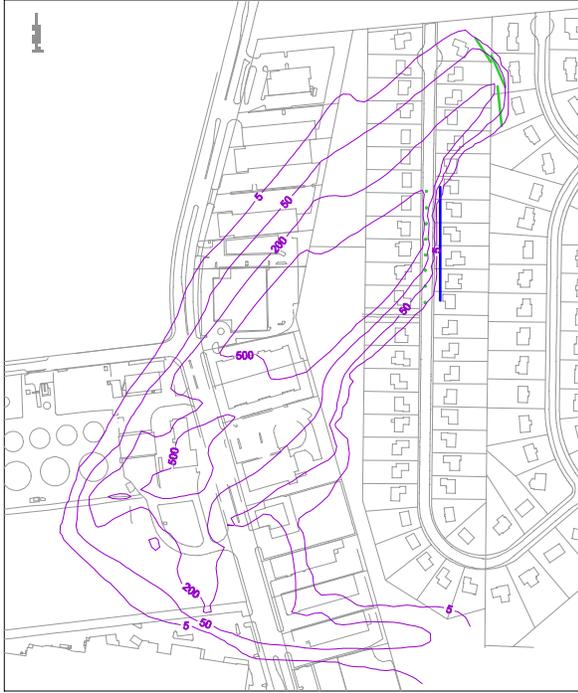
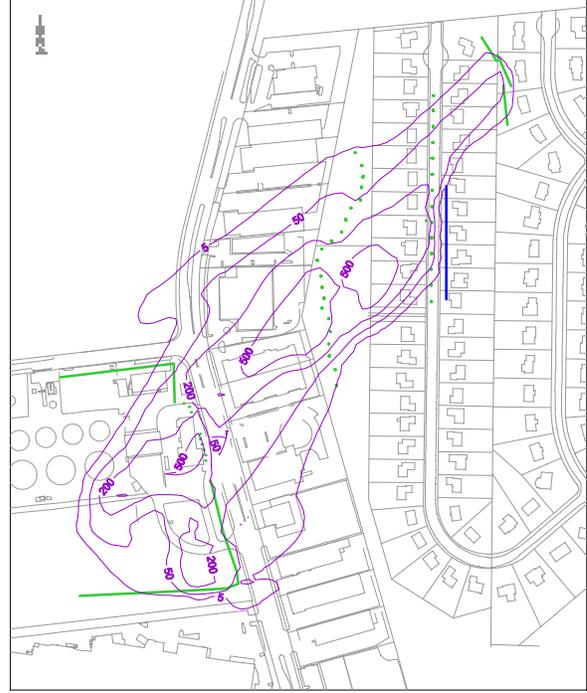


Figure 4.14. Comparison of source mass removal for the four remedial options.

**Natural Attenuation**



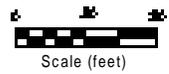
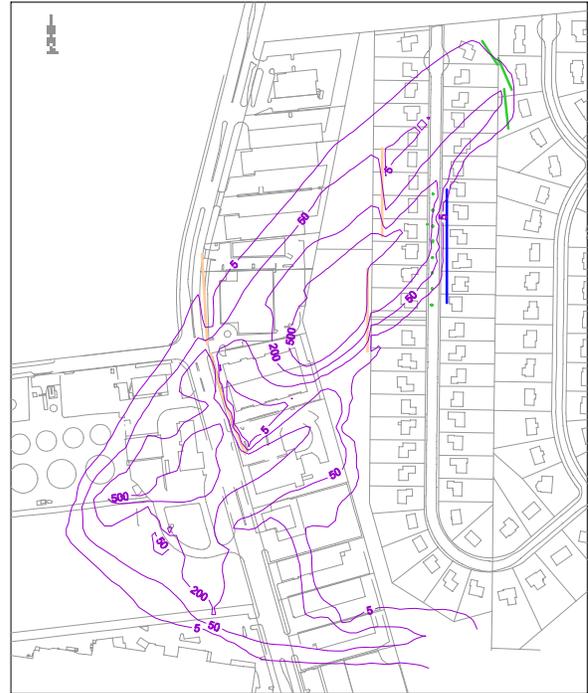
**Groundwater Extraction**



**Groundwater Flushing**

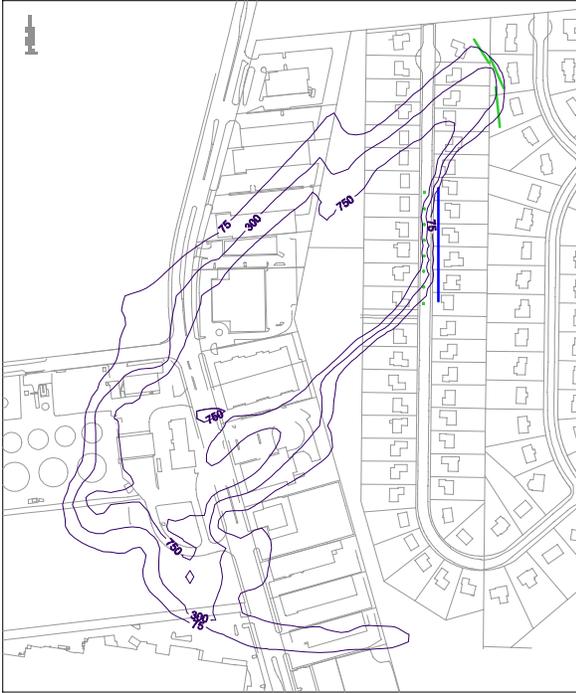


**Microbial Fences**

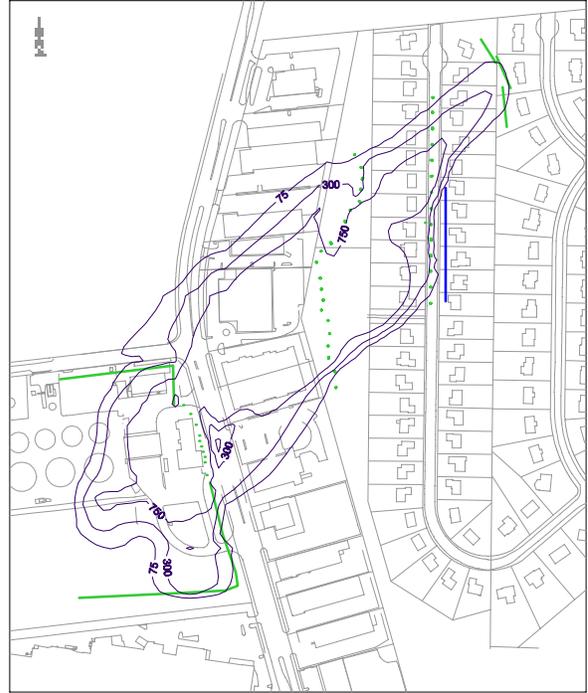


**Figure 4.15. Predicted dissolved benzene concentrations at Year 20 for the four remedial options.**

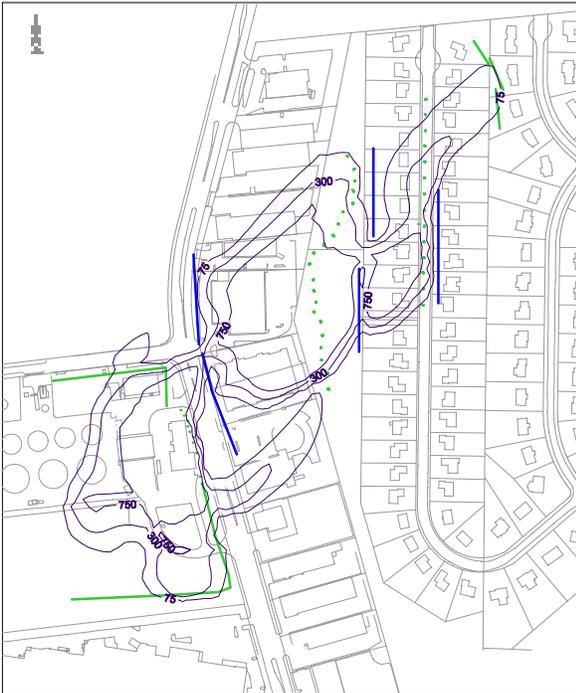
**Natural Attenuation**



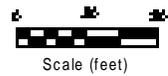
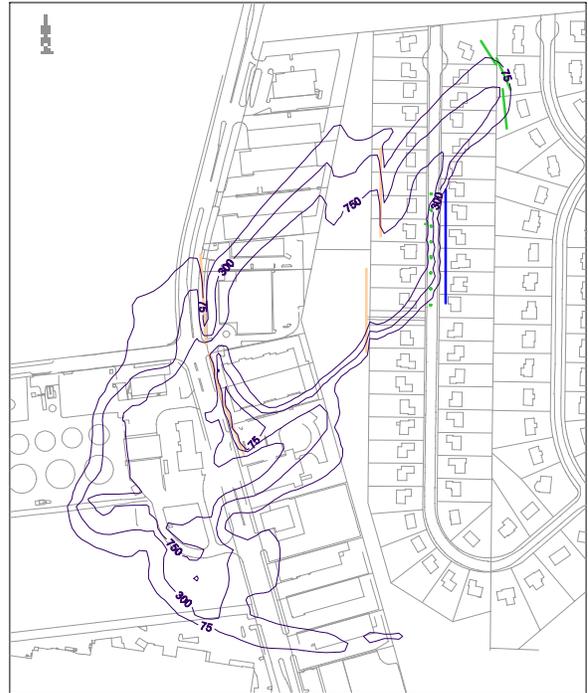
**Groundwater Extraction**



**Groundwater Flushing**



**Microbial Fences**



**Figure 4.16. Predicted dissolved TEX concentrations at Year 20 for the four remedial options.**

The modeling results presented in this chapter demonstrate that the groundwater flushing remedial option provides the greatest reduction of benzene and TEX mass from the PSH source as well as the lowest aquifer concentrations of benzene and TEX in the off-site area. The effectiveness of the groundwater flushing alternative can be attributed to several factors. First, the influx of clean water provides a means to dilute the aquifer concentrations. Secondly, as the clean water infiltrates from the horizontal wells, more mass can leach from the residual PSH. The increased head near the horizontal wells also increases the gradient, and hence groundwater velocities. Since mass transfer from the PSH to the aquifer is influenced by velocity in the BIOTRANS formulation, the increased groundwater velocities near the horizontal well will increase the rate of mass transfer. Finally, the assumption that the infiltrating water will provide dissolved oxygen to the aquifer, stimulates biodegradation and increases mass reduction.

Based on the results of the modeling analyses performed for this research, groundwater flushing appears to be the most efficient remedial option. However, before a remedial decision can be made, the costs associated with implementing each option must be considered. A cost analysis of each remedial option was performed by RETEC (1997). The estimated costs for each remedial option are presented in Table 4.6. The capital costs for each remedial option include costs associated with the long-term operation of HW-1. The operation and maintenance (O&M) costs associated with natural attenuation reflect the operation of the recovery systems at the leading edge of the plume. These costs are consistent between all the remedial options. The costs in Table 4.6 do not reflect other shared activities, such as project administration, site wide monitoring, and reporting. It was assumed that these activities would occur regardless of the remedial option selected. The capital costs associated with the groundwater flushing option are less than half the cost of implementing the microbial fence option. While the annual O&M costs associated with groundwater flushing are approximately \$100,000 greater than either the microbial fence or groundwater extraction options, the potential for a shorter remediation time utilizing the groundwater flushing option could yield cost savings in the long-term. Given the predicted effectiveness of the groundwater flushing option compared to the other remedial options and the relative cost comparison, groundwater flushing should be selected as the remedy for this site.

**Table 4.8. Estimated Costs of Remedial Options.**

Category	Remedial Option			
	Natural Attenuation	Groundwater Extraction	Groundwater Flushing	Microbial Fences
Capital Costs	\$134,000	\$134,000	\$1,266,000	\$3,057,000
O&M Costs per Year	\$138,000	\$350,000	\$450,000	\$361,000

Source: RETEC (1997)

## 4.4 Limitations

Although the modeling activities conducted during this research can be useful tools for the evaluation and selection of remedial alternatives, limitations do exist. Limitations are an inherent component of any modeling activity since numerical models are only a representation of the physical system. Specific limitations associated with this research are discussed in greater detail below.

Calibration of the dissolved phase plume could be enhanced by obtaining more measurements within the interior of the plume. Since the interior of the plume is not well delineated, the modeling relies on the assumption of effective solubility, which may not be true. In addition, the fate and transport model does not account for the potential of anaerobic biodegradation within the plume interior. Field measurements for alternative electron acceptors could provide insight into the possibility of anaerobic degradation at the site. If anaerobic biodegradation is active at this site, the potential effectiveness of natural attenuation could increase substantially compared to remedial options relying on aerobic degradation processes.

The simulation of aerobic degradation processes within the model relies on superposition of oxygen and hydrocarbon and assumes instantaneous degradation. Although the instantaneous solution does not account for any explicit microbial population dynamics, such as cell densities, the model has the capability to specify stoichiometric ratios and limits to biodecay, which can be used to represent inhibiting factors.

With respect to simulating the various remedial options, placement of the remedial system components can impact results of the modeling. Increasing the number and or changing the location of microbial fences and horizontal infiltration wells could alter the model predictions for benzene and TEX removal. A variety of sensitivity simulations could be performed to assess if different configurations of these remedial systems would influence predicted performance. These results would also have to be evaluated in conjunction with changes to capital and O&M costs.

One final note, the predicted effectiveness of each remedial option was evaluated based on the reduction of benzene and TEX from the source mass as well as a reduction in benzene and TEX aquifer concentrations. Although the groundwater flushing option was predicted to have the greatest mass removal and concentration reduction, this does not guarantee that these concentrations do not pose a risk to the environment or to human health. A separate risk analysis should be conducted to determine clean up goals that are protective of human health and the environment.

## 5. Conclusions

Research was conducted to evaluate, through the use of numerical groundwater flow and transport models, the potential of various remedial technologies to reduce dissolved hydrocarbon concentrations and source mass. The research approach involved:

- Site selection and review of historical site characterization data,
- Development and calibration of numerical flow and transport models to site data, and
- Utilization of the calibrated computer models to evaluate various remedial options.

A fuel distribution terminal in the Eastern United States was selected as the test site. A release of diesel and jet fuel from the terminal loading rack area contaminated the unconfined aquifer beneath the terminal and migrated off-site, impacting commercial and residential areas. This site was selected because extensive site characterization and monitoring data were available for the development and calibration of the groundwater flow and transport models.

Development of a groundwater flow model was previously initiated for this site. This research builds upon the preliminary calibration of that groundwater flow model and includes both hydrocarbon flow modeling and dissolved phase fate and transport modeling. The groundwater flow model served as the foundation for both the hydrocarbon flow model and the transport model. In addition, the initial groundwater flow model was modified to incorporate the results of recent site characterization activities and field studies.

Calibration of both the flow model and the fate and transport model was achieved. The flow model reliably simulated the observed groundwater elevations as well as water and product recovery volumes. The fate and transport model reliably simulated the dissolved plume shape and extent. The calibrated models were then applied to simulate four remedial options: (1) natural attenuation, (2) groundwater extraction, (3) groundwater flushing, and (4) microbial fences. The various remedial technologies were implemented in the models and changes from current site conditions were used to evaluate the effectiveness of each technology.

The potential effectiveness of each remedial option was evaluated based on a reduction of both aquifer concentrations and residual source mass for the benzene and TEX constituents. Results of the predictive simulations indicated that the groundwater flushing remedial option provides the greatest reduction of benzene and TEX mass from the PSH source as well as the lowest aquifer concentrations of benzene and TEX in the aquifer.

The calibrated numerical models were able to predict the effectiveness of various remedial options and provide a basis for comparison. The modeling in conjunction with other factors, such as cost, were utilized to facilitate the decision making process.

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# **Appendix A**

## **Modeling Parameters**

# A1. Flow Model Parameters

## A1.1 Recharge

The daily precipitation data and estimated recharge used in the flow model are provided in Figure A.1. The ten recharge zones defined to simulate variable surface cover conditions observed at the site are illustrated in Figure A.2. Table A1.1 contains the recharge factors and the mean annual recharge rate for each recharge zone.

**Table A1.1. Recharge Zone Descriptions, Factors, and Mean Recharge Rates.**

<b>Recharge Zone</b>	<b>Description</b>	<b>Recharge Zone Factors</b>	<b>Mean Recharge Rate (in/yr)</b>
1	Tank Farm/Gravel	1.30	12.3
2	Tank Farm/Gravel	0.60	5.7
3	Wooded	1.27	12.0
4	Grass/Landscaped	1.30	12.3
5	Grass/Landscaped	0.90	8.5
6	Grass/Landscaped	0.26	2.5
7	Pavement	0.18	1.7
8	Grass	0.70	6.6
9	Pavement/Landscaped	0.75	7.1
10	Grass/Landscaped	1.00	9.5

## A1.2 Soil Properties

The soil zone delineation is presented in Figure A.3. Soil Zones 3 and 9 represent fill material. The soil parameters associated with each soil zone are described below and their values are provided in Table A1.2.

Total Aquifer Porosity ( $\phi$ ). A total porosity of 0.44 was estimated from the average of saturated water contents measured on soil cores (Daniel B. Stephens Assoc., 1991). Since Soil Zones 3 and 9 represent unconsolidated fill material, the total porosity in these zones was assumed to be less and was assigned a value of 0.25.

Water Saturation at Field Capacity ( $S_m$ ). The water saturation after field drainage was derived by  $S_m = 1 - \phi_e/\phi$ , where  $\phi_e$  is the drainable porosity (or specific yield) measured to be 0.02 from pump and exfiltration tests (ESE, 1993) and  $\phi$  is total porosity. A value of 0.95 was used in the modeling effort for  $S_m$  and is considered representative of the soil conditions within the smear zone. For Soil Zones 3 and 9, the drainable porosity was assumed to be 0.15, which yielded a value of 0.4 for  $S_m$ .

Horizontal Saturated Hydraulic Conductivity ( $K_s$ ). Horizontal saturated hydraulic conductivity at the site is anisotropic and spatially variable. Values assigned to  $K_s$  were based on the range of measured data and were refined during calibration. The final values for  $K_s$  range from 0.3 to 7.0 feet per day.

Vertical Saturated Hydraulic Conductivity ( $K_v$ ). The vertical saturated hydraulic conductivity controls the drainage of hydrocarbon from the unsaturated zone.  $K_v$  was assigned to be twice the horizontal hydraulic conductivity for all soil zones except Soil Zones 3 and 9. This assumption is based on orientation of the foliations, which dip at a high angle, and on modeling of vacuum area of influence studies at the site (RETEC, 1995b; ES&T, 1997). Since Soil Zones 3 and 9 represent fill material and would not include the foliations,  $K_v$  was assumed to be the same as  $K_s$ .

Anisotropy Ratio ( $R$ ). The anisotropy ratio is the ratio of maximum principal conductivity to minimum principal conductivity. For isotropic soils,  $R$  is 1.0. Values assigned to  $R$  were based on the range of measured data and were refined during calibration. The final values for  $R$  range from 1 to 18.

Anisotropy Angle ( $\omega$ ). The anisotropy angle of conductivity is defined as the angle in degrees clockwise from north to the maximum principal conductivity direction. These values were based on measured angles of foliation and refined during calibration. The final values for  $\omega$  range from 0 to 135°.

van Genuchten “ $\alpha$ ”. This parameter is an empirical parameter that controls the shape of the water retention curve. It qualitatively describes the largest connected pore size. Typically, higher values of  $\alpha$  correspond to a smaller capillary fringe thickness above the water table. The range of  $\alpha$  for the calibration is 0.5 to 3.0 feet<sup>-1</sup>.

van Genuchten “ $n$ ”. This parameter is an empirical parameter that qualitatively describes the pore size distribution of the soil. Higher values of “ $n$ ” reflect narrow pore size distributions whereas lower values of “ $n$ ” reflect broader pore size distributions common in fine grained or poorly sorted soils. The value of “ $n$ ” for the model calibration was initially estimated as 2.2. This value was determined by fitting the van Genuchten model to laboratory moisture retention data in the range of water saturation from the field capacity water saturation ( $S_m$ ) to 1. During the calibration process, minor adjustments in “ $n$ ” were made for Soil Zones 1, 2, 8, 10, 11, and 12.

Maximum Saturated Residual Hydrocarbon Content ( $S_{or}$ ). This parameter defines the maximum residual hydrocarbon content in the saturated zone.  $S_{or}$  was based on measured soil TPH measurements and was refined during model calibration. The final value for  $S_{or}$  was 0.01 for all soil zones except Soil Zone 4, which represents the metasiltstone.

Maximum Unsaturated Residual Hydrocarbon Content ( $S_{og}$ ). This parameter defines the maximum residual hydrocarbon content in the unsaturated zone.  $S_{og}$  was based on measured soil TPH measurements and was refined during model calibration. The final value for  $S_{og}$  was 0.008 for all soil zones except Soil Zone 4, which represents the metasiltstone.

**Table A1.2. Soil Parameters for Soil Zones used in the Flow Model.**

<b>Soil Zone</b>	<b><math>\alpha</math> (ft<sup>-1</sup>)</b>	<b><math>n</math></b>	<b><math>\phi</math></b>	<b><math>S_m</math></b>	<b><math>S_{or}</math></b>	<b><math>S_{og}</math></b>	<b><math>K_s</math> (ft/day)</b>	<b><math>K_v</math> (ft/day)</b>	<b><math>R</math></b>	<b><math>\omega</math></b>
1	2.20	1.90	0.44	0.95	0.0100	0.0080	0.8	1.6	8.0	35.0
2	2.25	2.00	0.44	0.95	0.0100	0.0080	0.6	1.2	12.0	35.0
3	1.00	2.20	0.25	0.40	0.0100	0.0080	7.0	7.0	1.0	0.0
4	1.80	2.20	0.44	0.95	0.0001	0.0001	0.6	1.2	10.0	20.0
5	2.40	2.20	0.44	0.95	0.0100	0.0080	0.3	0.6	6.3	135.0
6	2.00	2.20	0.44	0.95	0.0100	0.0080	1.0	2.0	3.0	40.0
7	0.80	2.20	0.44	0.95	0.0100	0.0080	2.0	4.0	18.0	60.0
8	1.00	1.80	0.44	0.95	0.0100	0.0080	1.5	3.0	10.0	35.0
9	1.80	2.20	0.25	0.40	0.0100	0.0080	5.0	5.0	1.0	0.0
10	2.00	1.65	0.44	0.95	0.0100	0.0080	0.4	0.8	10.0	37.0
11	0.50	1.50	0.44	0.95	0.0100	0.0080	0.3	0.6	8.0	10.0
12	0.70	1.50	0.44	0.95	0.0100	0.0080	0.6	1.2	8.0	35.0
13	2.60	2.20	0.44	0.95	0.0100	0.0080	0.3	0.6	8.0	135.0
14	2.70	2.20	0.44	0.95	0.0100	0.0080	0.6	1.2	12.0	35.0
15	3.00	2.20	0.44	0.95	0.0100	0.0080	0.3	0.6	12.0	35.0
16	0.80	2.20	0.44	0.95	0.0100	0.0080	2.0	4.0	2.0	45.0

## A1.3 Hydrocarbon Properties

Hydrocarbon Specific Gravity ( $\rho_{ro}$ ). Hydrocarbon specific gravity is the density of hydrocarbon relative to water. A hydrocarbon specific gravity of 0.82 was determined in the laboratory and corroborated by field measurements (ESE, 1993).

Oil-Water Viscosity Ratio ( $\eta_{ro}$ ). The oil-water viscosity ratio is the ratio of hydrocarbon viscosity and water viscosity. The oil-water viscosity ratio was determined from laboratory measurements as 2.3 (ESE, 1993).

Capillary Pressure Parameter ( $\beta_{ao}$ ). This parameter is a scaling coefficient that may be approximated by the ratio of water surface tension to oil surface tension. The scaling factor  $\beta_{ao}$  was estimated as the ratio of water surface tension (72 dynes/cm) to the measured hydrocarbon surface tension of 27 dynes/cm (Price, 1991), yielding a value of 2.7.

Capillary Pressure Parameter ( $\beta_{ow}$ ). This parameter is a scaling coefficient that may be approximated by the ratio of water surface tension to oil-water interfacial tension. The scaling factor  $\beta_{ow}$  was estimated assuming  $1/\beta_{ao} + 1/\beta_{ow} = 1$ , yielding a value of 1.6.

## A2. Transport Model Parameters

### A2.1 Dissolved Hydrocarbon Species Parameters

Solubility. The aqueous solubility of species in pure phase is used to determine the equilibrium species solubility in multi-component PSH according to Raoult's Law. The literature value of 1,780 mg/L was assumed for benzene (U.S. EPA, 1990). The average solubilities for the TEX and TPH1 pseudo-species were estimated from PSH compositional analyses as 254 and 13 mg/L, respectively (Appendix B).

Molecular Weight. Species molecular weights are used to calculate species mole fractions, which are used to determine species equilibrium solubility in water during transport simulations. For benzene, a value of 78 g/mol was used. The average molecular weights for the TEX, TPH1, and TPH2 pseudo-species were estimated from PSH compositional analysis as 103, 144, and 208 g/mol, respectively (Appendix B).

Solid-Water Distribution Coefficient ( $k_d$ ). The solid-water distribution coefficient ( $k_d$ ) describes the tendency for organic contaminants to be sorbed to soil. The distribution coefficient may be estimated by

$$k_d = f_{oc} k_{oc} \quad (\text{A.1})$$

where  $f_{oc}$  is the fraction of organic carbon in the aquifer and  $k_{oc}$  is organic carbon partition coefficient of the solute. A mean soil organic carbon fraction of 0.001, which was measured from soil data (ESE, 1993), was utilized in the distribution coefficient calculations. A  $k_{oc}$  reported by Howard (1990) was utilized for benzene, and the  $k_{oc}$  for TEX was averaged from individual species organic carbon partition coefficients (Howard, 1990). The distribution coefficients for benzene, TEX, and TPH1 were assigned values of 0.086, 0.77, and 1.04 cm<sup>3</sup>/g, respectively.

### A2.2 Dissolved Oxygen Transport Parameters

Oxygen Solubility. A value of 8 mg/L was assigned as the solubility limit for dissolved oxygen based on average groundwater temperatures of 16°C.

Oxygen Stoichiometric Coefficient. The oxygen stoichiometric coefficient is the mass of oxygen that is consumed in the biodegradation of a unit mass of hydrocarbon species. The oxygen stoichiometric coefficient was assumed to be 4.0, based on the slurry phase respirometry study performed at the site (RETEC, 1995a).

Maximum Biodecay Rate. The maximum biodecay rate allows limitations to biodecay other than oxygen to be simulated. The maximum biodecay rate was calibrated during modeling of the microbial fence pilot study and was determined to be 1.3 mg/L-day (ES&T, 1997).

## A2.3 General Transport Parameters

Hydrocarbon Specific Gravity. The hydrocarbon specific gravity is the density of hydrocarbon relative to water and is used in the model to convert PSH source volume to mass. A specific gravity of 0.82 was determined in the laboratory (ESE, 1993).

Aquifer Thickness. The aquifer thickness for transport represents the depth over which dissolved phase hydrocarbon occurs. A value of 15 feet was used for aquifer thickness in this analysis based on the average thickness of the PSH smear zone.

Soil Bulk Density. The soil bulk density defines the mass of dry soil relative to the bulk soil volume. A soil bulk density of  $1.6 \text{ g/cm}^3$  was determined in the laboratory from field cores (Daniel B. Stephens and Assoc., 1991; RETEC, 1995a).

Total and Mobile Porosity. Total porosity ( $\phi$ ) was estimated as 0.44 from the average of saturated water contents measured on soil cores (Daniel B. Stephens and Assoc., 1991). The effective mobile porosity ( $\phi_m$ ) is the percent volume of aquifer in which fluids flow and was assigned the value of 0.03, which is approximately the mean field drainable porosity (ESE, 1993).

Dispersivities. Longitudinal and transverse dispersivities control the rate of dispersive transport in the direction of and perpendicular to groundwater flow, respectively. Longitudinal dispersivity was estimated to be 10 feet. This is approximately 20 percent of the observed dissolved transport distance from the PSH plume and is within the range observed by Anderson (1984). The transverse dispersivity was assumed to be 20 percent of the longitudinal dispersivity, or 2 feet.

PSH-Water Mass Transfer Coefficient. The PSH-water mass transfer coefficient describes the rate of species dissolution from PSH into groundwater flowing transversely past PSH in the aquifer. The PSH-water mass transfer coefficient was calibrated during modeling of the microbial fence pilot study and was determined to be 0.3 (ES&T, 1997).

**Table A2.1. BIOTRANS Transport Model Parameters.**

<b>Parameter</b>	<b>Calibration Value</b>		
<b>Dissolved Species</b>	<b>Benzene</b>	<b>TEX</b>	<b>TPH1</b>
Solubility (mg/L)	1780	254	13
Molecular weight (g/mol)	78	103	144
Solid-water distribution coefficient (cm <sup>3</sup> /g)	0.086	0.77	1.04
Initial concentration (µg/L)	variable	variable	variable
Initial mass fraction	variable	variable	0.3
<b>Dissolved Oxygen</b>			
Solubility (mg/L)			8.0
Stoichiometric coefficient			4.0
Maximum biodecay rate (mg/L-day)			1.3
Initial concentration (mg/L)			variable
Recharge concentration (mg/L)			5.0
Boundary concentration (mg/L)			5.0
<b>Transport</b>			
Oil specific gravity			0.82
Effective aquifer thickness (feet)			15
Bulk density (g/cm <sup>3</sup> )			1.6
Total porosity			0.44
Mobile porosity			0.03
Longitudinal dispersivity (ft)			10
Transverse dispersivity (ft)			2
PSH-water mass transfer coefficient			0.3

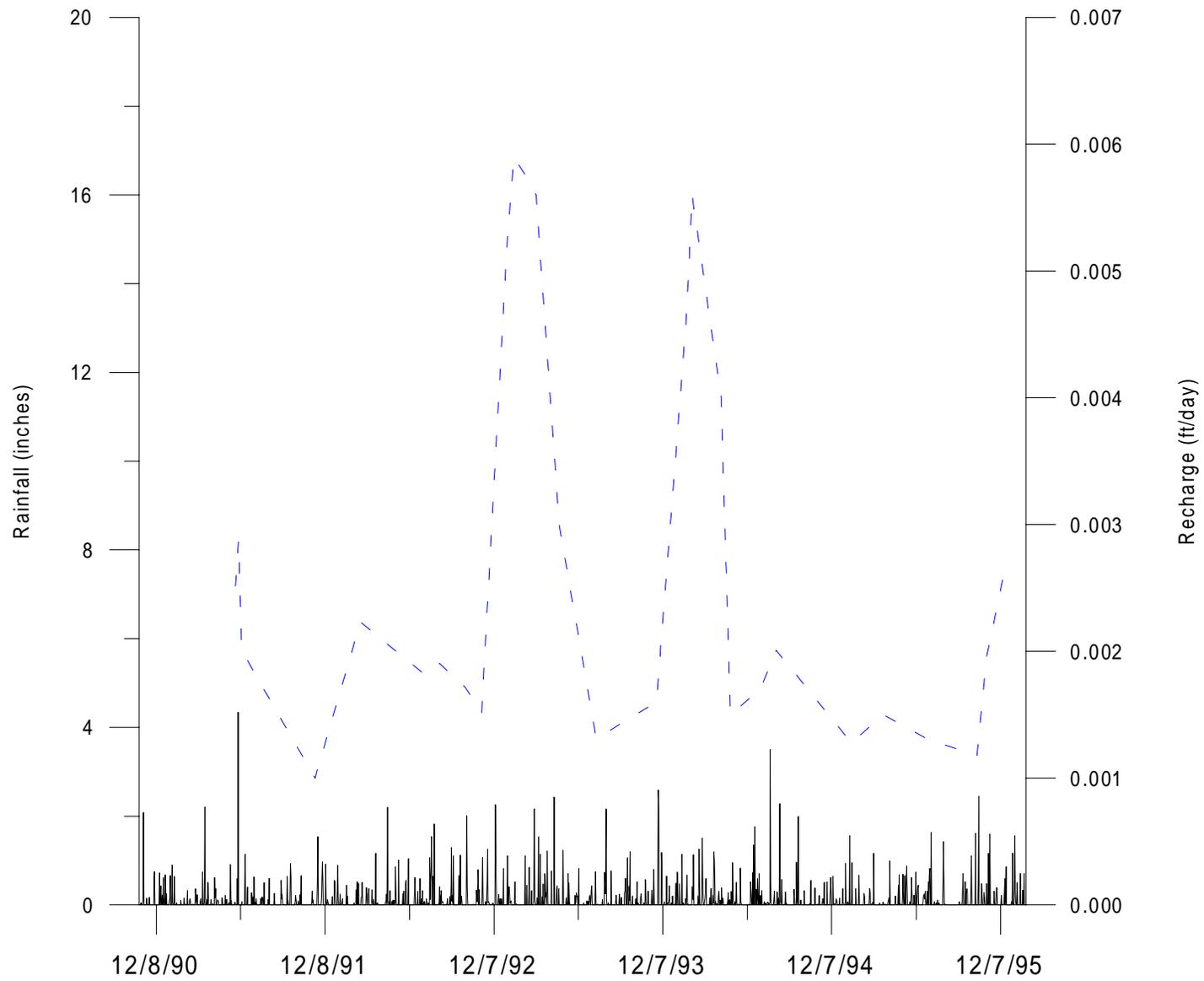


Figure A.1. Rainfall and estimated recharge used in the flow model.

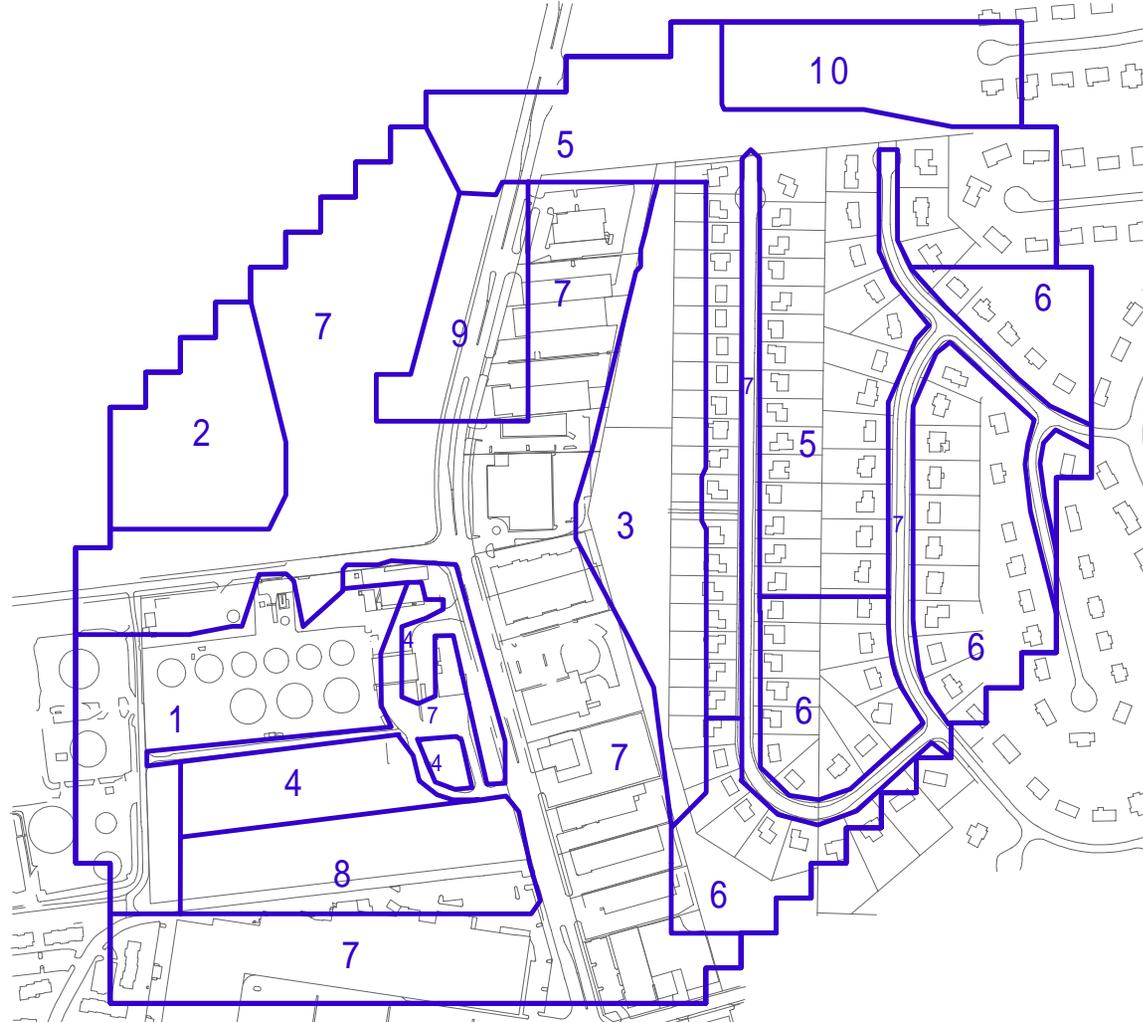


Figure A.2. Recharge zones used in the flow model.

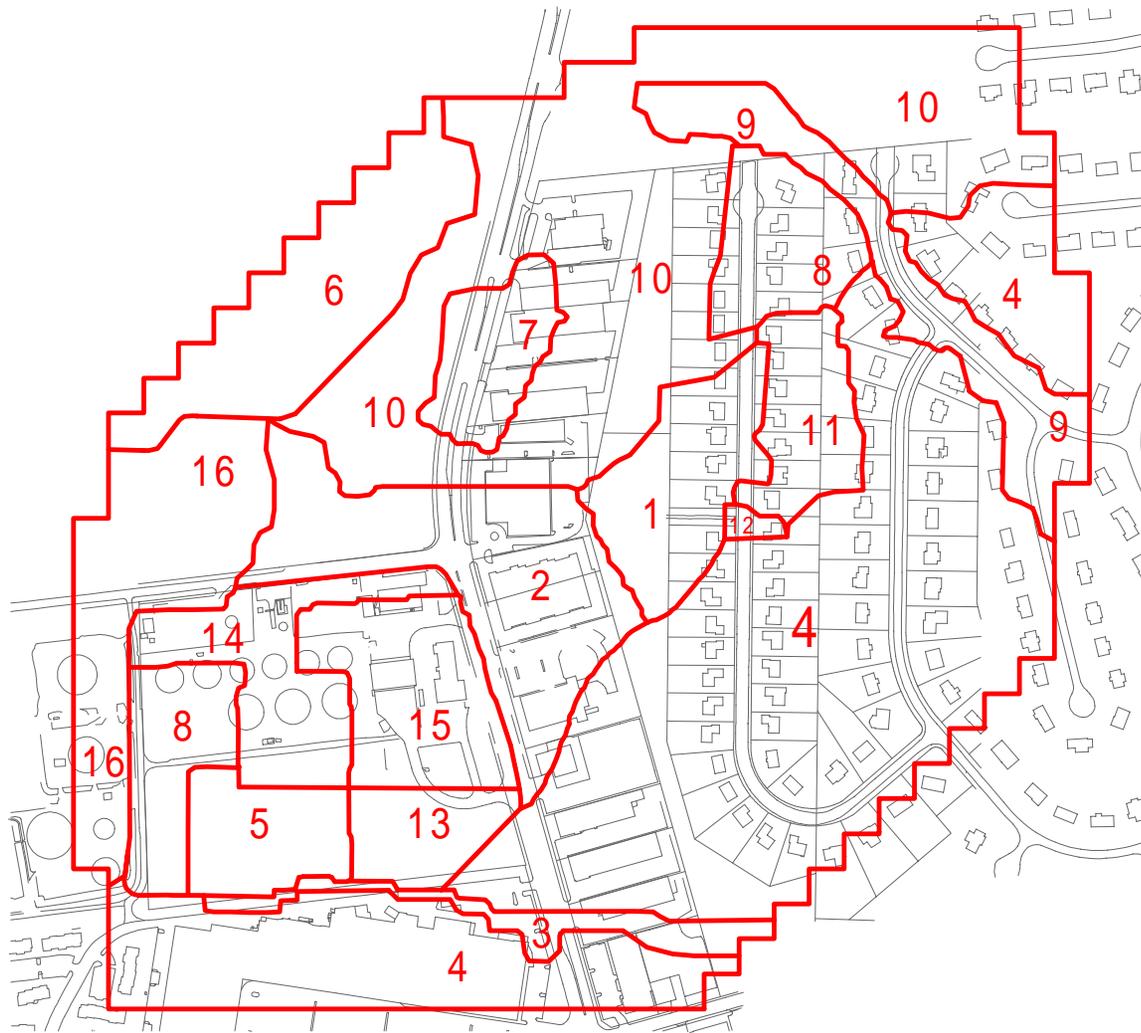


Figure A.3. Soil zones used in the flow model.

# **Appendix B**

## **PSH Composition Analysis**

To define site-specific parameter values for the TPH1 and TPH2 pseudo-species, PSH composition data were analyzed. A complete compositional analysis was performed on a PSH sample collected from a monitoring well at the terminal in October 1992. For each hydrocarbon constituent detected, the laboratory provided the molecular weight, estimated mole fraction, and estimated pure phase solubility.

The mole fraction data were converted to mass fractions as the transport model BIOTRANS uses the mass fraction data to calculate the effective solubility at each time step. The mass fractions for TPH1 and TPH2 were calculated as the sum of the mass fractions for the individual hydrocarbon constituents composing each pseudo-species. After each hydrocarbon constituent had been specified as part of either the TPH1 or TPH2 pseudo-species, the mass fractions of each constituent within each pseudo-species were normalized to one. These values are presented in the *Pseudo-Species Fraction* column in the accompanying table. These values were used to calculate a weighted average for the molecular weight of TPH1 and TPH2 and for a weighted average for the solubility of TPH1. A weighted solubility was not calculated for TPH2 as TPH2 was defined as being insoluble.

Compound	MW	Mole Fraction (estimated)	Mass Fraction (calculated)	Compound Solubility (mg/L)	Pseudo Species Fraction	Weighted Solubility (mg/L)	Weighted MW
<b>TEX</b>							
tol	92	3.1151E-03	1.6101E-03	542	0.1989	108	18
xyl	106	3.5791E-03	2.1314E-03	202	0.2633	53	28
xyl	106	5.8811E-03	3.5022E-03	174	0.4327	75	46
EtBz	106	1.4273E-03	8.4994E-04	165	0.1050	17	11
						<b>254</b>	<b>103</b>
Average							
<b>TPH1</b>							
C5=	70	4.5327E-04	1.7825E-04	203	0.0006	0.1224	0.0422
cC5	70	3.6255E-04	1.4258E-04	156	0.0005	0.0753	0.0338
BzC3	120	1.2933E-03	8.7190E-04	93	0.0029	0.2743	0.3540
BzC3	120	9.4396E-03	6.3637E-03	93	0.0215	2.0024	2.5837
C6=	84	1.3051E-04	6.1591E-05	69.7	0.0002	0.0145	0.0175
BzC3	120	3.6499E-03	2.4606E-03	57	0.0083	0.4745	0.9990
BzC3	120	8.6441E-03	5.8275E-03	57	0.0197	1.1239	2.3660
C4	58	6.3991E-05	2.0851E-05	48.9	0.0001	0.0034	0.0041
BzC3	120	6.7880E-03	4.5762E-03	48	0.0155	0.7432	1.8580
Naph	128	9.4959E-03	6.8285E-03	30	0.0231	0.6931	2.9573
C1Naph	142	1.3086E-02	1.0439E-02	28	0.0353	0.9890	5.0156
BzC4	134	1.5212E-03	1.1452E-03	25	0.0039	0.0969	0.5192
BzC4	134	8.5483E-03	6.4352E-03	25	0.0218	0.5443	2.9176
C1Naph	142	1.9808E-02	1.5802E-02	25	0.0535	1.3366	7.5920
C6	86	3.4070E-04	1.6461E-04	20.5	0.0006	0.0114	0.0479
cC7=	96	1.7583E-04	9.4832E-05	20	0.0003	0.0064	0.0308
cC7=	96	8.8073E-05	4.7500E-05	20	0.0002	0.0032	0.0154
C6	86	3.7287E-04	1.8015E-04	17.9	0.0006	0.0109	0.0524
BzC4	134	3.6093E-03	2.7171E-03	14	0.0092	0.1287	1.2319
BzC4	134	4.8915E-03	3.6824E-03	14	0.0125	0.1744	1.6695
BzC4	134	5.9838E-03	4.5047E-03	14	0.0152	0.2134	2.0423
BzC4	134	7.4085E-03	5.5772E-03	14	0.0189	0.2642	2.5286
C2Naph	156	3.7407E-03	3.2784E-03	14	0.0111	0.1553	1.7304
C2Naph	156	3.7407E-03	3.2784E-03	14	0.0111	0.1553	1.7304
cC7	98	1.1153E-04	6.1405E-05	14	0.0002	0.0029	0.0204
cC7	98	3.8248E-04	2.1058E-04	14	0.0007	0.0100	0.0698
cC7	98	8.8977E-04	4.8987E-04	14	0.0017	0.0232	0.1624
C6	86	5.0991E-04	2.4636E-04	13.3	0.0008	0.0111	0.0717
BzC4	134	9.0232E-03	6.7928E-03	12	0.0230	0.2758	3.0797
BzC4	134	4.1079E-03	3.0925E-03	12	0.0105	0.1256	1.4021
BzC4	134	1.9700E-03	1.4830E-03	12	0.0050	0.0602	0.6724
BzC4	134	6.2213E-03	4.6834E-03	10	0.0158	0.1585	2.1234
BzC4	134	6.4112E-03	4.8264E-03	10	0.0163	0.1633	2.1882
C2Naph	156	1.4318E-02	1.2549E-02	10	0.0425	0.4246	6.6234
bicC9	124	3.4148E-05	2.3788E-05	6	0.0001	0.0005	0.0100
cC8	112	1.1339E-04	7.1349E-05	6	0.0002	0.0014	0.0270
cC8	112	2.0543E-04	1.2926E-04	6	0.0004	0.0026	0.0490
cC8	112	3.2277E-05	2.0309E-05	6	0.0001	0.0004	0.0077
cC8	112	4.3292E-04	2.7240E-04	6	0.0009	0.0055	0.1032
cC8	112	4.6268E-04	2.9112E-04	6	0.0010	0.0059	0.1103
cC8	112	1.0722E-03	6.7464E-04	6	0.0023	0.0137	0.2556
C7	100	3.7484E-04	2.1058E-04	5.9	0.0007	0.0042	0.0712
BzC4	134	1.2110E-02	9.1166E-03	5	0.0308	0.1542	4.1333
C1Biphenyl	168	8.5608E-03	8.0798E-03	5	0.0273	0.1367	4.5927

Compound	MW	Mole Fraction (estimated)	Mass Fraction (calculated)	Compound Solubility (mg/L)	Pseudo Species Fraction	Weighted Solubility (mg/L)	Weighted MW	
C1tetralin	146	4.5549E-03	3.7360E-03	5	0.0126	0.0632	1.8455	
C1tetralin	146	6.0586E-03	4.9694E-03	5	0.0168	0.0841	2.4548	
C2Naph	156	3.5123E-02	3.0782E-02	5	0.1041	0.5207	16.2471	
C2Naph	156	2.1988E-02	1.9270E-02	5	0.0652	0.3260	10.1709	
C7	100	4.6490E-04	2.6118E-04	4.4	0.0009	0.0039	0.0884	
BzC5	148	7.6537E-03	6.3637E-03	3.8	0.0215	0.0818	3.1866	
BzC5	148	7.7827E-03	6.4710E-03	3.8	0.0219	0.0832	3.2403	
BzC5	148	5.8048E-03	4.8264E-03	3	0.0163	0.0490	2.4168	
BzC5	148	7.9977E-03	6.6498E-03	3	0.0225	0.0675	3.3298	
C1tetralin	146	6.1240E-03	5.0231E-03	3	0.0170	0.0510	2.4813	
C1tetralin	146	6.3420E-03	5.2018E-03	3	0.0176	0.0528	2.5696	
C1tetralin	146	5.8843E-03	4.8264E-03	3	0.0163	0.0490	2.3842	
C7	100	2.6429E-04	1.4848E-04	3	0.0005	0.0015	0.0502	
cC9	126	6.8451E-04	4.8454E-04	3	0.0016	0.0049	0.2066	
cC9	126	1.1989E-04	8.4867E-05	3	0.0003	0.0009	0.0362	
cC9	126	7.6278E-05	5.3994E-05	3	0.0002	0.0005	0.0230	
cC9	126	6.0422E-04	4.2770E-04	3	0.0014	0.0043	0.1823	
cC9	126	8.4220E-05	5.9617E-05	3	0.0002	0.0006	0.0254	
cC9	126	1.2946E-04	9.1640E-05	3	0.0003	0.0009	0.0391	
C7	100	1.0242E-03	5.7538E-04	2.6	0.0019	0.0051	0.1947	
C8	114	9.7665E-04	6.2550E-04	2.2	0.0021	0.0047	0.2413	
cC8	112	3.0197E-04	1.9000E-04	2.2	0.0006	0.0014	0.0720	
BzC5	148	5.2243E-03	4.3438E-03	2	0.0147	0.0294	2.1751	
BzC5	148	7.2237E-03	6.0062E-03	2	0.0203	0.0406	3.0076	
C1tetralin	146	3.0947E-03	2.5383E-03	2	0.0086	0.0172	1.2539	
cC8	112	9.8305E-04	6.1855E-04	2	0.0021	0.0042	0.2344	
cC9	126	2.5500E-04	1.8050E-04	2	0.0006	0.0012	0.0770	
cC9	126	1.1455E-04	8.1084E-05	2	0.0003	0.0005	0.0346	
C8	114	4.8680E-04	3.1177E-04	1.5	0.0011	0.0016	0.1203	
cC8	112	1.1872E-04	7.4698E-05	1.4	0.0003	0.0004	0.0283	
C8	114	1.6966E-04	1.0866E-04	1.3	0.0004	0.0005	0.0419	
C8	114	1.5681E-04	1.0043E-04	1.3	0.0003	0.0004	0.0387	
bicC9	124	4.5383E-04	3.1615E-04	1	0.0011	0.0011	0.1326	
BzC5	148	3.4240E-03	2.8469E-03	1	0.0096	0.0096	1.4256	
BzC8	190	3.9522E-03	4.2187E-03	1	0.0143	0.0143	2.7120	
C1tetralin	146	1.2292E-02	1.0082E-02	1	0.0341	0.0341	4.9802	
C1tetralin	146	7.8893E-03	6.4710E-03	1	0.0219	0.0219	3.1965	
C1tetralin	146	1.4820E-02	1.2155E-02	1	0.0411	0.0411	6.0045	
cC10	140	1.4185E-04	1.1157E-04	1	0.0004	0.0004	0.0528	
cC10	140	8.9509E-05	7.0400E-05	1	0.0002	0.0002	0.0333	
cC9	126	1.3234E-03	9.3680E-04	1	0.0032	0.0032	0.3994	
cC9	126	6.0540E-04	4.2854E-04	1	0.0014	0.0014	0.1827	
cC9	126	1.5249E-04	1.0794E-04	1	0.0004	0.0004	0.0460	
cC9	126	2.3206E-04	1.6427E-04	1	0.0006	0.0006	0.0700	
cC9	126	2.2756E-04	1.6108E-04	1	0.0005	0.0005	0.0687	
cC9	126	2.5328E-04	1.7929E-04	1	0.0006	0.0006	0.0764	
cC9	126	1.5567E-03	1.1020E-03	1	0.0037	0.0037	0.4698	
decalin	138	3.5047E-03	2.7171E-03	1	0.0092	0.0092	1.2686	
<b>0.296</b>				<b>12.89</b>		<b>143.73</b>		<b>Average</b>

<b>TPH2</b>							
C8	114	2.7933E-04	1.7890E-04	0.9	0.0003		0.0291

Compound	MW	Mole Fraction (estimated)	Mass Fraction (calculated)	Compound Solubility (mg/L)	Pseudo Species Fraction	Weighted Solubility (mg/L)	Weighted MW
C8	114	7.6553E-04	4.9028E-04	0.9	0.0007		0.0799
C1decalin	152	6.3219E-03	5.3985E-03	0.8	0.0077		1.1728
cC11	154	4.0274E-03	3.4844E-03	0.6	0.0050		0.7670
C9	128	1.8701E-04	1.3448E-04	0.5	0.0002		0.0246
C8	114	1.2122E-03	7.7633E-04	0.5	0.0011		0.1265
cC9	126	6.5420E-04	4.6309E-04	0.5	0.0007		0.0834
cC10	140	2.5596E-04	2.0132E-04	0.5	0.0003		0.0403
cC10	140	1.9899E-03	1.5651E-03	0.5	0.0022		0.3132
cC10	140	7.8993E-04	6.2129E-04	0.5	0.0009		0.1243
C1tetralin	146	4.0625E-03	3.3322E-03	0.5	0.0048		0.6954
C9	128	2.0274E-04	1.4579E-04	0.4	0.0002		0.0267
C2decalin	166	4.6578E-03	4.3438E-03	0.4	0.0062		1.0306
C9	128	8.3937E-05	6.0359E-05	0.3	0.0001		0.0110
C9	128	5.3370E-05	3.8379E-05	0.3	0.0001		0.0070
C9	128	1.6311E-04	1.1729E-04	0.3	0.0002		0.0215
C9	128	1.3250E-04	9.5284E-05	0.3	0.0001		0.0174
C9	128	5.0525E-04	3.6333E-04	0.3	0.0005		0.0665
cC10	140	3.2261E-03	2.5374E-03	0.3	0.0036		0.5077
cC10	140	7.8420E-04	6.1679E-04	0.3	0.0009		0.1234
cC10	140	6.6779E-04	5.2523E-04	0.3	0.0008		0.1051
cC10	140	3.3908E-03	2.6669E-03	0.3	0.0038		0.5337
C9	128	1.1892E-03	8.5513E-04	0.1	0.0012		0.1564
C9	128	4.0324E-03	2.8997E-03	0.1	0.0041		0.5305
C10	142	1.4512E-04	1.1577E-04	0.1	0.0002		0.0235
C10	142	1.5689E-03	1.2516E-03	0.1	0.0018		0.2540
C10	142	1.4868E-03	1.1861E-03	0.1	0.0017		0.2407
C10	142	7.7530E-03	6.1850E-03	0.1	0.0088		1.2553
cC11	154	1.8684E-03	1.6164E-03	0.1	0.0023		0.3558
cC11	154	1.7803E-03	1.5402E-03	0.1	0.0022		0.3390
cC11	154	1.7141E-03	1.4830E-03	0.1	0.0021		0.3264
cC11	154	2.8108E-03	2.4318E-03	0.1	0.0035		0.5353
cC12	168	3.9584E-03	3.7360E-03	0.1	0.0053		0.8971
C10	142	1.6451E-03	1.3124E-03	0.05	0.0019		0.2664
C11	156	1.6471E-03	1.4435E-03	0.04	0.0021		0.3219
C11	156	2.6116E-03	2.2888E-03	0.04	0.0033		0.5103
C11	156	3.5286E-03	3.0925E-03	0.04	0.0044		0.6895
nC11	156	1.7663E-02	1.5480E-02	0.03	0.0221		3.4517
nC12	170	2.2872E-02	2.1844E-02	0	0.0312		5.3077
C13	184	4.8593E-03	5.0231E-03	0	0.0072		1.3210
cC13	182	5.0875E-03	5.2018E-03	0	0.0074		1.3532
cC13	182	4.7204E-03	4.8264E-03	0	0.0069		1.2555
cC13	182	2.4826E-03	2.5383E-03	0	0.0036		0.6603
C14	198	8.0350E-03	8.9378E-03	0	0.0128		2.5294
C1tetralin	180	7.0708E-03	7.1503E-03	0	0.0102		1.8396
C3decalin	170	4.4172E-03	4.2187E-03	0	0.0060		1.0251
nC13	184	1.7742E-02	1.8340E-02	0	0.0262		4.8234
C2tetralin	160	1.3284E-02	1.1941E-02	0	0.0171		2.7308
C2tetralin	160	1.4438E-02	1.2978E-02	0	0.0185		2.9679
C2tetralin	160	4.6535E-03	4.1829E-03	0	0.0060		0.9566
cC13	182	9.5456E-03	9.7601E-03	0	0.0140		2.5389
C14	198	3.7925E-03	4.2187E-03	0	0.0060		1.1939
C14	198	5.9138E-03	6.5783E-03	0	0.0094		1.8617

Compound	MW	Mole Fraction (estimated)	Mass Fraction (calculated)	Compound Solubility (mg/L)	Pseudo Species Fraction	Weighted Solubility (mg/L)	Weighted MW
C14	198	7.4244E-03	8.2586E-03	0	0.0118		2.3372
C14	198	5.0460E-03	5.6130E-03	0	0.0080		1.5885
C15	212	1.3838E-02	1.6481E-02	0	0.0236		4.9941
nC14	198	2.3578E-02	2.6227E-02	0	0.0375		7.4223
C16	226	1.2136E-02	1.5409E-02	0	0.0220		4.9774
C5decalin	208	8.7502E-03	1.0225E-02	0	0.0146		3.0398
cC16	224	5.2274E-03	6.5783E-03	0	0.0094		2.1061
nC15	212	1.9181E-02	2.2845E-02	0	0.0327		6.9223
	200	1.2282E-02	1.3800E-02	0	0.0197		3.9449
	200	3.5955E-03	4.0399E-03	0	0.0058		1.1548
	200	9.5774E-03	1.0761E-02	0	0.0154		3.0762
	200	6.9047E-03	7.7581E-03	0	0.0111		2.2177
	200	5.3137E-03	5.9705E-03	0	0.0085		1.7067
	200	1.1996E-02	1.3478E-02	0	0.0193		3.8529
	200	4.2001E-03	4.7192E-03	0	0.0067		1.3490
	200	1.3809E-02	1.5516E-02	0	0.0222		4.4354
	200	5.6956E-03	6.3995E-03	0	0.0091		1.8294
nC16	226	2.5258E-02	3.2069E-02	0	0.0458		10.3590
	210	3.2122E-03	3.7896E-03	0	0.0054		1.1375
	210	3.7576E-03	4.4332E-03	0	0.0063		1.3306
	210	4.0910E-03	4.8264E-03	0	0.0069		1.4487
	210	9.4850E-03	1.1190E-02	0	0.0160		3.3588
	210	4.5455E-03	5.3627E-03	0	0.0077		1.6096
	210	3.6061E-03	4.2544E-03	0	0.0061		1.2770
	210	3.0607E-03	3.6109E-03	0	0.0052		1.0838
	210	7.0607E-03	8.3301E-03	0	0.0119		2.5003
nC17	240	1.0977E-02	1.4801E-02	0	0.0212		5.0772
pristane	268	5.4852E-03	8.2586E-03	0	0.0118		3.1635
	220	5.7852E-03	7.1503E-03	0	0.0102		2.2484
	220	5.1199E-03	6.3280E-03	0	0.0090		1.9898
	220	1.8404E-03	2.2747E-03	0	0.0033		0.7153
	220	6.6530E-03	8.2228E-03	0	0.0118		2.5856
	220	4.3389E-03	5.3627E-03	0	0.0077		1.6863
	220	4.0207E-03	4.9694E-03	0	0.0071		1.5626
	220	3.1819E-03	3.9327E-03	0	0.0056		1.2366
	220	2.4189E-03	2.9897E-03	0	0.0043		0.9401
	220	3.1819E-03	3.9327E-03	0	0.0056		1.2366
	220	3.0662E-03	3.7896E-03	0	0.0054		1.1916
nC18	254	6.2134E-03	8.8663E-03	0	0.0127		3.2189
phytane	282	4.2425E-03	6.7213E-03	0	0.0096		2.7091
	230	2.5550E-03	3.3014E-03	0	0.0047		1.0853
	230	2.5903E-03	3.3470E-03	0	0.0048		1.1003
	230	3.1265E-03	4.0399E-03	0	0.0058		1.3281
	230	4.3163E-03	5.5772E-03	0	0.0080		1.8335
	230	3.4309E-03	4.4332E-03	0	0.0063		1.4574
	230	5.4507E-03	7.0430E-03	0	0.0101		2.3153
	230	2.6292E-03	3.3973E-03	0	0.0049		1.1168
	230	3.7906E-03	4.8979E-03	0	0.0070		1.6101
nC19	268	4.5116E-03	6.7928E-03	0	0.0097		2.6020
	240	2.8902E-03	3.8969E-03	0	0.0056		1.3368
	240	3.3410E-03	4.5047E-03	0	0.0064		1.5452
	240	1.9793E-03	2.6688E-03	0	0.0038		0.9155

Compound	MW	Mole Fraction (estimated)	Mass Fraction (calculated)	Compound Solubility (mg/L)	Pseudo Species Fraction	Weighted Solubility (mg/L)	Weighted MW
	240	2.8372E-03	3.8254E-03	0	0.0055		1.3122
	240	3.4735E-03	4.6834E-03	0	0.0067		1.6066
	240	1.4117E-03	1.9034E-03	0	0.0027		0.6529
	240	2.7576E-03	3.7181E-03	0	0.0053		1.2754
	240	2.7841E-03	3.7539E-03	0	0.0054		1.2877
	240	2.3054E-03	3.1083E-03	0	0.0044		1.0663
	240	1.6656E-03	2.2457E-03	0	0.0032		0.7704
nC20	282	4.7841E-03	7.5793E-03	0	0.0108		3.0549
	250	2.8510E-03	4.0042E-03	0	0.0057		1.4308
	250	4.0728E-03	5.7202E-03	0	0.0082		2.0440
	250	2.3175E-03	3.2549E-03	0	0.0047		1.1631
	250	2.3789E-03	3.3411E-03	0	0.0048		1.1939
	250	2.5964E-03	3.6466E-03	0	0.0052		1.3030
	250	1.6580E-03	2.3286E-03	0	0.0033		0.8321
	250	2.8000E-03	3.9327E-03	0	0.0056		1.4052
nC21	296	1.4958E-03	2.4874E-03	0	0.0036		1.0523
	260	1.1562E-03	1.6888E-03	0	0.0024		0.6276
	260	2.5945E-03	3.7896E-03	0	0.0054		1.4083
	260	6.8493E-04	1.0005E-03	0	0.0014		0.3718
	260	1.0764E-03	1.5723E-03	0	0.0022		0.5843
	260	1.4151E-03	2.0670E-03	0	0.0030		0.7681
	260	4.9182E-04	7.1838E-04	0	0.0010		0.2670
nC22	310	1.9579E-03	3.4098E-03	0	0.0049		1.5108
	270	1.0210E-03	1.5487E-03	0	0.0022		0.5976
	270	9.6696E-04	1.4667E-03	0	0.0021		0.5660
	270	8.5971E-04	1.3041E-03	0	0.0019		0.5033
	270	4.7837E-04	7.2562E-04	0	0.0010		0.2800
	270	3.9787E-04	6.0351E-04	0	0.0009		0.2329
nC23	324	6.8939E-04	1.2548E-03	0	0.0018		0.5811
	275	1.3643E-04	2.1078E-04	0	0.0003		0.0828
	275	2.0642E-04	3.1890E-04	0	0.0005		0.1253
	275	5.5730E-05	8.6100E-05	0	0.0001		0.0338
	275	7.1533E-05	1.1051E-04	0	0.0002		0.0434
	275	2.4972E-04	3.8580E-04	0	0.0006		0.1516
	275	4.1705E-05	6.4431E-05	0	0.0001		0.0253
	275	6.3518E-06	9.8132E-06	0	0.0000		0.0039
	275	1.2712E-04	1.9639E-04	0	0.0003		0.0772
	275	1.1593E-05	1.7911E-05	0	0.0000		0.0070
	275	5.4409E-06	8.4058E-06	0	0.0000		0.0033
	275	8.7726E-06	1.3553E-05	0	0.0000		0.0053
	275	9.4709E-06	1.4632E-05	0	0.0000		0.0058
	275	2.6257E-05	4.0566E-05	0	0.0001		0.0159
	275	2.6555E-05	4.1027E-05	0	0.0001		0.0161
	275	2.6620E-05	4.1126E-05	0	0.0001		0.0162
	275	2.3455E-05	3.6237E-05	0	0.0001		0.0142
	275	2.5592E-05	3.9539E-05	0	0.0001		0.0155
	275	2.7200E-05	4.2023E-05	0	0.0001		0.0165
	275	1.9636E-05	3.0336E-05	0	0.0000		0.0119
	275	5.8383E-05	9.0199E-05	0	0.0001		0.0355
	275	5.2850E-05	8.1651E-05	0	0.0001		0.0321
	275	3.0232E-05	4.6706E-05	0	0.0001		0.0184
	275	4.2195E-05	6.5189E-05	0	0.0001		0.0256

Compound	MW	Mole Fraction (estimated)	Mass Fraction (calculated)	Compound Solubility (mg/L)	Pseudo Species Fraction	Weighted Solubility (mg/L)	Weighted MW
	275	4.4767E-05	6.9162E-05	0	0.0001		0.0272
	275	2.8678E-05	4.4305E-05	0	0.0001		0.0174
	275	2.2512E-05	3.4780E-05	0	0.0000		0.0137
	275	2.4976E-05	3.8586E-05	0	0.0001		0.0152
	275	1.3643E-05	2.1078E-05	0	0.0000		0.0083
	275	1.3725E-05	2.1204E-05	0	0.0000		0.0083
	275	3.1144E-05	4.8116E-05	0	0.0001		0.0189
	275	3.1214E-05	4.8225E-05	0	0.0001		0.0190
	275	3.6638E-05	5.6604E-05	0	0.0001		0.0222
	275	8.8278E-06	1.3638E-05	0	0.0000		0.0054
	275	4.0825E-05	6.3072E-05	0	0.0001		0.0248
	275	1.7611E-05	2.7209E-05	0	0.0000		0.0107
	275	1.7693E-05	2.7335E-05	0	0.0000		0.0107
	275	1.9775E-05	3.0552E-05	0	0.0000		0.0120
	275	1.1960E-05	1.8478E-05	0	0.0000		0.0073
	275	1.6848E-05	2.6029E-05	0	0.0000		0.0102
	275	1.6103E-05	2.4878E-05	0	0.0000		0.0098
	275	3.0775E-05	4.7546E-05	0	0.0001		0.0187
	275	9.5440E-06	1.4745E-05	0	0.0000		0.0058
	275	2.0184E-05	3.1183E-05	0	0.0000		0.0123
<b>0.700</b>				<b>208 Average</b>			

Note: Some solubilities and molecular weights are estimated

## Mary Ann Parcher

### *Professional Positions:*

- Project Engineer, Environmental Systems & Technologies, Inc., 1997 to present
- Staff Engineer, Environmental Systems & Technologies, Inc., 1994-1996
- Teaching/Research Assistant, Virginia Polytechnic Institute and State University, 1993-1994
- Environmental Scientist, Tetra Tech, Inc., 1991-1993

### *Education:*

B.S. Natural Resource Management, University of Maryland, 1990.

### *Areas of Specialization:*

- Modeling of multiphase flow and transport for NAPLs
- Chemical transport computer modeling
- Modeling of airflow in the unsaturated zone
- Land use and surface water quality modeling
- Site characterization for surface and subsurface environments
- Proposal development and project planning
- Project, budget, and personnel management

### *Honors and Awards:*

- Phi Beta Kappa
- Chi Epsilon
- Gamma Sigma Delta
- Recipient of Pratt Fellowship 1993-1994

### *Memberships in Professional Organizations:*

- American Water Resources Association – Professional Advisor to the Virginia Polytechnic Institute and State University Student Chapter