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**MODELING CATALYTIC DESTRUCTION OF SUBSURFACE CONTAMINANTS IN  
RECIRCULATING WELLS**

THESIS

Kerry J. Cadena, Captain, USAF

AFIT/GEE/ENV/03-02

**DEPARTMENT OF THE AIR FORCE  
AIR UNIVERSITY**

**AIR FORCE INSTITUTE OF TECHNOLOGY**

**Wright-Patterson Air Force Base, Ohio**

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AFIT/GEE/ENV/03-02

MODELING CATALYTIC DESTRUCTION OF SUBSURFACE CONTAMINANTS  
IN RECIRCULATING WELLS

THESIS

Presented to the Faculty

Department of Systems and Engineering Management

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Air Education and Training Command

In Partial Fulfillment of the Requirements for the  
Degree of Master of Science in Engineering and Environmental Management

Kerry J. Cadena, B.S.

Captain, USAF

March 2003

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IN RECIRCULATING WELLS

Kerry J. Cadena, B.S.  
Captain, USAF

Approved:

/SIGNED/  
Dr. Mark N. Goltz (Chairman)

21 Mar 03  
date

/SIGNED/  
Lt Col Alfred E. Thal, Jr (Member)

21 Mar 03  
date

/SIGNED/  
Dr. Junqi Huang (Member)

21 Mar 03  
date

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Kerry J. Cadena

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Groundwater and soil contamination is a significant problem throughout the nation, with approximately 300,000 to 400,000 sites affected (National Research Council, 1994). Examples of groundwater contaminants of special interest to DoD and AF installations include fuel hydrocarbons, chlorinated hydrocarbons, and nitroaromatic compounds.

Traditional remediation technologies, which include pump-and-treat, permeable reactive barriers, and natural attenuation, have numerous drawbacks associated with them. These drawbacks have prompted researchers to look for innovative contamination clean-up methods. The technology investigated in this thesis, recirculating horizontal flow treatment wells (HFTWs) with in-well palladium (Pd) catalyst reactors, offers the potential for destruction of groundwater contaminants commonly found at USAF and DoD installations at less expense, more safely and effectively, and without the need to pump contaminated water to the surface.

In this study, a numerical model was used to simulate application of the remediation technology under different site conditions for a number of contaminants of interest. It was found that the HFTW system with in-well Pd catalyst reactors had potential to remediate groundwater contaminants of DoD interest. Based only on this modeling study, however, it was unclear whether the technology could reduce contaminant concentrations enough to meet regulatory standards downgradient of the treatment system. Further experimental study is recommended, both in the laboratory and in the field, to quantify the efficacy of the technology in treating various contaminants of concern.

# MODELING CATALYTIC DESTRUCTION OF SUBSURFACE CONTAMINANTS IN RECIRCULATING WELLS

## 1.0 INTRODUCTION

### 1.1 MOTIVATION

Groundwater and soil contamination is a significant problem throughout the nation, with approximately 300,000 to 400,000 sites affected (National Research Council, 1994). The estimated cost for remediating all these sites exceeds \$1 trillion over a 30-year period (National Research Council, 1994). The number of sites belonging to the Department of Defense (DoD) that require restoration is estimated at 28,500 (DERP, 2001). In 2001 alone, the budget for cleaning up these sites was \$1.3 billion (DERP, 2001).

The U.S. Environmental Protection Agency's (EPA) Center for Environmental Research Information (CERI) estimates that over 200 different chemicals, both natural and man-made, have been found in groundwater throughout the United States (EPA, 1992). Some of these groundwater contaminants are possible or probable carcinogens. Examples of carcinogenic groundwater contaminants commonly encountered are fuel hydrocarbons (benzene, toluene, ethylbenzene, and xylene), chlorinated hydrocarbons (*e.g.* trichloroethylene (TCE) and tetrachlorethylene (PCE)) and nitroaromatic compounds (National Research Council, 1994; Gui and others, 2000). Groundwater contamination by chlorinated ethenes alone is estimated to be present at approximately 70 percent of Air Force installations (Stoppel, 2001). Additionally, new contaminants are still being found at DoD facilities. One example is N-

Nitrosodimethylamine (NDMA), a soluble substance which is problematic at very low concentrations (NIEHS, 2002). The wide-spread presence of these and many other contaminants in groundwater at United States Air Force (USAF) and other DoD sites worldwide, has led to the investigation of groundwater remediation technologies which may be useful for managing them (Stoppel, 2001).

Containment is one very common strategy for dealing with contaminated groundwater. The goal of containment is not contaminant destruction or the removal of the contaminant source (Domenico and Schwartz, 1998). Instead, containment systems use chemical, biological, or physical processes to prevent the spread of a contaminant to human or environmental receptors (National Research Council, 1994). Groundwater remediation technologies commonly applied to contain a dissolved contaminant plume generally fall into three broad categories: collection and treatment systems, permeable reactive barrier systems (*i.e.* funnel-and-gate systems), and natural attenuation systems (Stoppel, 2001; Starr and Cherry, 1994).

Collection and treatment, more commonly referred to as pump-and-treat, involves pumping contaminated groundwater to the surface and treating it (National Research Council, 1994). The chief drawbacks to this process are the high cost and risk associated with bringing the contaminant to the surface for treatment, as well as the problems associated with disposing of the contaminant and the treated water (Stoppel, 2001).

A permeable reactive barrier (PRB) system involves construction of an *in situ* reactor in the aquifer capable of destroying or immobilizing the contaminant through physical, chemical or

biological means (Domenico and Schwartz, 1998; Starr and Cherry, 1994). PRBs are often emplaced using a so-called “funnel-and-gate” system. These systems involve construction of low hydraulic conductivity cutoff walls (the funnels), which direct contaminated groundwater toward the *in situ* reactor (the gate). The reactor is filled with a permeable media that destroys or immobilizes the contaminant as the contaminated groundwater flows through it (Starr and Cherry, 1994). One commonly installed funnel-and-gate system uses zero-valent iron to dehalogenate chlorinated ethenes (Stoppel, 2001). The main drawback to a PRB system is that it is passive; that is, the system is designed for use under one set of conditions; if those conditions change, the system may be bypassed or the residence time in the reactor may be inadequate (Stoppel, 2001). Also, PRBs are not applicable under all conditions (*e.g.* if the plume is too deep for the barrier to intercept it) (Stoppel, 2001).

"Natural attenuation is the effect of natural processes (*i.e.*, those which do not require human intervention such as engineered enhancements or controls) which reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater" (EPA OUST 2a, 2002b). Environmental factors such as pH, nutrient availability, contaminant concentration, and dissolved oxygen concentration, are known to influence the rate and effectiveness of contaminant destruction. There are a number of drawbacks to natural attenuation. First, the remediation time is lengthier than that of active remediation technologies for a particular site (EPA OUST 10, 2002b). Second, natural attenuation is ineffective under many subsurface hydraulic and geochemical conditions (EPA OUST 10, 2002b). With the exception of fuel hydrocarbons, many DoD contaminants of concern, such as the chlorinated compounds, nitroaromatics, and NDMA, are known or suspected to not naturally attenuate except under

very specific geochemical conditions (Ferland, 2000; Spain and others, 2000; Gui and others, 2000). Finally, the belief that natural attenuation is a “no action” or “walk away” approach to environmental contamination creates a negative public perception of the approach (EPA OUST 4, 2002b; Stoppel, 2001).

The drawbacks associated with the traditional remediation technologies discussed above have prompted researchers to look for innovative contamination clean-up methods. One such innovation involves recirculating horizontal flow treatment wells (HFTWs) with in-well palladium (Pd) catalyst reactors (Stoppel, 2001). This new technology offers the potential for effective contaminant containment with the safety and cost advantages that result from *in situ* remediation; that is, no contaminated water need be brought to the ground surface for treatment, as contaminant destruction is “in place”. Additionally, unlike a PRB system, the HFTW is an active system; engineered system parameters, such as water flow rate in the treatment wells, can be adjusted in response to changes in subsurface conditions (Stoppel, 2001). Figure 1-1 shows both a cross-section and plan view of an HFTW system with in-well Pd reactors.



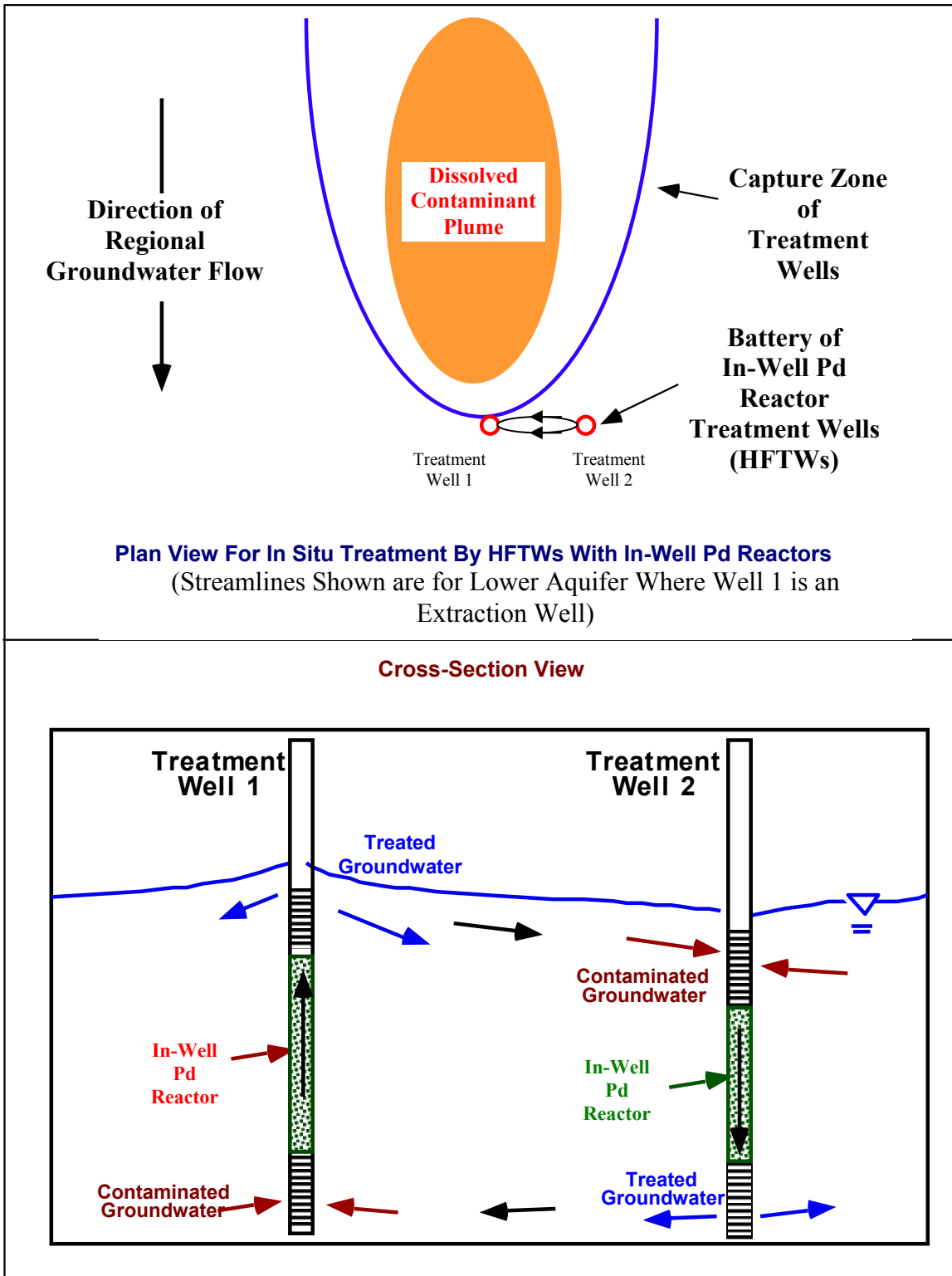


Figure 1-1: HFTW System Cross-Section and Plan View (Stoppel, 2001)

As depicted in Figure 1-1, in an HFTW system, one treatment well pumps water in through a lower screened interval, up through the reactor, and out through an upper screened interval. As the contaminant passes through the reactor it is chemically destroyed. A second well works identically except that flow is in the opposite direction – water travels in through the upper screen, downward through the reactor, and out through the lower screen (Ferland, 2000). The fact that adjacent treatment wells pump in opposite directions results in recirculation of contaminated groundwater through the two wells, so that contaminated water passes through the reactors multiple times. This significantly increases the effectiveness of the system compared to a single-pass system.

A field evaluation of the HFTW technology was conducted at a site with TCE-contaminated groundwater at Edwards Air Force Base, California. The HFTW system installed at Edwards did not use the in-well Pd catalytic reactors described above, but instead used the HFTWs to inject nutrients into circulating groundwater, in order to stimulate *in situ* biodegradation. The site at Edwards consists of two aquifers – an eight-meter thick upper aquifer and a five-meter thick lower aquifer separated by a two-meter thick aquitard, so that the upper screens of the treatment wells injected and extracted water from the upper aquifer while the lower screens injected and extracted water from the lower aquifer. TCE concentrations at the site were measured at 0.5 to 1.5 mg/L. The HFTW system worked as designed. Due to recirculation of groundwater between the two treatment wells, TCE concentrations downgradient of the HFTW system were 97 – 98 percent less than upgradient concentrations, even though there was only about 85% contaminant destruction with a single-pass of contaminated groundwater

through a treatment well (McCarty and others, 1998). In 2003, an HFTW system with in-well Pd catalysts is scheduled to begin operation to treat TCE-contaminated groundwater at this same site (Munakata and others, 2002).

## **1.2 RESEARCH OBJECTIVE**

This thesis will evaluate the potential for use of HFTWs with in-well Pd reactors to manage groundwater contaminants of concern at DoD and USAF installations.

## **1.3 RESEARCH APPROACH**

The general approach of this study will be to apply a numerical model of HFTWs with in-well Pd reactors at various real and hypothetical sites to evaluate technology effectiveness at containing plumes of DoD groundwater contaminants of concern. During the literature review phase of this study, we must address two questions: (1) what groundwater contaminants of concern at USAF and DoD installations can be destroyed by palladium catalysis and (2) what models are available to simulate contaminant plume containment using Pd catalytic reactors installed in-well as part of an HFTW system?

Based on the answer to the latter question, either an existing model or a new model will be used to predict how effective the in-well Pd catalyst technologies will be when managing groundwater contamination at “typical” USAF and DoD sites. If a new model is developed, it will be verified by comparing results with simpler models that have already been verified. Then, using data from the Edwards AFB TCE contaminated site, along with design parameters from the system being installed there, simulations will be run to predict and

evaluate system performance. Model simulations will also be run for real or hypothetical sites contaminated with other contaminants, to evaluate the feasibility of using the technology to manage these contaminant plumes.

#### **1.4 SCOPE AND LIMITATIONS OF RESEARCH**

(1) This research will only consider catalysis by Pd. That is, the applicability of palladium catalysis to treat DoD contaminants of concern will be investigated. Other catalysts will not be studied, even though for a particular contaminant, there may be a catalyst that has more potential for use than Pd.

(2) This study will only focus on the applicability of the HFTW technology to contaminants with DoD relevance.

(3) Where possible, the rate of destruction of various contaminants using Pd catalysis will be obtained from prior work reported in the literature. Where rate studies for a particular contaminant of interest have not been reported in the literature, destruction rate constants will be obtained by extrapolating from studies of Pd catalytic destruction of related contaminants, or by extrapolating from studies that investigated use of other catalysts to destroy the contaminant of interest.

(4) Contaminant concentrations for the model runs will be determined in two ways. For the runs simulating TCE treatment at the Edwards AFB site, contaminant levels used in the model will be based on field data. For the other contaminants, concentrations used in the model will

be based on typical concentrations of the contaminant at other sites as reported in the literature.

## **2.0 LITERATURE REVIEW**

### **2.1 INTRODUCTION**

In this chapter we review literature relevant to modeling the remediation of contaminated groundwater using horizontal flow treatment wells (HFTWs) with in-well palladium (Pd) catalyst reactors. First, the contaminants of interest will be discussed in Section 2.2. The contaminants to be discussed will be divided into two groups. The first group contains those contaminants of special interest to the US Air Force (USAF) because of their prevalence at USAF installations. Contaminants in this category include pesticides, polyaromatic hydrocarbons (PAHs), fuels, and solvents. A second category of contaminants that will be discussed are those which have only recently emerged as problematic groundwater constituents. These include contaminants such as nitroaromatics, perchlorate, Methyl Tertiary-Butyl Ether (MTBE), 1,4-Dioxane, and *N*-Nitrosodimethylamine (NDMA). Next, in Section 2.3 we describe how Pd catalysis works and examine the feasibility of using the Pd catalyst system for remediation of the contaminants discussed in Section 2.2. Section 2.4 is a detailed explanation of how the HFTW system works. Finally, the models available to simulate contaminant plume remediation using an HFTW system with in-well Pd catalytic reactors will be covered. The two types of models, analytical and numerical, will be discussed and examples of model application for each model-type presented.

### **2.2 GROUNDWATER CONTAMINANTS**

As discussed earlier, the contaminants we will look at in this study fall into two categories. Category one contains contaminants of interest to the US Air Force (USAF) because of their

prevalence at USAF installations. These contaminants are detailed in Section 2.2.1 below. The second category is made up of contaminants that have recently emerged as problematic groundwater constituents. These contaminants are covered in Section 2.2.2. Contaminant sources, problems associated with the contaminant, and traditional remediation technologies will be covered for each contaminant.

## **2.2.1 CONTAMINANTS PREVALENT AT USAF INSTALLATIONS**

### **2.2.1.1 Fuel Hydrocarbons**

Fuel hydrocarbons are compounds that contain only hydrogen and carbon. These compounds are found on AF installations worldwide. There are four fuel hydrocarbons on the list of organic constituents most commonly detected in groundwater at AF installations; these compounds are toluene - the second most common groundwater contaminant at Air Force installations, benzene, ethylbenzene, and xylene. Additionally, chlorobenzene, is also listed as a fuel contaminant (Hunter, 2002). These contaminants come from petroleum products used on military installations. These petroleum products include gasoline, diesel fuel, jet fuels, and numerous oil and lubrication products (Lehr and others, 2002).

Tanker trucks, trains, and watercraft are used to transport petroleum products onto and around facilities. These products are stored both above and below ground in storage tanks. Above and below ground piping networks are used to transfer fuel from storage areas to where it will be used. The main cause of fuel hydrocarbon groundwater contamination is accidental spills and leaks from the transport vehicles, storage tanks, and pipelines. Additionally, spills during operational activities are a cause of contamination. Once spilled onto soil, the hydrocarbons

find their way into subsurface aquifers over time (Lehr and others, 2002; Testa and Winegardner, 1991).

A number of serious human health effects are caused by exposure to fuel hydrocarbons. Toluene is known to cause nervous system, kidney, and liver problems. Benzene can cause anemia, decreases in blood platelet count, and increased risk of cancer. Both ethylbenzene and chlorobenzene can cause liver and kidney problems. Xylene is known to cause nervous system damage (EPA, 2002a). Groundwater contaminated by fuel hydrocarbons at a high enough level is not suitable for human consumption, thus reducing the availability of valuable groundwater resources. The US Environmental Protection Agency (USEPA) has set Maximum Contaminant Levels (MCLs) for many common organic and inorganic contaminants. These MCLs, which are primary drinking water standards, are enforceable by law and intended to avoid adverse human health effects (Sellers, 1999). In addition to health effects, release of these substances may result in environmental problems, such as destruction of vegetation (Lehr and others, 2002).

Though remediation of fuel hydrocarbon contaminated groundwater is highly dependent on site-specific characteristics, such as the type and concentration of contaminant and subsurface hydrogeology, traditional methods include pump-and-treat, *in situ* air sparging, *in situ* bioremediation, and natural attenuation (Lehr and others, 2002). The limitations of pump-and-treat and natural attenuation were both discussed in Section 1.1. *In situ* air sparging involves injection of air below the water table. As the air moves upward toward a vapor capture zone above the water table, the fuel hydrocarbons, which are volatile, move from the



water into the air and are thus removed from the groundwater. Problems associated with this technology include: (1) it can only be applied at relatively shallow depths - usually less than 30 feet and (2) it's difficult to assure good contact between the air and contaminant – especially in low permeability soils or when the air channels, as is frequently the case (Lehr and others, 2002; Sellers, 1999). *In situ* bioremediation requires pumping nutrients and/or oxygen into the contaminated subsurface area to encourage microbial growth. The microorganisms then biodegrade the contaminant. A limitation of this process is that it is often difficult, especially in heterogeneous soils, to ensure that the microbes and the nutrient/oxygen/hydrocarbon contaminant mixture are in contact, in order to effect biodegradation. (Lehr and others, 2002; Sellers, 1999).

#### 2.2.1.2 Polynuclear Aromatic Hydrocarbons (PAHs)

A number of PAHs appear on the AF's list of Top 35 Organic Constituents Detected in Groundwater; these include naphthalene, fluorene, and pyrene (Hunter, 2002). PAHs are formed during incomplete combustion of organic fuels such as coal, oil, gas, wood, and garbage. PAHs, which rarely occur as individual compounds, have low solubility and high sorption capacity. Despite these characteristics, many PAHs are capable of finding their way into subsurface aquifers from surface waters and waste sites. The associated human health risk is the carcinogenic nature of many PAHs (WHO, 2002).

Owing to their low solubility and need of aerobic conditions to degrade, traditional remediation technologies for PAHs are few. However, short chain PAHs can be bioremediated under strict aerobic conditions (WHO, 2002).

### 2.2.1.3 Chlorinated Hydrocarbons and Solvents

Examples of chlorinated hydrocarbons of particular importance to the AF include trichloroethylene (TCE), tetrachloroethylene (PCE), vinyl chloride (VC), and 1,1,1-trichloroethane (1,1,1-TCA). These four chlorinated hydrocarbons are ranked one, five, 12, and 15, respectively, on the AF's list of Top 35 Organic Constituents Detected in Groundwater (Hunter, 2002). Some chlorinated hydrocarbons, such as TCE, PCE, and 1,1,1-TCA are solvents while others, such as VC, are daughter products produced during the degradation of solvents. 1,4-Dioxane, although not a chlorinated hydrocarbon, is frequently associated with groundwater contamination by chlorinated solvents. As 1,4-dioxane has only recently been recognized as an important groundwater contaminant to test for, it is not on the AF list. However, it appears to be quite common. 1,4-dioxane has been used as a solvent and is a chemical component of many products. It can be found in paints, varnishes, greases, and automotive coolant liquids (Nyer and others, 2001).

Chlorinated hydrocarbons and solvents are often released as the result of leaks from storage containers - such as underground storage tanks, spills during operational activities, or improper disposal at waste and refuse sites. These substances then find their way into subsurface aquifers and contaminate the groundwater (Semprini, 1995).

There are a number of problems associated with the presence of these contaminants in groundwater. Pertaining to human health, many of these products and substances are known or suspected human carcinogens. Additionally, these substances are relatively recalcitrant to degradation, fairly mobile, and denser than water when present as a separate phase. The

result is that professionals have significant difficulty when attempting to design remediation systems to remove these contaminants from the environment.

Conventional remediation technologies for chlorinated hydrocarbons include pump-and-treat and reductive dechlorination by zero-valent metal. Pump-and-treat remediation systems are described in Section 1.1. Reductive dechlorination by zero-valent metal involves using the metal as an electron donor to donate electrons to reduce the chlorinated hydrocarbon, which acts as an electron acceptor (Lehr and others, 2002). Numerous metals, including zero-valent iron, zero-valent zinc, and zero-valent tin, have been investigated for use in this type of process. *In situ* reductive dechlorination by zero-valent metal typically involves installation of a permeable reactive barrier (PRB) system, as described in Chapter 1, at the downgradient end of a contaminant plume. The contaminated water flows through the permeable barrier and the contaminant is chemically destroyed (Kearny and Roberts, 1998). A problem associated with this technology is the formation of precipitates on the metal surface causing the system effectiveness to be reduced or destroyed (Ferland and others, 2000).

#### 2.2.1.4 Pesticides

Soil and groundwater contamination by pesticides is common throughout the world. Pesticide contamination in general is due to two activities – pesticide manufacture and use (Kearny and Roberts, 1998).

Pesticides are applied to surfaces to kill insects and other unwanted organisms. A wide variety of human health effects are associated with exposure to pesticides during their

production, distribution, and use. Additionally, there are health effects that result from exposure to the residual compounds that remain after pesticide application. These health effects include nerve damage, perhaps leading to paralysis and blindness; brain damage; and liver and kidney disorders. Some pesticides have been found to be carcinogenic, teratogenic, and mutagenic (Trautmann and Porter, 2003a; Trautmann and Porter, 2003b).

Conventional methods to remediate pesticide contamination are numerous. These methods include bioremediation, *in situ* oxidation, phytoremediation (the use of trees and plants for contaminant uptake), and use of zero-valent iron. There are limitations associated with these technologies. Problems associated with bioremediation have been discussed in Section 2.2.1.1. Oxidation requires the use of strong oxidants, and there are safety concerns with storing and handling these oxidants, problems distributing the oxidant uniformly throughout the contaminated area, and the potential to produce toxic compounds as a result of incomplete oxidation. Phytoremediation is limited to application on shallow contaminated sites, the contaminated plant material may need to be treated and disposed of, and the toxicity of the contaminant can hamper plant growth (Sellers, 1999). Of greatest relevance to this thesis effort is the treatment of pesticide-contaminated groundwater using zero-valent iron in a PRB. This technology and its limitations are described Section 2.2.1.3 above.

## **2.2.2 NEWLY EMERGING CONTAMINANTS**

### **2.2.2.1 Nitroaromatic Compounds**

Nitroaromatic compounds are found in pesticides, in industrial feedstocks, and in military explosives (Spain and others, 2000). In this thesis, we are most interested in nitroaromatic compound contamination originating from the production, assembling, packaging, and distribution of explosives, as this has the most relevance to DoD. Typical compounds originating from these activities include 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX). Activities involving the use of explosives have led to significant soil and groundwater contamination by these products at many munitions sites, including military installations (Price and others, 2001; Spain and others, 2000).

Numerous problems are associated with contamination by nitroaromatic compounds. First, because these compounds do not function as bacterial growth substrates they do not biodegrade. Thus, in general, they are less degradable and more persistent in the environment. These substances, which are listed as US EPA Priority Pollutants, are powerful human carcinogens and, when reduced by chemical reaction, become even more carcinogenic, possibly mutagenic, and reactive (Spain and others, 2000).

Traditional technologies for remediation of nitroaromatic contaminated sites are limited. Pump-and-treat, with carbon sorption as the treatment method, is used almost exclusively as the remediation method for such sites (Spain and others, 2000). Reduction using zero-valent

iron, natural attenuation, and phytoremediation, are other methods which can be used for remediation (Spain and others, 2000).

#### 2.2.2.2 Methyl Tertiary-Butyl Ether (MTBE)

MTBE is a gasoline additive used to improve the octane rating of gasoline and to increase combustion efficiency by supplying oxygen. Due to discharge from leaking underground fuel storage tanks, MTBE, which is highly soluble and mobile, has been found contaminating groundwater (Nyer and others, 2001).

MTBE has been conventionally treated using pump-and-treat, though aboveground treatment methods such as activated carbon and air stripping have been less than successful, due to the low volatility and affinity for activated carbon of MTBE. Attempts to bioremediate MTBE in situ have been hampered by low rates of biodegradation (Nyer and others, 2001).

#### 2.2.2.3 Perchlorate

Perchlorate salts have a variety of uses including: as a component in rocket solid propellant and electronic tubes; as an additive in lubricating oils; and during production of paints and enamels. However, ammonium perchlorate, which is specifically used in rocket and missile propellants, is of particular interest within DoD as a groundwater contaminant. Spent and waste perchlorate has been disposed of in landfills and by burning and detonation in open pits. These disposal methods have allowed the compound to infiltrate and contaminate groundwater reservoirs. This highly reactive oxidizer causes human health problems by

competing with iodine in the thyroid, thereby causing a reduction in hormone production (Nyer and others, 2001).

Ion exchange, reverse osmosis, and biodegradation have all been used as aboveground technologies to manage perchlorate-contaminated groundwater. Unfortunately, in order for any of these remediation technologies to be applied, the contaminated groundwater must be pumped to the surface, with the attendant disadvantages that brings (Nyer and others, 2001).

#### 2.2.2.4 N-Nitrosodimethylamine (NDMA)

NDMA, an EPA Priority Pollutant, though mainly used in research, is also used in a number of industrial processes and found in a number of products. NDMA, an odorless yellow liquid, is produced during liquid rocket fuel production. Its other uses are as an antioxidant, a nematocide, a copolymer softener, and a lubricant additive (Nyer and others, 2001).

NDMA is a known carcinogen that causes liver damage in humans and animals. Though breakdown of NDMA in sunlight occurs in minutes, when released to soil or water it is much more persistent. The rate of breakdown in these media is not currently known (Nyer and others, 2001).

Technologies under investigation for remediating NDMA contaminated sites include aboveground UV destruction or adsorption by granular activated carbon, and degradation by granular iron and nickel-enhanced iron (Ni/Fe) (Gui and others, 2000).

## 2.3 Pd CATALYSIS

Significant study has recently been devoted to the use of Pd as a catalyst for the degradation of contaminants in water, specifically chlorinated compounds. Much of this research has centered on the pathways and kinetics by which contaminant reduction occurs. These studies will be presented in Sections 2.3.1 and 2.3.2. Additionally, the viability of using Pd to remediate the contaminants discussed in Section 2.2 will be discussed below, in Section 2.3.3.

### 2.3.1 Pathway

As discussed by Lowry and Reinhard (1999) the primary pathway of Pd-catalyzed reduction of a chlorinated aliphatic hydrocarbon in the presence of hydrogen is hydrodehalogenation. This pathway involves the replacement of the halide ions of a chlorinated compound with hydrogen ions. As shown in Figure 2-1, TCE is catalyzed via hydrodehalogenation in steps  $k_1$  through  $k_7$ . Step  $k_8$ , the reduction of ethene to ethane, is via hydrogenation. However, based on the extremely low levels of chlorinated intermediates, Lowry and Reinhard (1999) concluded that the primary pathway is via step  $k_9$ . That is, the TCE is transformed directly to ethane at the catalyst surface. The end product of the hydrodehalogenation/hydrogenation process is harmless daughter products.

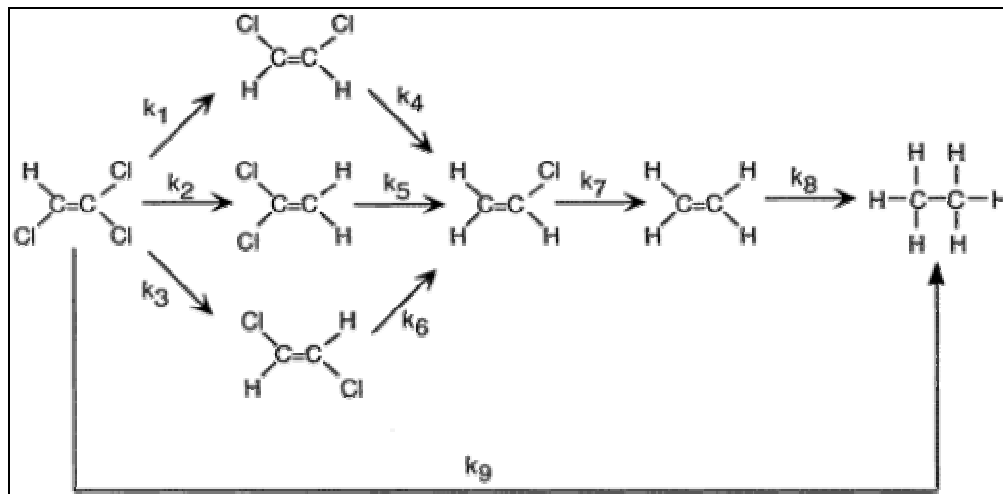


Figure 2-1: Sequential and Direct Reaction Pathways for Conversion of TCE to Ethane (Lowry and Reinhard, 1999)



### 2.3.2 Kinetics

As reported by Ferland and others (2000), chlorinated compound degradation by Pd catalysis can be described using pseudo first-order kinetics. The rate, though apparently not affected by the available surface area of metal, is dependent on catalyst concentration. Hydrogen, which is used as an electron donor, is needed for the reaction (Ferland and others, 2000). However, though dependency on the hydrogen gas concentration has not been fully studied, the hydrogen gas concentration does not appear to influence the reaction rate. As discussed by Lowry and Reinhard (1999), this lack of observed dependence on hydrogen concentration may simply be that the studies conducted thus far maintain excess hydrogen. Lowry and Reinhard (1999) do indicate that transformation of the chlorinated compounds may be by processes other than hydrodehalogenation, however, as stated in Section 2.3.1, the predominant mechanism appears to be first-order hydrodehalogenation.

Figure 2-2 shows the degradation pathways for tetrachloroethylene (PCE) and the less chlorinated ethenes to ethane (Ferland and others, 2000). The  $k_1$ ,  $k_2$ , and  $k_3$  values shown in the figure have been determined by research conducted by McNab and Ruiz (1998). Values for these rate constants are listed in Table 2-1. Ferland and others showed that based on these rates, in-well application of Pd catalysis showed great potential for *in situ* remediation of chlorinated ethene-contaminated groundwater. In contrast, chlorinated ethene degradation rates using zero-valent iron (ZVI) are several orders of magnitude lower. For instance, the pseudo-first-order rate constant for TCE degradation using ZVI is  $1.06 \times 10^{-4} \text{ min}^{-1}$  (Stoppel, 2001)

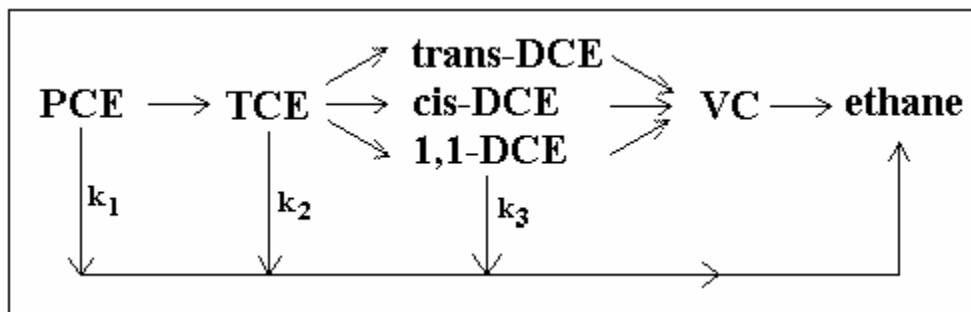


Figure 2-2: Pd-Based Catalytic Degradation Pathways for Chlorinated Ethenes (after Ferland, 2000)

Step	Laboratory k values (min <sup>-1</sup> ) for column experiments
k <sub>1</sub>	1.2
k <sub>2</sub>	1.26 ± 0.005
k <sub>3</sub>	1.14 ± 0.002

Table 2-1: Pseudo-First Order Reaction Constants for Dehalogenation of Chlorinated Ethenes (after Ferland, 2000)

An important note in reference to these pseudo first-order reaction rate constants is that in reality the reaction rate isn't constant (Lowry and Reinhard, 1999). Specifically, during an experiment where a headspace reactor was used to reduce TCE in the presence of Pd catalyst, the rate of TCE transformation was initially under predicted by a first-order rate constant and then over predicted as the model run continued (Lowry and Reinhard, 1999). The researchers concluded that this was the result of catalyst deactivation. However, they also determined that simple pseudo first-order kinetics were still a good approximation to model chlorinated compound destruction by Pd catalysis (Lowry and Reinhard, 1999; Munakata and others, 2002).

### 2.3.3 Applicability of Pd Catalysis to Remediate other Contaminants of Interest

The studies discussed above focused on the use of Pd catalysis to remediate chlorinated hydrocarbon-contaminated groundwater. We now investigate the potential of this technology to remediate the other common groundwater contaminants discussed in Section 2.2.

#### 2.3.3.1 Fuel Hydrocarbons

Bucker and Förster (1998) studied the use of Pd on Y-type zeolites (PdY) to decompose benzene, xylene, and toluene in batch experiments. The researchers looked at each of the compounds individually, not as a mixture as they are found in fuels. The results of the study indicate that PdY can be used to catalyze the oxidation of these compounds to produce carbon

dioxide and water. Contaminant conversions of 65 percent or better were routinely obtained. Moreover, under extreme conditions, at a temperature of 533 K, only a 0.08 second residence time was required to completely convert the target compounds to carbon dioxide and water using only 1 wt% Pd. From these findings, it seems remediation of fuel hydrocarbons by Pd may be possible (Bucker and Förster, 1998).

### 2.3.3.2 Polynuclear Aromatic Hydrocarbons (PAHs)

No information was located documenting research involving Pd, or other metals, being utilized to destroy or degrade PAHs. Perhaps this is due to the low solubility of PAHs in water, making research into technologies that can treat dissolved phase PAHs a low priority. It is unlikely that Pd-catalysis is applicable to PAH remediation (Agrawal, 2002).

### 2.3.3.3 Pesticides

A number of studies involving a variety of pesticides and Pd have been published. Engelmann and others (2001) used magnesium/Pd bimetallic particles to dechlorinate 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane, commonly known as DDT, using batch experiments. Though no rate information was reported, total dechlorination of the DDT was achieved (Engelmann and others, 2001). A second study of interest was conducted by Siantar and others (1996). This research investigated use of a hydrogen/Pd catalyst to treat 1,2-dibromo-3-chloropropane (DBCP). The study, run in a batch mode, measured an average pseudo-first order reaction rate constant of  $0.22 \pm 0.03 \text{ min}^{-1}$ . It appears likely that pesticides with nitrite or carbon-chlorine bonds could be remediated using Pd (Agrawal, 2002).

#### 2.3.3.4 Nitroaromatic Compounds

Though research into nitroaromatic destruction by Pd has begun in recent years for use in groundwater remediation applications, there is still little published data currently available. Researchers have investigated Pd-catalysis using palladium-containing polymers, Pd salts, and Pd on carbon, iron, and aluminum supports (Ugo and others, 1991; Klyuyev and Vainshtein, 1997; Rodgers and Bunce, 2001). Figueras and Coq (2001) determined that the reaction between the Pd catalyst and the nitroaromatic compounds is both very rapid and exothermic. Unfortunately, no information was located in the published literature regarding reaction rate constants.

#### 2.3.3.5 Methyl Tertiary-Butyl Ether (MTBE)

No information was located documenting research involving Pd, or other metals, being utilized to destroy or degrade MTBE. This appears to be a compound that may be amenable to destruction by Pd-catalysis, further research is needed (Agrawal, 2002).

#### 2.3.3.6 Perchlorate

No information was found on research involving Pd-catalyzed reduction of perchlorate. However, research involving other metals is available in published literature. One example involves the use of UV light and metallic iron ( $\text{Fe}^0$ ) which was researched by Gurol and Kim (2000). The results of this study were that, under anoxic conditions, perchlorate is reduced to chloride and water. Unfortunately, very intense UV light was required to affect high reaction rates.

### 2.3.3.7 N-Nitrosodimethylamine (NDMA)

Though no information was found covering research involving NDMA destruction using Pd, there have been studies investigating the use of granular iron and nickel-enhanced iron to catalyze NDMA destruction (Gui and others, 2000). It thus is very probable that Pd-catalyzed destruction of NDMA is feasible (Agrawal, 2002).

## **2.4 APPLICATION OF IN-WELL TREATMENT SYSTEM TO REMEDIATE GROUNDWATER**

In order for Pd-catalyzed destruction to occur *in situ*, it is necessary to mix the contaminant together with either an oxidizing agent (in the case of Pd-catalyzed oxidation, such as in the case of fuel hydrocarbon contamination) or a reductant (in the case of Pd-catalyzed reduction, such as for chlorinated hydrocarbons, nitroaromatics, pesticides, perchlorate, etc.) in the presence of the catalyst. An HFTW can effect this mixing in-well, without the need to pump contaminated water to the surface, thus avoiding the disadvantages of a groundwater extraction system, which were discussed in Chapter 1.

An HFTW system involves a pair of treatment wells, one pumping in an upward direction and the other in a downward direction (Ferland and others, 2000). A number of different in-well treatment systems have been proposed or employed to effect destruction of groundwater contaminants. Examples of such treatment systems include remediation via biodegradation (McCarty et al., 1998) and the use of in-well catalytic reactors (McNab and others, 2000; Stoppel and Goltz, 2003; Munakata and others, 2002).

### **2.4.1 HFTW SYSTEM OPERATION**

An HFTW system typically has two wells. Each well is screened at two different depths. In one well, groundwater is extracted from a lower horizon of the aquifer and pumped upwards through an in-well reactor. As contaminated water passes through the reactor, it is treated, or perhaps, as in the case of a bioremediation application, nutrients are amended to the flowing groundwater. The treated water is then discharged through the upper screen into an upper horizon of the aquifer. Well 1 in the cross-section view of Figure 2-3 shows this operation. Well 2 in the figure works identically to Well 1 except that the water is being pumped in the opposite direction. That is, contaminated groundwater is being drawn in through the upper screen and treated water is being discharged through the lower screen (Munakata and others, 2002; Stoppel and Goltz, 2003). The plan view in Figure 2-3, shows the capture zones and water flows between the wells. In addition to mixing, HFTW operation induces groundwater recirculation between the two treatment wells. This recirculation allows some portion of the treated groundwater to be recaptured by the treatment system and passed through the catalyst treatment reactors multiple times (Munakata and others, 2002; Stoppel and Goltz, 2003). Thus, although one pass of contaminated water through the system may be inadequate to achieve required down-gradient contaminant concentrations, being able to affect multiple passes of contaminated water through the reactors may result in achievement of the required downgradient concentration levels (Fernandez, 2001; Stoppel and Goltz, 2003).

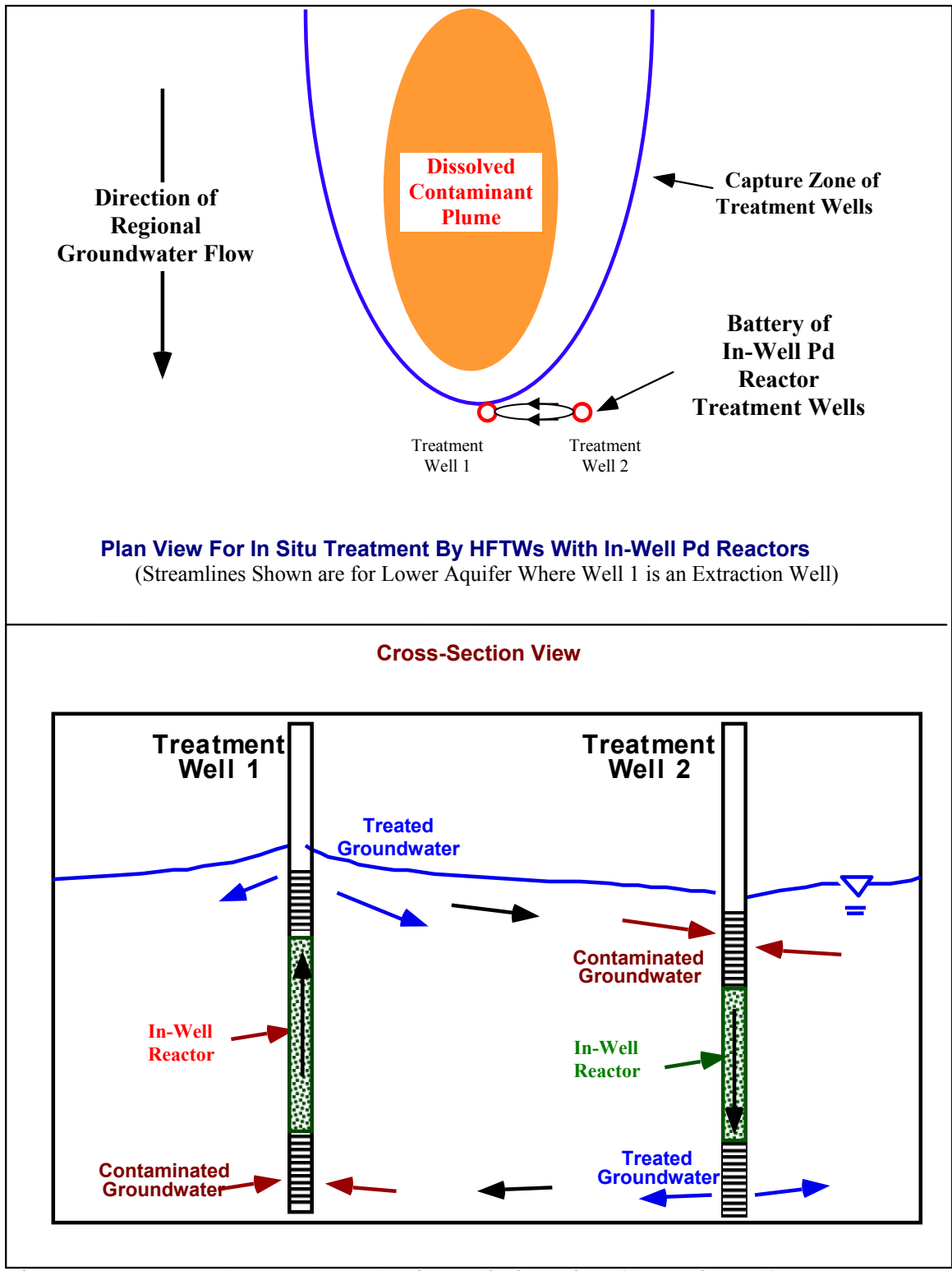


Figure 2-3: HFTW System Cross-Section and Plan View (Stoppel, 2001)

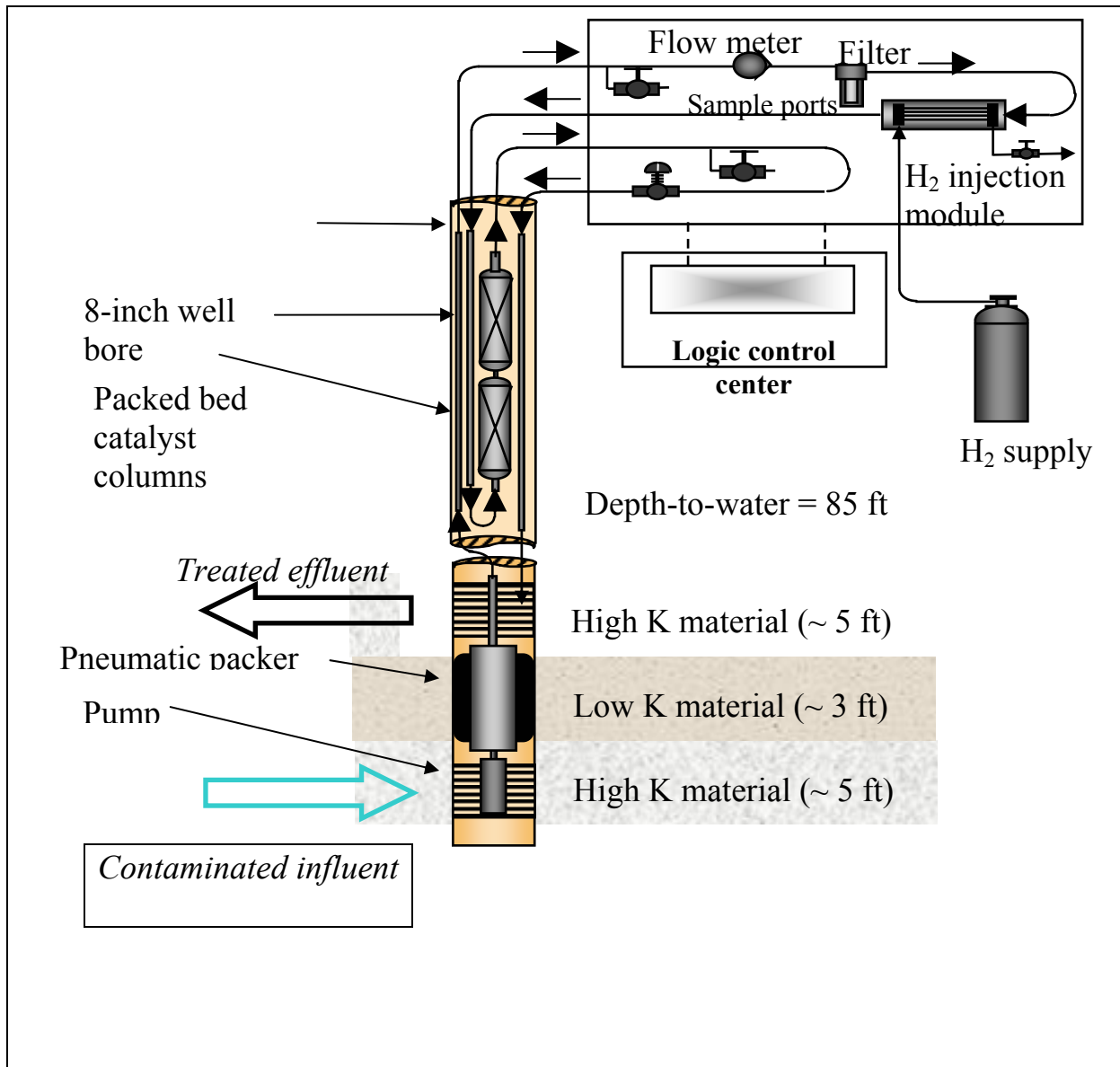


Figure 2-4: Horizontal Flow Treatment Well with In-Well Reactor (McNab and others, 1999)



## **2.4.2 BIOREMEDIATION USING HFTWs**

McCarty and others (1998) evaluated application of an HFTW to effect biodegradation of TCE at Edwards AFB's Site 19. Specifically, aerobic cometabolic biodegradation was investigated (McCarty and others, 1998).

The site had two aquifers, an eight meter thick upper aquifer and a five meter lower aquifer, separated by a two meter thick aquitard. The HFTW system operated as described in Section 2.4.1. Toluene (an electron donor) and oxygen (an electron acceptor) was mixed into TCE-contaminated groundwater as it flowed through each HFTW treatment well. Oxygen was supplied as hydrogen peroxide and oxygen gas, while neat toluene was added. Toluene, oxygen gas, and hydrogen peroxide were mixed into the flowing water using static mixers. When the groundwater was injected into the aquifer, bioactive zones were established around the injection well screens. In these zones, indigenous microorganisms aerobically oxidized the toluene, which served as a primary substrate for microbial metabolism and growth. Fortuitously, the enzyme produced by the microorganisms to oxidize the toluene also served to co-oxidize (or "co-metabolize") the TCE (McCarty and others, 1998).

It was estimated that with each pass of contaminated water through a bioactive zone, 83-87% of the TCE was destroyed. However, when the investigators compared TCE concentrations upgradient and downgradient of the HFTW system, overall removals of 97-98% were measured. This is because of the recirculation of water between the two treatment wells that was discussed above, whereby contaminated water was recycled multiple times through the bioactive zones (McCarty and others, 1998).

### 2.4.3 HFTWs WITH IN-WELL METALLIC REACTORS

McNab and Ruiz (1999) and McNab and others (2000) report a field evaluation of a circulating well with an in-well Pd reactor that was operated at a chlorinated solvent-contaminated site at Lawrence Livermore National Laboratory. Unlike the HFTW system described above, the Lawrence Livermore study used only a single dual-screened well with an in-well treatment system. As shown in Figure 2-4, the well spanned two aquifers. The two aquifers were separated by an aquitard. The lower well screen extracted contaminated water from the lower aquifer while treated water was injected into the upper aquifer through the upper well screen. The treatment system consisted of two packed bed reactors containing Pd coated alumina,  $\text{Al}_2\text{O}_3$ , spheres. In this system, molecular hydrogen is used as a reductant, and the  $\text{H}_2$  injection module shown in Figure 2-4 supplies the electron donor needed to reductively dehalogenate the chlorinated contaminant.

This field evaluation verified the viability of using circulating wells to promote *in situ* catalytic reductive dehalogenation of chlorinated solvent contaminants. The system effectively remediated a number of chlorinated hydrocarbons, including TCE, PCE, 1,1-dichloroethene (1,1-DCE), and carbon tetrachloride. Specifically, with a four hour per day operation cycle, the removal efficiencies for many chlorinated contaminants were above 90 percent. For the four chlorinated hydrocarbons mentioned above, the removal efficiencies were >99 percent. For example, in the case of TCE, the system influent and effluent levels were 3,612-3,777 ppb and <0.4-0.8 ppb, respectively. Additionally, no daughter products, such as vinyl chloride, were detected.

Another example of research using in-well Pd reactors to manage chlorinated solvent contaminated groundwater was described by In this effort, which is still underway, a dual-well HFTW system, as described in Section 2.4.1, with in-well Pd catalyst was proposed to remediate TCE- contaminated groundwater at the same Edwards AFB site as was discussed in Section 2.4.2. Figure 2-4 depicts one of the treatment wells. Both a field project and laboratory study was done during this research effort.

As indicated earlier, the field project for this study has not yet been conducted. However, results from the laboratory study have shown TCE removal rates of 50 to 80 percent, though this rate dropped over time due to catalyst deactivation. A TCE reaction rate constant of  $0.43 \text{ min}^{-1}$  was determined in the laboratory and methods of catalyst regeneration are being investigated (Munakata and others, 2002).

## **2.5 MODELING AN HFTW SYSTEM WITH IN-WELL Pd CATALYSTS**

A number of models have been developed to simulate how HFTW systems work to manage contaminated groundwater. These models fall into two general categories, analytical and numerical. In section 2.5.1, we will discuss analytical models that have been developed to simulate the flow field induced by HFTWs (Christ and others, 1999), as well as analytical models that simulate flow induced by HFTWs coupled with contaminant transport and destruction using in-well Pd reactors (Ferland and others, 2000; Stoppel and Goltz, 2003). Although to our knowledge the only study that applied a numerical model to simulate flow induced by HFTWs coupled with contaminant transport and destruction using in-well Pd reactors was conducted by Fernandez (2001), other investigators have numerically modeled

*in situ* bioremediation using HFTWs (Huang and Goltz, 1998; Gandhi and others, 2002a;b). These numerical modeling studies will be discussed in Section 2.5.2.

### **2.5.1 ANALYTICAL MODELS**

Analytical models are easy to understand and apply. An analytical model is an exact solution to the differential equation(s) that describe the process of interest. Many simplifying assumptions, for example unidirectional groundwater flow, are usually required to obtain an analytical solution. Though these models are often too simplistic to be applied to simulate real-world systems, they are commonly used as screening tools to test and benchmark numerical codes, and to help the modeler understand how a system works (Gershenfeld, 1999).

#### **2.5.1.1 Christ and others (1999) - HFTW Flow Model**

Christ and others (1999) developed a model to simulate the two-dimensional steady-state flow field induced in a homogeneous aquifer by constant pumping of an HFTW system. The main focus of the study was the development of equations to determine the interflow between the treatment wells ( $I_{avg}$ ) and the capture zone width (CZW). For a two-well HFTW system, interflow is defined as the ratio of flow through the extraction well that originated in the injection well. As we will see below, interflow is an important parameter in determining the overall treatment efficiency of an HFTW system. The detailed derivation for these parameters is beyond the scope of this study. However, following Christ and others (1999), we are able to determine  $I_{avg}$  and CZW if we know such things as the regional Darcy groundwater velocity (speed and direction), the distance between the treatment wells, the

aquifer thickness, the treatment well pumping rates, and the orientation of the treatment wells to the regional flow.

Another important parameter characterizing a treatment system is removal efficiency. First, let us define the single-pass treatment efficiency,  $\eta_{sp}$ , of a system as the fraction of contaminant removed during a single pass of contaminated water through the treatment reactor (*e.g.* the catalyst bed). The equation for  $\eta_{sp}$  is

$$\eta_{sp} = \frac{C_{in} - C_{out}}{C_{in}} \quad (1)$$

where  $C_{in}$  is the influent contaminant concentration and  $C_{out}$  is the effluent contaminant concentration (Stoppel and Goltz, 2003). We may also define overall treatment efficiency of an HFTW system as the fraction of contaminant flowing into the system from upgradient that remains after treatment and flows downgradient. That is:

$$\eta = \frac{C_{up} - C_{down}}{C_{up}} \quad (2)$$

where  $C_{up}$  and  $C_{down}$  are the contaminant concentrations upgradient and downgradient of the HFTW treatment system, respectively. Using mass balance, and the above definitions, we find (Christ and others, 1999):

$$\eta = \frac{\eta_{sp}}{1 - I_{avg}(1 - \eta_{sp})} \quad (3)$$

### 2.5.1.2 Ferland and others (2000) - HFTW Flow with First-Order Contaminant Destruction by an In-Well Pd Reactor

Ferland and others (2000) developed an analytical model which coupled the steady-state flow model of Christ and others (1999) with a model of chlorinated ethene fate-and-transport as affected by first-order destruction in an in-well Pd reactor.

Ferland and others (2000) used pseudo first-order reaction kinetics as the basis for their analytical model. The pseudo first-order equation is:

$$\frac{dC}{dt} = -kC$$

where  $k$  is the contaminant first-order reaction rate constant, and  $C$  is the contaminant concentration. Integrating this equation gives

$$\frac{C(t)}{C_{in}} = e^{-kt}$$

where  $C(t)$  is the contaminant concentration at time  $t$  and  $C_{in}$  is the initial contaminant concentration (Ferland and others, 2000). Thus, if we know the first-order rate constant,  $k$ , and the residence time in a catalytic reactor, which is a function of the reactor volume, porosity, and flow rate through the reactor, we can calculate the concentration of contaminant leaving the reactor ( $C_{out}$ ) for a given influent concentration ( $C_{in}$ ). We may then use equation (1) to calculate the single-pass removal efficiency ( $\eta_{sp}$ ). Then, using the methods of Christ and others (1999), for given aquifer hydraulic parameters, well pumping rates, and well locations, we can determine  $I_{avg}$ , and use equation (3) to calculate the overall removal efficiency ( $\eta$ ) of the HFTW system.

Ferland's goal in developing this model was to provide remediation system designers a tool to determine if an HTFW with an in-well reactor system is a viable technology at a given site (Ferland and others, 2000). As mentioned earlier, in order to apply the Christ and others (1999) flow model, which is a component of the overall model, significant site-specific information is required, such as groundwater Darcy velocity, the aquifer thickness, and the orientation of the treatment wells to the regional flow. In addition, simplifying conditions such as homogeneity of aquifer material, and two-dimensional steady-state flow, must be assumed. These simplifying assumptions cause the model, though adequate for use as a screening tool and to help a user gain understanding about system operation, to be insufficient for design purposes. Numerical models are necessary for this purpose (Fernandez, 2001).

#### 2.5.1.3 Stoppel and Goltz (2003) - HFTW Flow with First-Order Contaminant Destruction by an In-Well Pd Reactor Accounting for Catalyst Deactivation/Regeneration

The modeling effort conducted by Stoppel and Goltz (2003) extended the work of Ferland and others (2000) by accounting for deactivation and regeneration of the catalyst material in the reactor. Specifically, the deactivation of the catalyst is incorporated into the original Ferland model by treating the first-order rate constant,  $k_{obs}$ , as a function of time. Stoppel and Goltz (2003) assume regeneration of the catalyst to be complete and instantaneous; thus, after completion of a regeneration cycle the catalyst is assumed to have regained its original efficiency.

Stoppel and Goltz' (2003) modeling effort was intended to improve the existing Ferland and others (2000) model. The research found that catalyst deactivation can indeed be modeled by making the first-order rate constant a function of time. This allows for a qualitative description of how the catalyst, and thus how the remediation system, will work over time. This is an improvement to the Ferland and other's (2000) original model in that deactivation was found to be slow for an in-well reactor pumping at "typical" rates.

## **2.5.2 NUMERICAL MODELS**

In a numerical groundwater model, the partial differential equations that govern groundwater flow and contaminant transport are approximated by a set of algebraic equations which can be solved to determine contaminant concentration as a function of space and time throughout the domain of interest. Numerical models do not require the number of simplifying assumptions that must be made in an analytical model. For instance, non-linear equations in a heterogeneous aquifer can be solved numerically. Thus, a numerical model may be more appropriate to simulate actual site conditions to effect a system design (Zheng and Bennett, 2002).

### **2.5.2.1 Huang and Goltz (1998) – HFTW Flow and *In Situ* Bioremediation**

Huang and Goltz (1998) developed a three-dimensional numerical model to simulate remediation of a contaminated aquifer using an HFTW system to promote *in situ* bioremediation. This model uses MODFLOW, a groundwater flow model developed by Harbaugh and McDonald (1996), to simulate the steady-state flow of groundwater in an aquifer being influenced by pumping HFTWs. When given required parameters such as the



locations and pumping rates of wells, hydraulic conductivities, and initial and boundary conditions, MODFLOW determines the hydraulic heads and velocity fields for the system of interest. Then, a second modeling tool, MT3D, which is a three-dimensional fate and transport model, was modified to incorporate the subsurface biodegradation processes that were being induced through nutrient addition at the treatment wells. The modified transport model was used to simulate contaminant concentrations throughout the aquifer over time. These simulations are accomplished using groundwater velocity information from MODFLOW and contaminant specific information, such as initial contaminant concentration values, which are input by the modeler (Fernandez, 2001).

The modeling effort, which simulated the Edwards AFB *in situ* cometabolic bioremediation evaluation discussed in Section 2.4.2, investigated the effects of sorption and contaminant bioavailability on *in situ* bioremediation of the groundwater contamination. The goal of the effort was to provide remediation managers with increased knowledge of the fate and transport of contaminants leading, ultimately, to better design and implementation of HFTW remediation systems (Huang and Goltz, 1998).

The researchers determined that whether sorption was modeled as a rate-limited process or an equilibrium process, overall HFTW system efficiency as determined by downgradient contaminant concentrations was the same (Huang and Goltz, 1998).

#### 2.5.2.2 Gandhi and others (2002a; b) – HFTW Flow and *In Situ* Bioremediation

In a two-part paper, Gandhi and others (2002a; b) also modeled operation of the Edwards AFB *in situ* bioremediation technology system. In the first paper, the investigators “examine controls on the flow and transport behavior in two aquifers subject to a two-well recirculation system” (Gandhi and others, 2002a). This two-well recirculation system is what has been referred to as the HFTW system in this thesis. The three-dimensional, finite-element model developed included both a flow component and an advective-dispersive transport component. The model was used to simulate groundwater heads that resulted from operation of the HFTW system, as well as transport of a non-biodegrading, non-sorbing bromide tracer. The area at which the technology was operated was well instrumented, and after calibration, the model did a good job of simulating the head and bromide transport data at a number of monitoring wells.

The second part of the modeling effort was to simulate cometabolic biodegradation of the target contaminant (TCE). As discussed in the previous section, nutrients were added to the system at the treatment wells to stimulate TCE biodegradation (Gandhi and others, 2002b). The treatment system installed at the Edwards AFB site was run successfully for a 410-day period. Information from the system operation was used in the modeling effort. The results of the simulation, that is a comparison of the model simulation results and the field data, show significant correlation between what is expected and what is actually occurring (Gandhi and others, 2002b).

### 2.5.2.3 Fernandez (2001) -- HFTW Flow with First-Order Contaminant Destruction by an In-Well Pd Reactor

Fernandez modified the model developed by Huang and Goltz (1998) discussed above by replacing bioremediation with Pd-catalyzed dehalogenation using an in-well reactor as the remediation method. TCE destruction in the reactor was modeled as a first-order process. Just as in the Huang and Goltz (1998) model, Fernandez (2001) used MODFLOW to model the steady-state groundwater flow and a modified version of MT3D to model the fate and transport of the contaminant in the aquifer.

The goal of this research effort was to optimize the HFTW system. The parameters Fernandez investigated for optimization were the number of HFTW wells, well location, pumping rate, and catalytic reactor size. The basis for determining success of the optimization was cost and downgradient TCE concentration. That is, Fernandez used the model to determine the parameter conditions that resulted in the most cost effective contaminant mass destruction while also achieving downgradient TCE concentrations within regulatory limits. The results of the study were site specific; however, the need for use of a multi-well HFTW system for effective remediation was determined (Fernandez, 2001).

An optimal solution in reference to cost was found in the modeling effort. Unfortunately, the most cost-effective solution did not result in acceptable downgradient TCE concentrations.

For the optimal solution, the downgradient TCE concentration was 0.148 mg/L, a value much higher than the 0.005 mg/L EPA regulatory limit (Fernandez, 2001).

## **3.0 METHODOLOGY**

### **3.1 INTRODUCTION**

Recall that the objective of this study is to evaluate the potential of HFTWs with in-well Pd reactors to remediate groundwater contaminants of concern at DoD and USAF installations. Our general approach to achieving this objective is to apply a numerical model of HFTWs at sites to evaluate the technology's effectiveness. In this chapter we will discuss the model. First, in Section 3.2, we will present the model itself. This section will discuss the equations upon which the numerical model is based, provide an explanation of how the model works, and justify the reason this particular numerical model was chosen for this study.

Section 3.3 will detail the scenarios that will be simulated using the model. Scenarios will include the Edwards AFB TCE contamination site, as well as another site with different hydrogeologic conditions, that is also contaminated with TCE. Additionally, remediation of a number of other contaminants will be simulated, using site parameters from the Edwards AFB site. Model runs under these different scenarios will allow us to evaluate the feasibility of using the technology to manage contaminant plumes under various site and contamination conditions.

### **3.2 NUMERICAL MODEL**

#### **3.2.1 FLOW AND TRANSPORT MODEL**

Christ and others (1998) developed a two-dimensional analytical model to simulate flow induced by an HFTW system. The analytical model, which assumed a homogeneous aquifer,

calculated the interflow and capture zone width of an HFTW system, for given aquifer (Darcy velocity, aquifer thickness, etc.) and HFTW (pumping rate, distance between wells, etc.) parameter values. Interflow is defined as the fraction of water in the extraction well which came from the injection well. Capture zone width defines the boundaries of contaminated water upgradient of the HFTW system that is captured by the wells. The derivation of the analytical model and the relationships between interflow, capture zone width, and aquifer and HFTW parameters can be found in Christ and others (1998).

The analytical model developed by Christ and others (1998) was not chosen for this modeling effort because the simplifying assumptions needed for an analytical model, like two-dimensionality and homogeneous hydrology, make the model too restrictive and unrealistic. Instead, the model used in this thesis is a numerical model that simulates the transport of the contaminant under the flow conditions induced by the HFTW and then a first-order reaction model is used to simulate contaminant destruction in the in-well reactor. The equations this is based on are detailed in Section 2.5.1.2. As described below, the three-dimensional steady-state flow field induced by HFTW operation is simulated using MODFLOW. The groundwater velocities calculated by MODFLOW are then used as inputs by a numerical transport model to simulate advective/dispersive/sorptive transport of the contaminant in the aquifer.

MODFLOW is the U.S. Geological Survey modular finite difference groundwater flow model. The software is capable of modeling transient and steady state groundwater flow in three-dimensions. Groundwater velocity and direction is given in MODFLOW's graphical

and text-based outputs (Harbaugh and McDonald, 1996). The data files created by MODFLOW are then used in the transport model developed by Huang and Goltz (1998) which is described in Section 2.5.2.1. The transport model outputs contaminant concentration as a function of spatial location and time. The model also keeps track of total contaminant mass, so that it can be used to determine cumulative contaminant destruction over time.

As noted above, a first-order kinetic model to simulate contaminant destruction in the in-well reactors was incorporated into the HFTW flow and transport model. Based on the work of Lowry and Reinhard (1999), the hydrodehalogenation of chlorinated ethylenes, such as TCE, in the presence of a palladium catalyst does exhibit pseudo first-order kinetics. Thus, Ferland and others (2000) first-order kinetics model was chosen to model the degradation of contaminant in this thesis effort. Note that although the reactor model used by Ferland and others (2000) is the same as the model used in this study, in this study we use a numerical model to simulate flow and contaminant transport in the aquifer, whereas Ferland and others (2000) relied on an analytical model (Christ and others, 1999) to describe the flow field induced by HFTW operation.

The design parameters of the in-well Pd reactor, particularly the residence time, have an important influence on contaminant destruction in the HFTW system. Dr. Jeffery Cunningham, who is working on the development and production of the actual HFTW system to be used during the real world evaluation of this technology at the Edwards AFB Area 19 site (Munakata and others, 2002), provided the reactor design parameter values given in Table 3-1 (Cunningham, 2002).

Table 3-1: HFTW Pd Reactor Parameters

<b>Parameter</b>	<b>Value</b>
Reactor Radius	0.0635 m
Reactor Volume	25 L
Reactor Length	1.97 m
Pd Pellet Porosity	40%
Flow Rate through Reactor	14.4 m <sup>3</sup> /d
Reactor Residence Time	1 min

### **3.2.2 MODEL CHOICE JUSTIFICATION**

As indicated in the previous section, the transport model being used in this thesis effort was developed by Huang and Goltz (1998). The ease of conferring with the model authors; the three-dimensional capabilities of the model; and the model's mergence of steady-state flow, advective and dispersive transport, and easy incorporation of the first-order kinetics discussed above are specific reasons for choosing the Huang and Goltz (1998) model.

## **3.3 SCENARIOS**

### **3.3.1 EDWARDS AFB WITH TCE**

For Edwards AFB the model will be set up to simulate plume containment with a continuous contaminant source in place; this is as the site appears to be for the real-world situation at the Edwards AFB site (McCarty and others, 1998).

Site 19 at Edwards AFB has been characterized by both McCarty and others (1998) and Gandhi and others (2002a). We model the aquifer system, as shown in Figure 3-1, as consisting of an upper aquifer and a lower aquifer separated by a low hydraulic conductivity

aquitard. The aquifers consist of sand and gravel with silt and clay fingers (Gandhi and others, 2002a). Also shown in Figure 3-1 is the HFTW well-pair configuration.

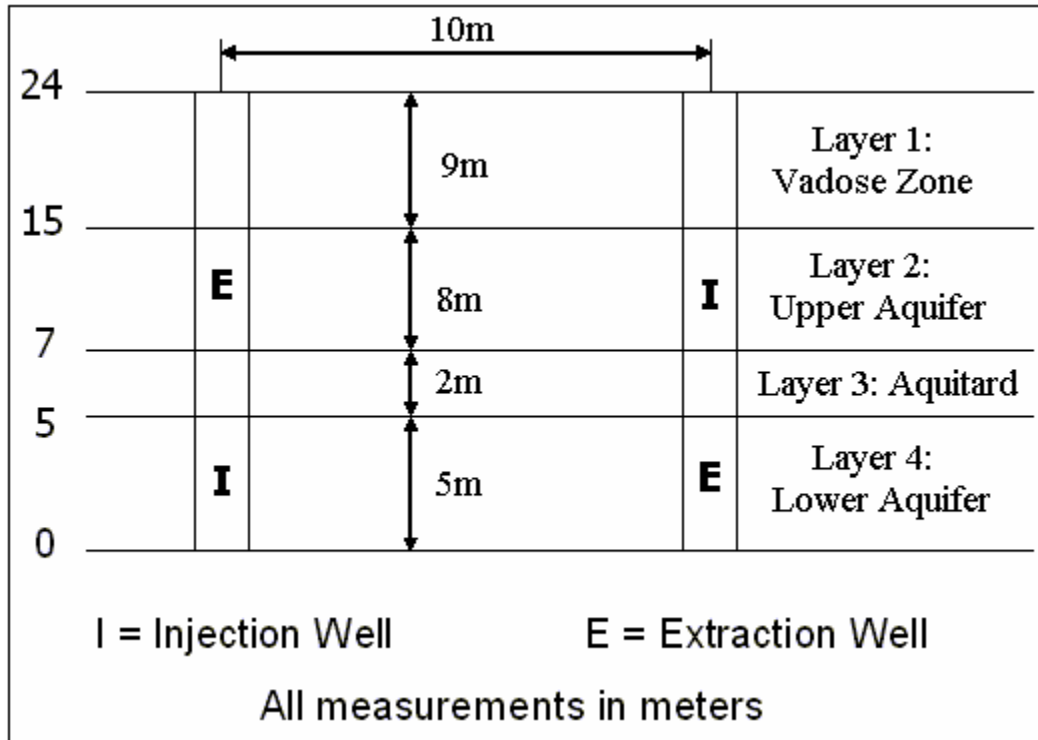


Figure 3-1: Cross-section View of HFTW Well Pair Configuration

Figure 3-2 shows the plan view of the aquifer system model. The dimensions of the model area are 200 m by 200 m with each cell being 10 m by 10 m. The background concentration of TCE for both aquifers, as well as other site and technology parameters, are listed in Table 3-2. As a conservative assumption, TCE is assumed not to sorb to the aquifer solids. In the model run where a continuous source is simulated, the source area is shown in Figure 3-2 as the vertical column of darkened cells. The TCE concentration in the source area is equal to the background concentration. For the model run involving only a plume, this source area is



not present. The HFTWs, which are 10 m apart as shown in Figure 3-1, are depicted by the black dots in the center of the grid.

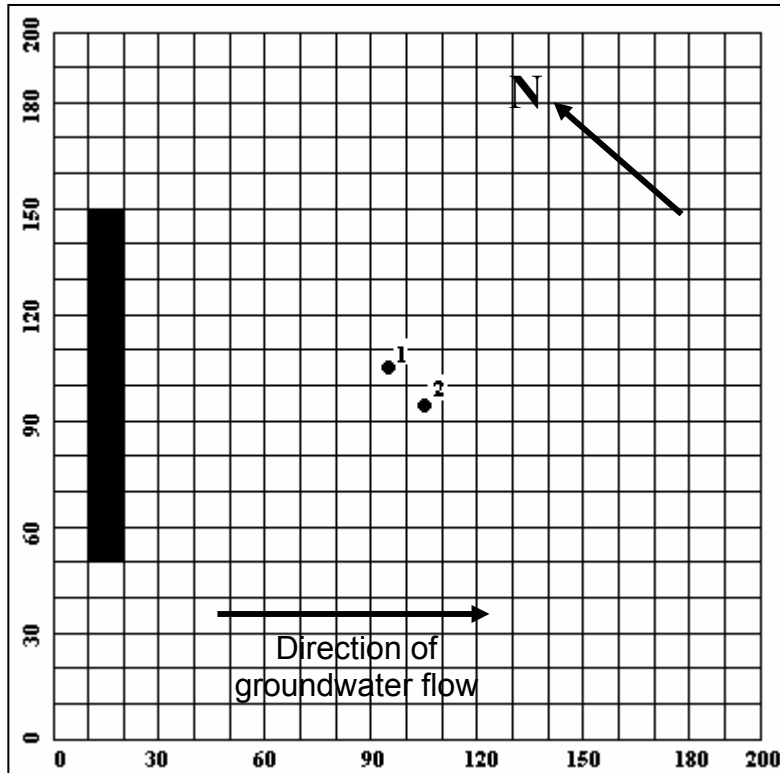


Figure 3-2: Plan View of Site with HFTW Well Pair

### 3.3.2 EDWARDS AFB WITH OTHER CONTAMINANTS

In order to compare the effectiveness of in-well Pd catalysis for treating different contaminants, the hydrogeologic conditions at Edwards AFB will be used for a number of contaminants. That is, the model of the Edwards AFB site described in the previous section will be used, but instead of TCE, the transport and in-well destruction of other contaminants will be simulated. These contaminants are 1,2-dibromo-3-chloropropane (DBCP),

Table 3-2: Edwards AFB Simulation Parameters

Parameter	Value	Source
Horizontal hydraulic conductivity of upper and lower aquifer ( $K_x$ and $K_y$ )	0.0034 cm/s	McCarty and others (1998)
Vertical hydraulic conductivity of upper and lower aquifer ( $K_z$ )	10% $K_x = 0.00034$ cm/s	Domenico and Schwartz (1998)
Hydraulic gradient (dh/dL)	Upper aquifer – ~0.004 Lower aquifer – ~0.007	McCarty and others (1998)
Pumping rate	14.4 m <sup>3</sup> /d	Cunningham (2002)
Soil porosity	30%	McCarty and others (1998)
Specific yield ( $S_y$ )	23%	Domenico and Schwartz (1998)
Background TCE Concentration	Upper aquifer – 680 µg/L Lower aquifer – 750 µg/L	McCarty and others (1998)
Groundwater Flow Direction	Northwest to Southeast	Gandhi and others (2002)
TCE reaction rate with Pd/AL <sub>2</sub> O <sub>3</sub>	1960 day <sup>-1</sup>	Stoppel (2001)

nitrobenzene, and perchlorate. These contaminants were chosen because they have been relatively well-studied and there are a number of papers dealing with their fate in the subsurface. In particular, enough information was available for these contaminants so that a rate constant for contaminant destruction by Pd-catalysis could be estimated. The parameters associated with these contaminants are given in Table 3-3. Again, as a conservative assumption, we assume all contaminants are non-sorbing.

The rate constant for Pd-catalyzed reduction of DBCP tabulated in Table 3-3 was measured in the laboratory (Siantar and others, 1996). The rate constants in Table 3-3 for the degradation of nitrobenzene and perchlorate using palladium as the catalyst were estimated based on the experimental reaction rate constants for those contaminants' degradation using zero-valent

iron (ZVI). It was assumed that the increase in rate constant that was observed when using Pd rather than ZVI to degrade TCE would be the same as the increase that would be observed when using Pd rather than ZVI to degrade nitrobenzene and perchlorate. We see that the rate of Pd-catalyzed reduction of TCE ( $1960 \text{ day}^{-1}$ ) is approximately 13,000 times the rate of TCE degradation by ZVI ( $0.153 \text{ day}^{-1}$ ). Applying this factor of 13,000 to the rate constant for nitrobenzene degradation by ZVI measured by Agrawal and Tratnyek (1995) of  $50.4 \text{ day}^{-1}$ , we estimate that the rate constant for Pd-catalyzed reduction of nitrobenzene would be  $6.48 * 10^5 \text{ day}^{-1}$ . Westerhoff (2003) determined the first-order rate constant for the degradation of chlorate in the presence of ZVI is  $25.9 \text{ day}^{-1}$ . This value was used as a conservative approximation of the reaction rate constant for degradation of perchlorate by ZVI (Agrawal, 2003). Multiplying this rate by 13,000 gives us a rough approximation of the rate constant for Pd-catalyzed reduction of perchlorate, for use in the model.

The final column in Table 3-3 lists the MCL/Levels of regulatory concern for each of these contaminants. Of specific interest, because there are no USEPA set MCLs, are the levels of regulatory concern for nitrobenzene and perchlorate. The value listed for nitrobenzene comes from the groundwater corrective action value developed by the Louisiana Association for Environmental Health and Sciences (AEHS, 2003). The value listed for perchlorate is the action level developed by the state of California (USEPA, 1999).

Table 3-3: Contaminant Parameters

Contaminant	ZVI First-Order Rate Constant	Approximate Pd Catalyzed First-Order Rate Constant <sup>4</sup>	Initial and Source Concentration	MCL/Level of Regulatory Concern
TCE	0.153 day <sup>-1</sup> (1)	1.96 * 10 <sup>3</sup> day <sup>-1</sup> (1)	0.68 - 0.75 mg/L (2)	5 µg/L (7)
DBCP	N/A	3.20 * 10 <sup>2</sup> day <sup>-1</sup> (3)	0.01 mg/L (3)	0.2 µg/L (7)
Nitrobenzene	50.4 day <sup>-1</sup> (4)	6.48 * 10 <sup>5</sup> day <sup>-1</sup> (*)	93.0 mg/L (4)	5 µg/L (8)
Perchlorate	25.9 day <sup>-1</sup> (5)	3.33 * 10 <sup>5</sup> day <sup>-1</sup> (*)	800.0 mg/L (5)	18 µg/L (9)

<sup>1</sup> Stoppel, 2001

<sup>2</sup> McCarty and others (1998)

<sup>3</sup> Siantar and others, 1996

<sup>4</sup> Agrawal and Tratnyek, 1995

<sup>5</sup> Westerhoff, 2003 for chlorate (perchlorate rate constant unavailable)

<sup>6</sup> Based on extrapolating from rate constants of contaminant and zero-valent iron reactions

<sup>7</sup> USEPA Maximum Contaminant Level

<sup>8</sup> AEHS, 2003

<sup>9</sup> USEPA, 1999

\* Extrapolated

### 3.3.3 PLANT 44 SITE WITH TCE

In order to allow comparison of system performance under different hydrogeologic conditions, a second site was chosen for modeling. This site, known as Plant 44, is located in Tucson, Arizona. The aquifer being remediated contains both TCE and 1,1-DCE, though only TCE is considered in this study. TCE contamination is in a shallow groundwater zone (SGZ) which is an approximately 11 meter thick layer of relatively low hydraulic conductivity composed of clay and silt. This site was chosen for comparison with the Edwards AFB site to see how a reduction in hydraulic conductivity of nearly two orders of magnitude would impact performance of the HFTW system. Figure 3-3 is a cross-section of the aquifer system model used to simulate the site. Figure 3-4 is a plan view of the site model.

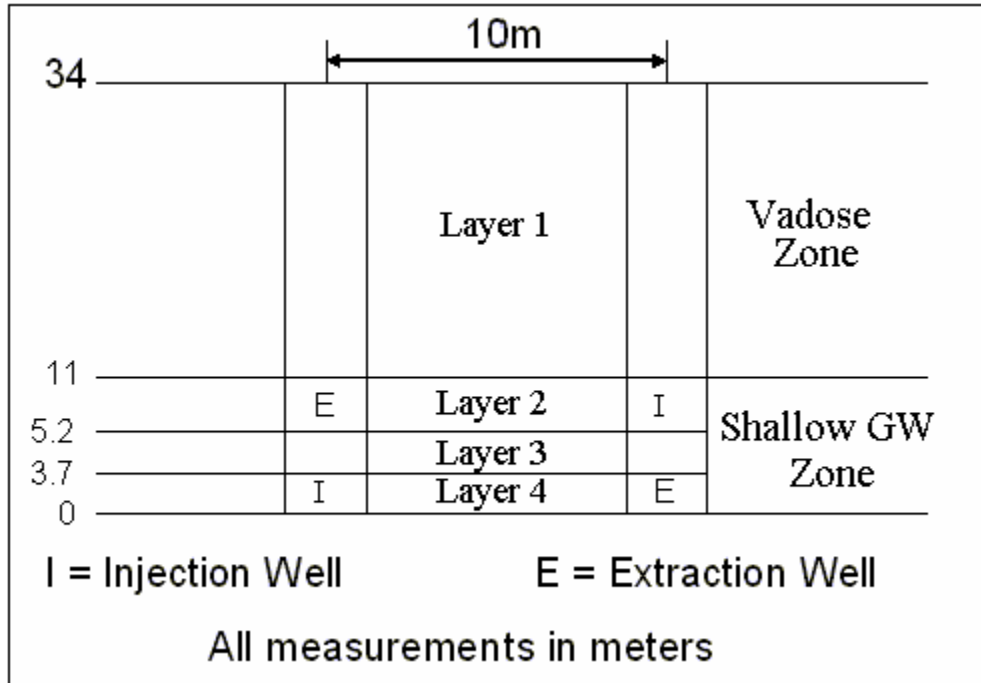


Figure 3-3: HFTW Well Pair Configuration

As shown in Figure 3-4, the dimensions of the model area, as for the Edwards AFB site, are 200 m by 200 m with each cell being 10 m by 10 m. The grey blocks in Figure 3-4 represent an inner ring with initial TCE concentrations of 1,000 mg/L while the dark blocks represent an outer ring with initial TCE concentrations of 100 mg/L. TCE is assumed to be non-sorbing. The HFTWs are again depicted by the black dots in the center. There is no source area included in this simulation. As the effects of the HFTW system never reach outside the immediate area of the wells, it is not believed this influences the simulation outcome.

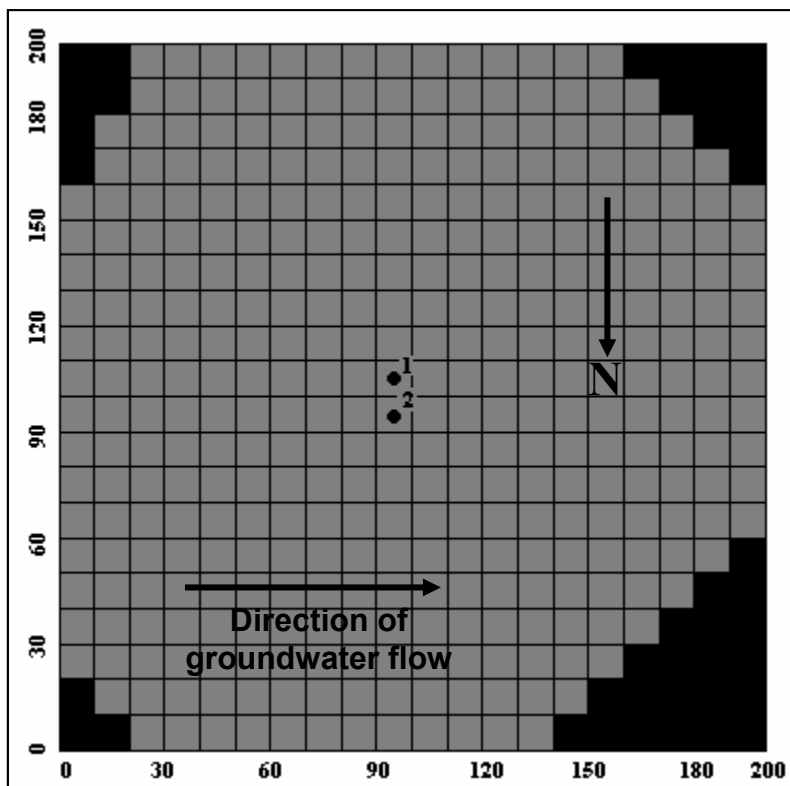


Figure 3-4: Plan View of Site with HFTW Well Pair

Table 3-4: Area 44 Simulation Parameters

Parameter	Value	Source
Horizontal hydraulic conductivity ( $K_x$ and $K_y$ )	$9.17 * 10^{-5}$ cm/s	Hargis and Associates, 1996
Vertical hydraulic conductivity ( $K_z$ )	10% $K_x = 9.17 * 10^{-6}$ cm/s	Domenico and Schwartz, 1998
Hydraulic gradient (dh/dL)	0.045 (average)	Hargis and Associates, 1996
Pumping rate	14.4 m <sup>3</sup> /d	Cunningham, 2002
Soil porosity	40%	Hargis and Associates, 1996
Specific yield ( $S_y$ )	5.5%	Domenico and Schwartz, 1998
Initial TCE Concentration <sup>1</sup>	Inner ring – 1000 µg/L Outer ring – 100 µg/L	Hargis and Associates, 1996
Groundwater Flow Direction	East to West	Hargis and Associates, 1996

<sup>1</sup> See Figure 3-4

### **3.4 TECHNOLOGY PERFORMANCE EVALUATION**

Results of the model simulations were used to decide whether or not the technology was “successful” in achieving remediation goals for given site and contaminant conditions. A number of different model outputs were considered for use in determining success. Two of these outputs were contaminant concentration at a downgradient compliance point and mass of contaminant destroyed. As indicated in Section 3.2.1, the transport model is capable of determining these values.

Contaminant concentration contours throughout the 200 meter by 200 meter area being modeled in each simulation were plotted. The simulation time period is 1,500 days for each run. Surfer<sup>®</sup> Version 8.01 surface mapping system software was used to construct these concentration contours based on the model output data. The contour map was then used to determine if contaminant concentrations leaving the model area were below the levels of regulatory concern listed in Table 3-3.

The second output parameter, mass destroyed was also used to quantify the effectiveness of the remediation system at different sites and with different contaminants. This comparison will help us to determine the appropriateness of using the HFTW system for a given contaminant or at a given site. Model output of mass of contaminant destroyed versus time was plotted for the different scenarios using Excel.

## **4.0 ANALYSIS**

### **4.1 OVERVIEW**

In this chapter the results of the model runs will be presented and discussed. The results for each scenario are described in separate sections. Some comparison between scenario results will be included in this chapter; however, an overall discussion on the appropriateness of the technology to manage various contaminants under differing site conditions will be included in Chapter 5.

### **4.2 ANALYSIS OF SCENARIO OUTCOMES**

#### **4.2.1 TCE REMEDIATION AT EDWARDS AFB**

As discussed in Chapter 3, a run simulating TCE remediation at Edwards AFB assumed there was a constant concentration source of TCE. The source area was located as indicated in Figure 3-2. Constant concentrations for the upper (layer 2) and lower (layer 4) aquifer horizons were set at the background TCE concentrations listed in Table 3-2. It was assumed that there was no source in the aquitard (layer 3) or the vadose zone (layer 1). The concentration contour maps for layers two and four, where the HFTW injection/extraction screens are located, and a plot of cumulative mass destroyed over time for this model run are given in Figures 4-1, 4-2, and 4-3, respectively. Figures 4-1 and 4-2 present simulated concentration contours after 1,500 days of HFTW operation. 1,500 days was chosen as the appropriate time to present the “snapshots” of the concentration contours in Figures 4-1 and 4-2, as it was assumed the system would be at steady-state, based on the linearity of the mass



destroyed versus time plot in Figure 4-3 after about 500 days. Unfortunately, this steady-state assumption proved false, as will be discussed subsequently.

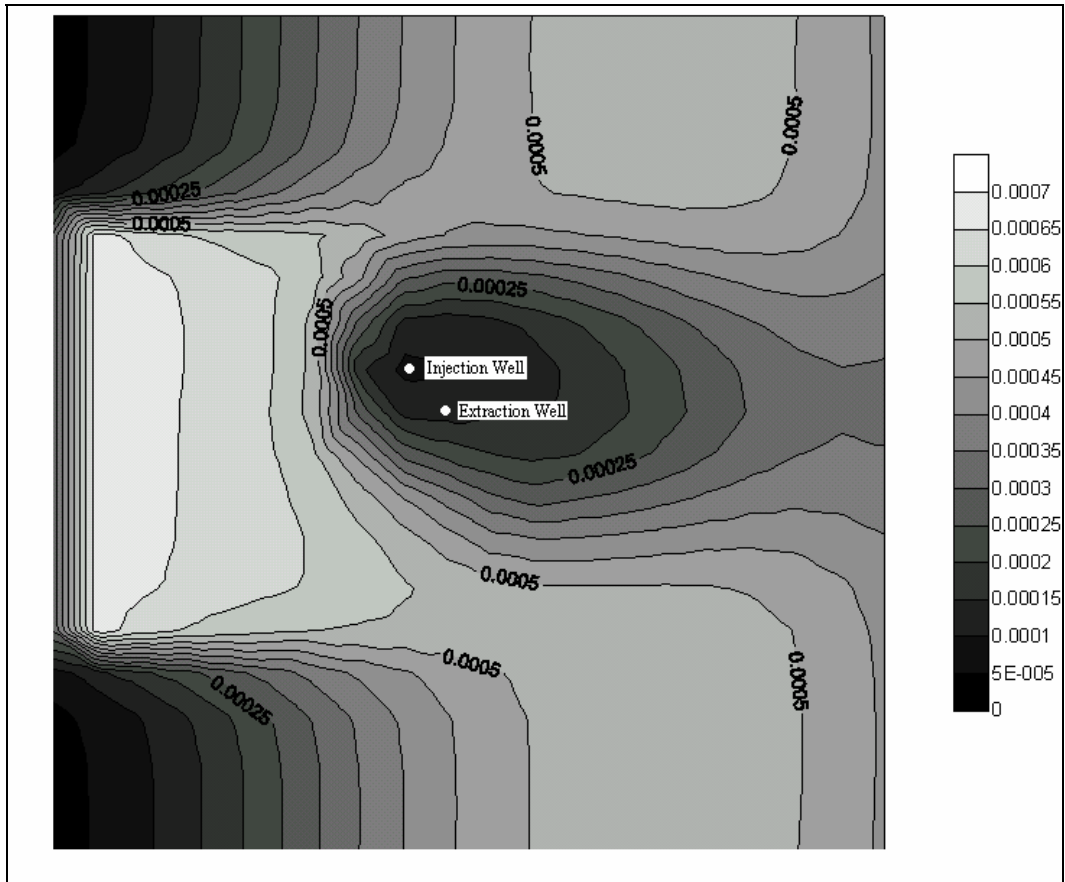


Figure 4-1: TCE Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Two at Edwards AFB Site with Source Area

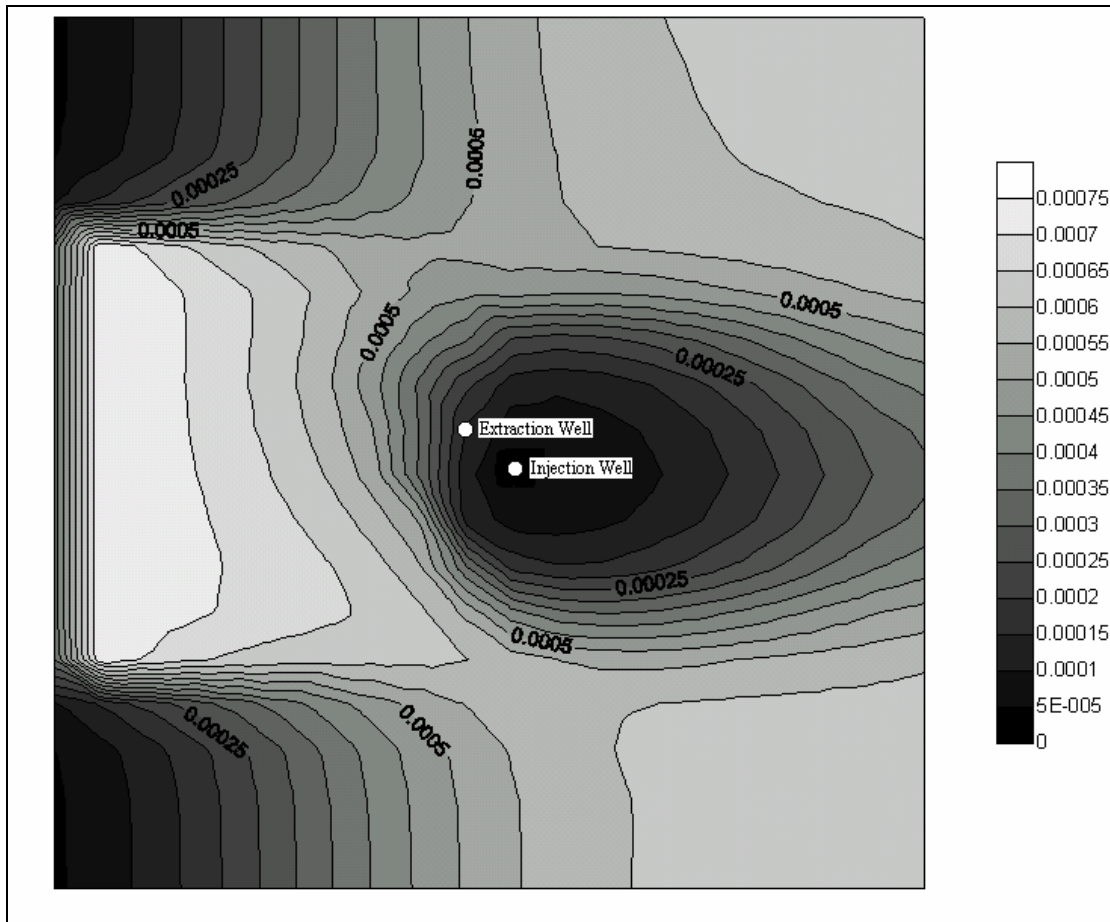


Figure 4-2: TCE Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Four at Edwards AFB Site with Source Area

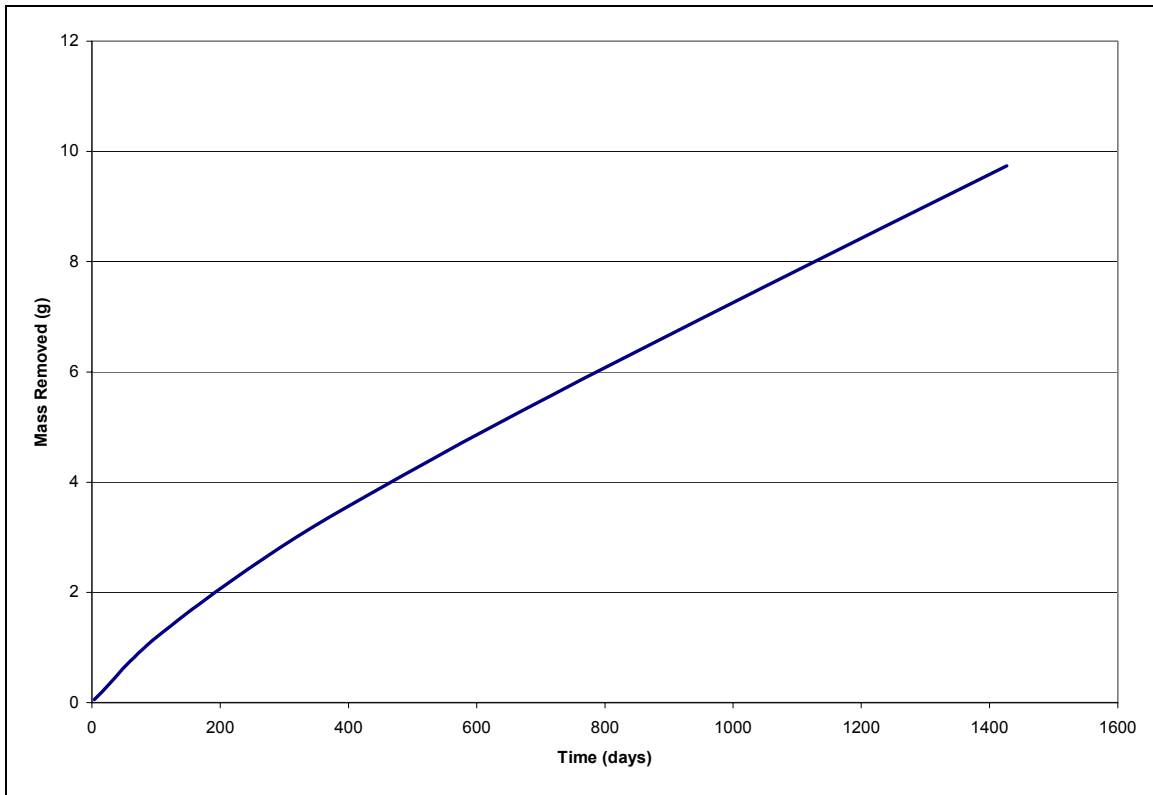


Figure 4-3: Cumulative Mass Destroyed for Edwards AFB Site with Source Area

The EPA maximum contaminant level (MCL) for TCE, as reported in Chapter 2, is five  $\mu\text{g/L}$  or  $5\text{e-}06$  g/L. Figures 4-1 and 4-2 show the contaminant concentrations leaving the site (recall from Figure 3-2 that the site boundary is 100 m downgradient of the treatment wells). Based on the 1,500 day simulation run time, the concentration of TCE leaving the site directly downgradient of the treatment wells does not meet the MCL in either aquifer. We note, however, that contaminant concentrations close to the injection wells appear to approach the MCL. If the system is at steady-state, as was assumed, these low concentrations would be irrelevant to achieving downgradient concentration goals. However, it appears the system is not at steady-state after 1,500 days. Based on some rough calculations, the groundwater in the upper aquifer is only moving about four cm per day. Thus, water that has been treated in

the HFTW system will only have moved about 60 meters after 1,500 days, and will not have arrived at the downgradient boundary, which is 100 m from the treatment wells. Thus, it is clear the system is not at steady state after 1,500 days and it is unknown from these simulations whether the treatment system will be capable of achieving concentration goals below the MCL at the site boundary.

#### **4.2.2 REMEDIATION OF OTHER CONTAMINANTS AT EDWARDS AFB**

The next set of runs involved using the Edwards AFB site with contaminants other than TCE.

##### **4.2.2.1 1-2-dibromo-3-chloropropane (DBCP)**

The first simulation involved the pesticide DBCP. The initial and source concentrations used in the simulation runs, which are listed in Table 3-3, were determined based on values found in published literature about each contaminant. Other than the initial and source concentration, the only change in model inputs was the reaction rate constant. The concentration contours for layers two and four at 1,500 days, the layers in which contaminant destruction occurred, and the plot of cumulative mass destroyed over time for this model run are given in Figures 4-4, 4-5, and 4-6, respectively.

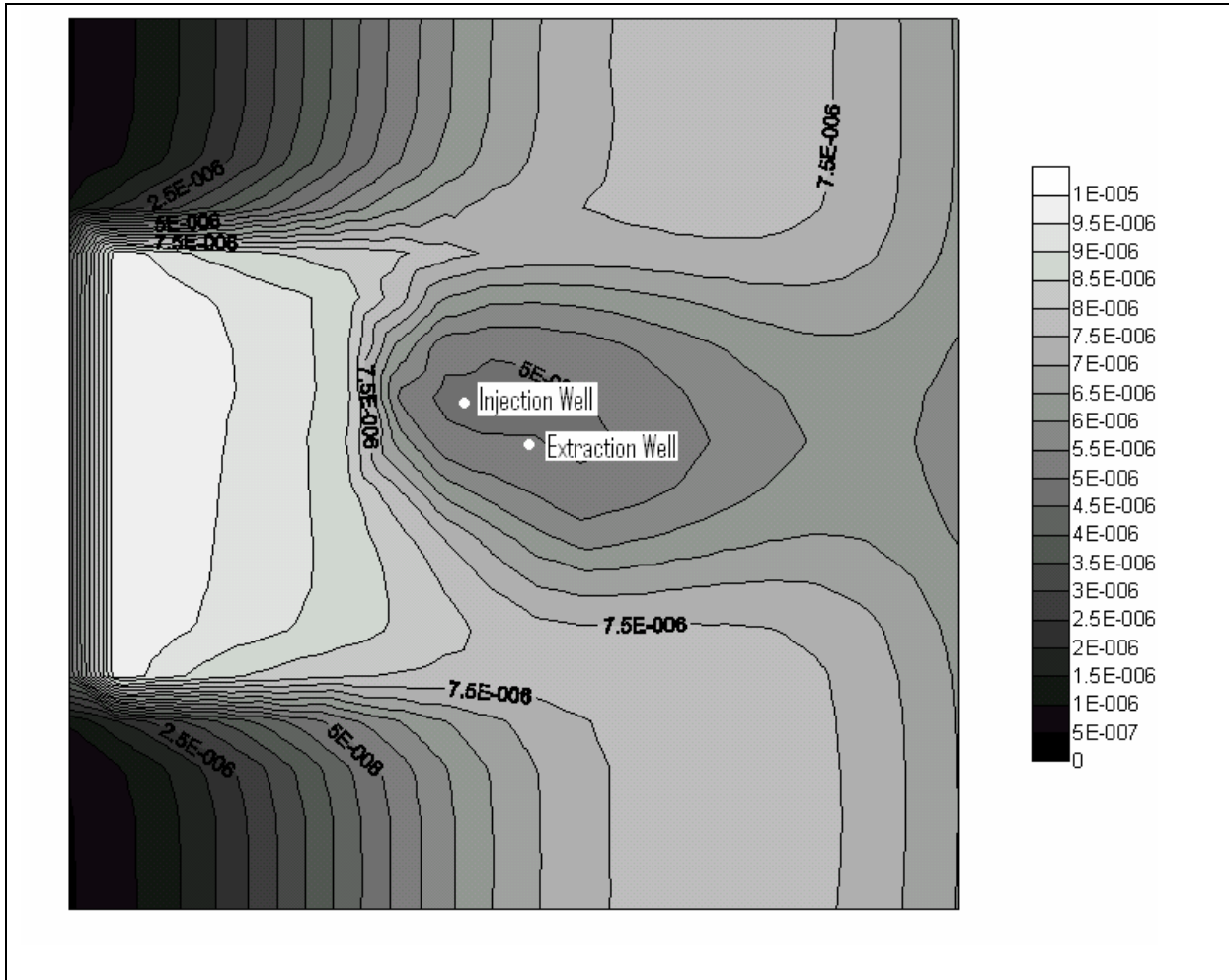


Figure 4-4: DBCP Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Two at Edwards AFB Site

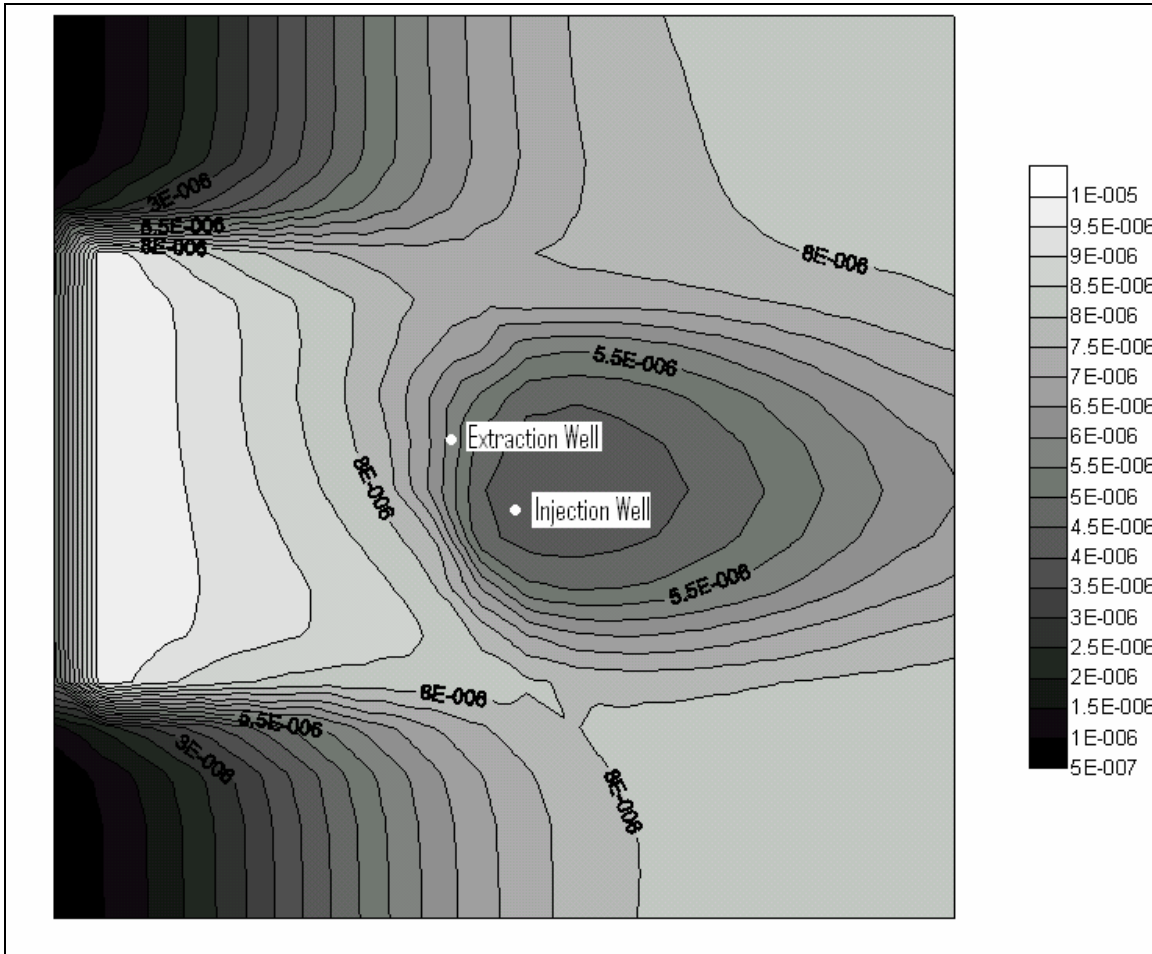


Figure 4-5: DBCP Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Four at Edwards AFB Site

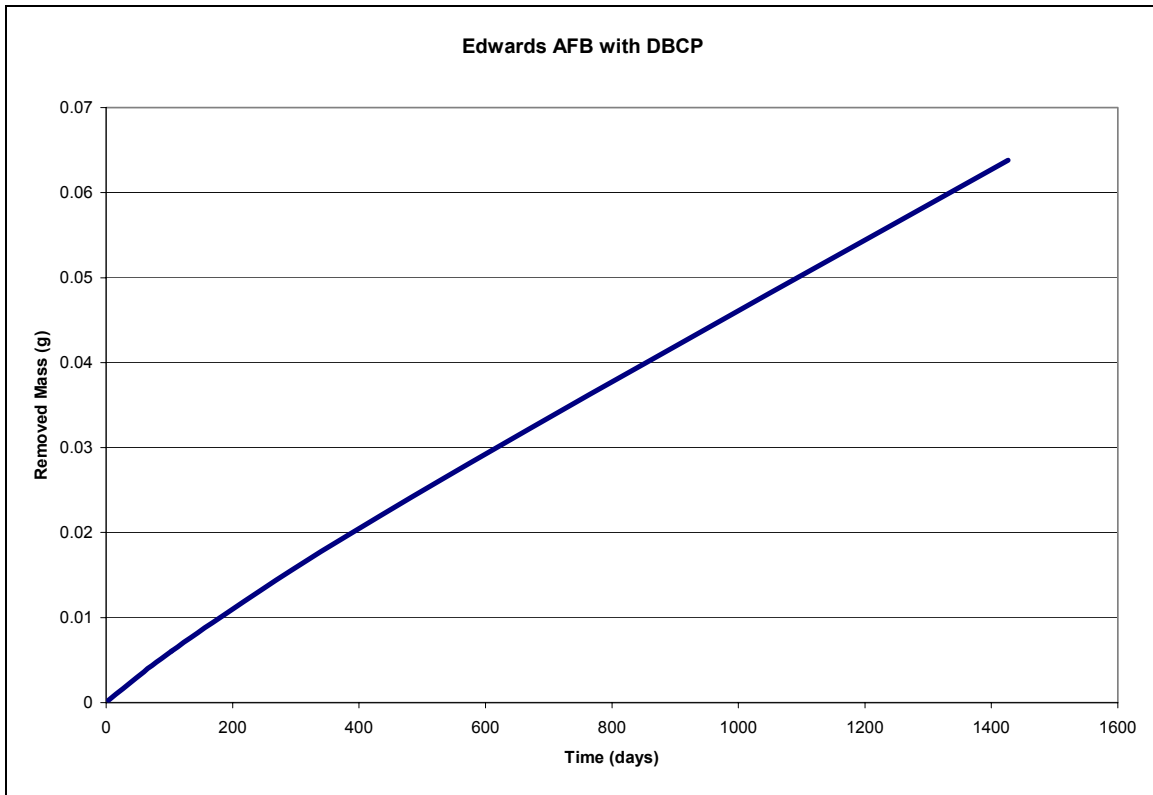


Figure 4-6: Cumulative Mass Destroyed Graph for Edwards AFB Site with DBCP

The MCL for DBCP, as reported in Chapter 2, is 0.2  $\mu\text{g/L}$  or  $0.2\text{e-}06 \text{ g/L}$ . As shown in Figures 4-4 and 4-5, the concentrations of DBCP leaving the remediation area are not below the MCL in either aquifer. However, as discussed in Section 4.2.1, groundwater flow calculations indicate the system is not yet at steady state. Thus, despite the system's inability to achieve concentration goals at the site boundary within 1,500 days, this does not indicate that the system is not able to eventually meet the requirement. A comparison of Figures 4-1, 4-2, and 4-3 with Figures 4-4, 4-5, and 4-6 shows very similar outcomes for the two contaminants, though due to the significantly lower initial and source concentrations for DBCP, the concentrations and mass removals of DBCP are much lower than those for TCE.

#### 4.2.2.2 Nitrobenzene

The second simulation involved the nitroaromatic nitrobenzene. The initial and source concentrations for nitrobenzene, used in the simulation runs, are listed in Table 3-3. Other than the initial and source concentrations, the only change in model inputs was the reaction rate constant. The concentration contours for layers two and four at 1,500 days and the plot of cumulative mass destroyed over time for this model run are given in Figures 4-7, 4-8, and 4-9, respectively.

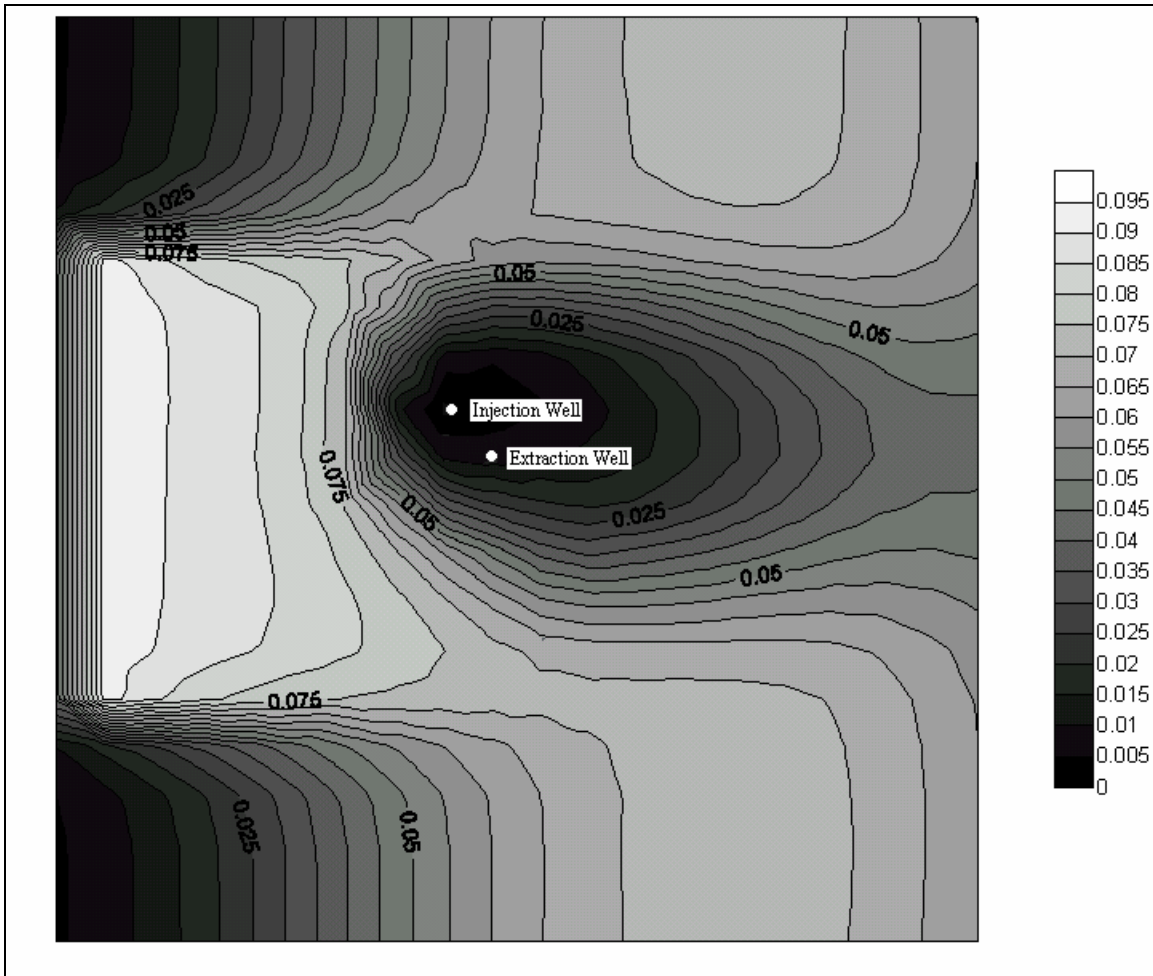


Figure 4-7: Nitrobenzene Concentration Contours in g/L after 1,500 Days of HFTW

Operation for Layer Two at Edwards AFB Site



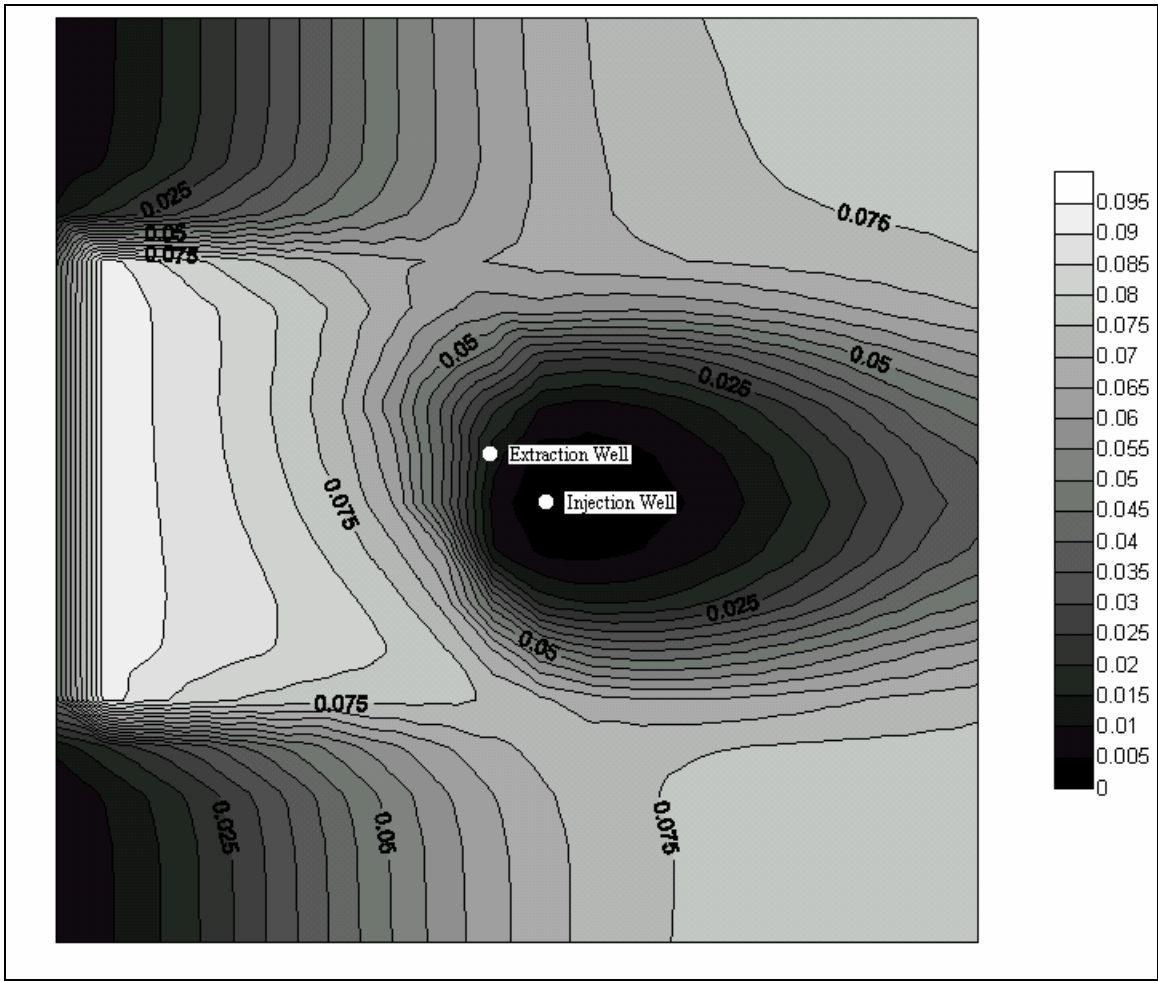


Figure 4-8: Nitrobenzene Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Four at Edwards AFB Site

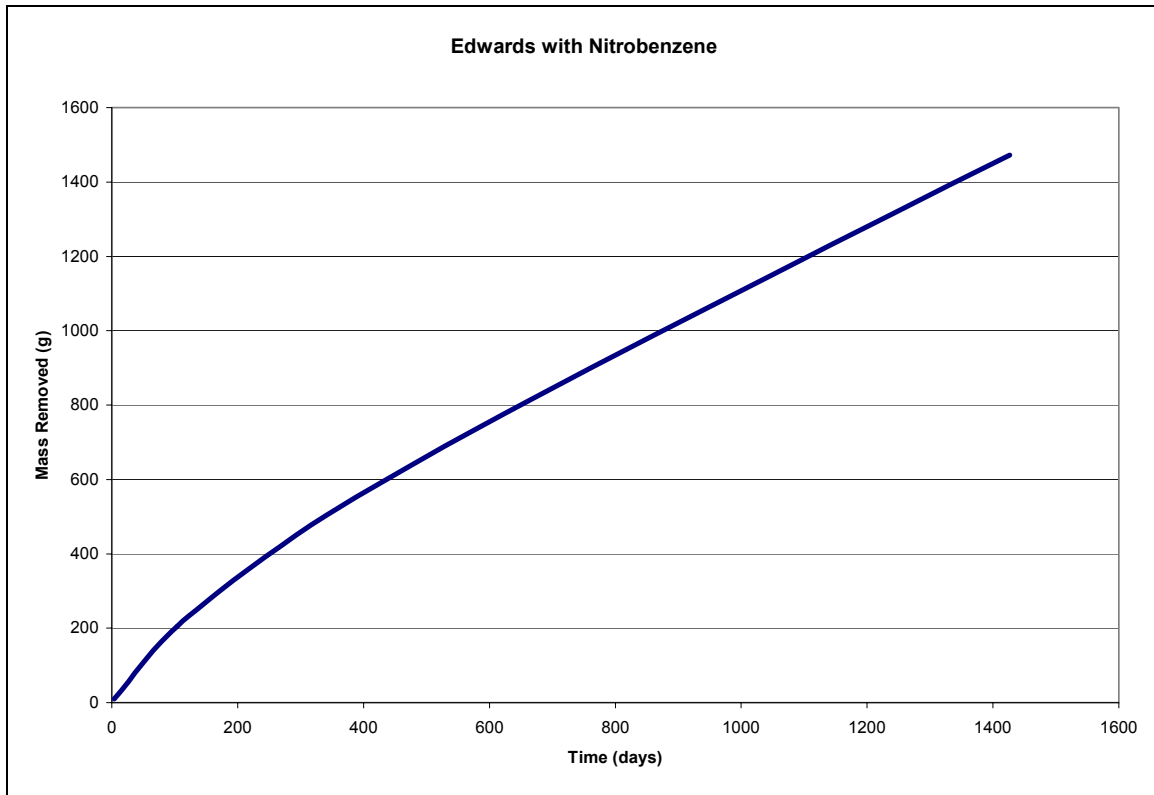


Figure 4-9: Cumulative Mass Destroyed Graph for Edwards AFB Site with Nitrobenzene

The clean-up standard chosen for evaluation of the results of the nitrobenzene run, as reported in Chapter 2 and listed in Table 3-3, is 5 µg/L or 5e-06 mg/L. As shown in Figures 4-7 and 4-8, the concentration of nitrobenzene leaving the remediation area does not meet the clean-up standards, though as discussed in Section 4.2.1, the system is not yet at steady state. Thus, despite the system's inability to achieve concentration goals at the site boundary within 1,500 days, this does not indicate that the system is not able to eventually meet the requirement. A comparison of Figures 4-1, 4-2, and 4-3 with Figures 4-7, 4-8, and 4-9 shows very similar concentration and mass removal behavior for the two contaminants. However, because of the much higher initial concentrations for nitrobenzene, as indicated in Table 3-3, the final concentrations and mass removals of nitrobenzene are much higher than those for TCE.

### 4.2.2.3 Perchlorate

The final simulation involved perchlorate. The initial and source concentrations for perchlorate, used in the simulation runs, are listed in Table 3-3. Other than the initial and source concentrations, the only change in model inputs was the reaction rate constant. The concentration contours for layers two and four and the plot of mass destroyed over time after 1,500 days of simulation run time for this model run are given in Figures 4-10, 4-11, and 4-12, respectively.

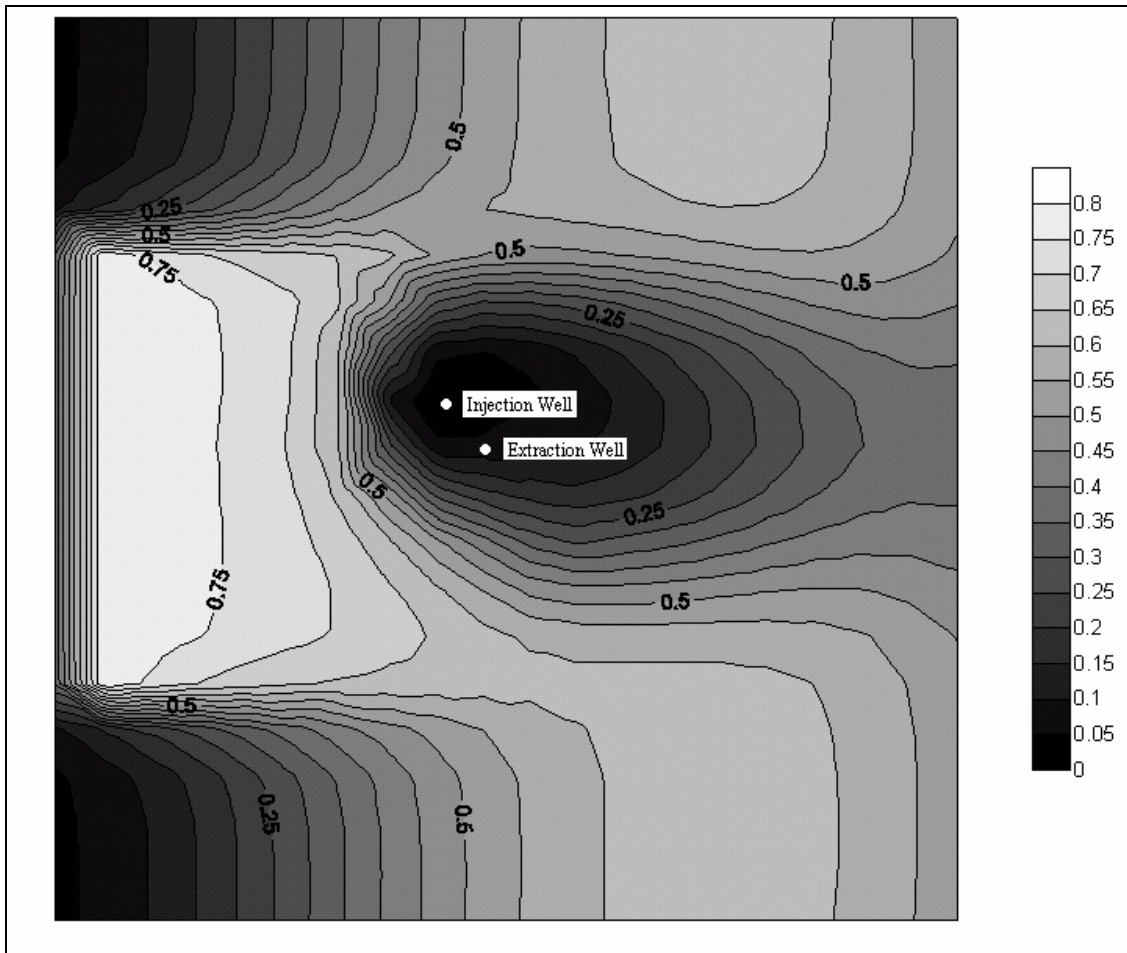


Figure 4-10: Perchlorate Concentration Contours in g/L after 1,500 Days of HFTW

Operation for Layer Two at Edwards AFB Site

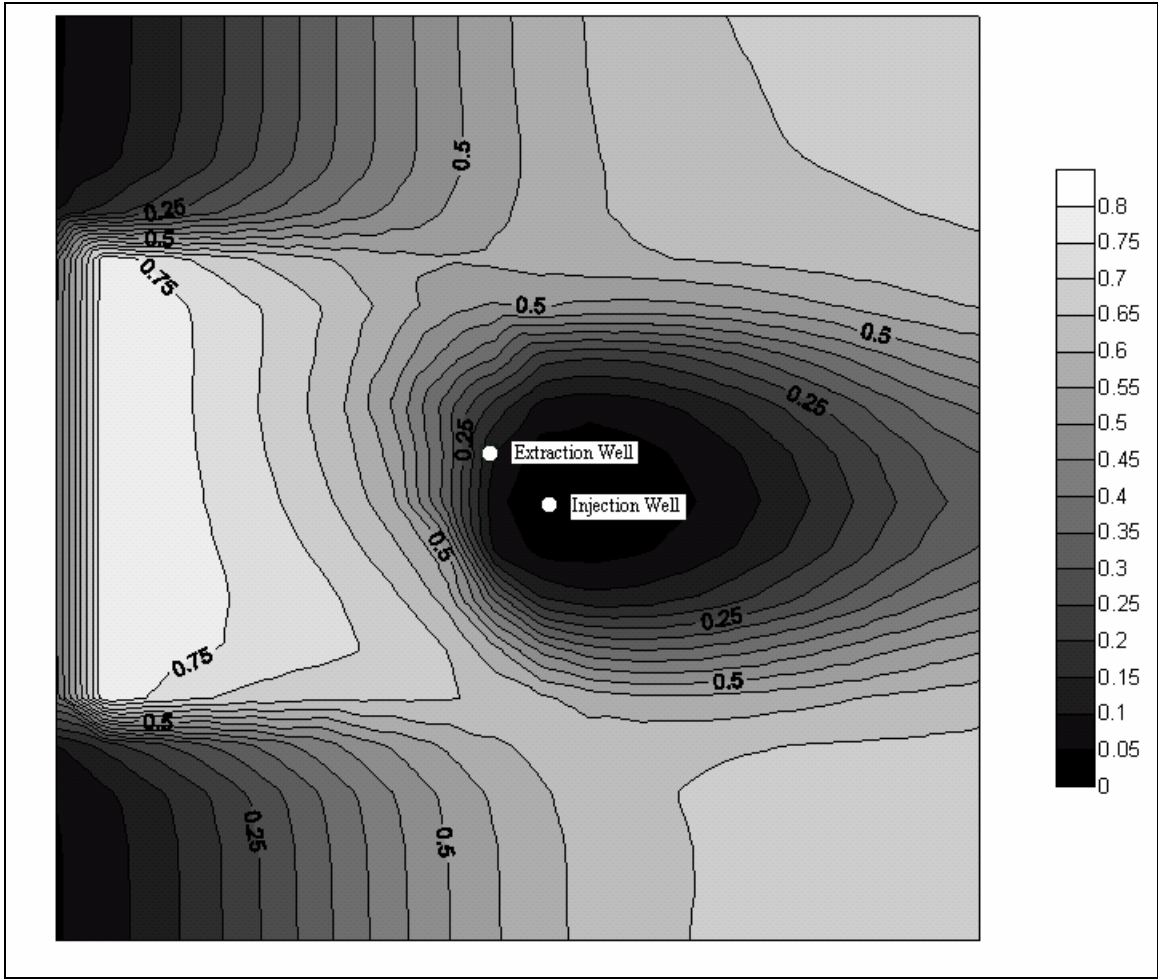


Figure 4-11: Perchlorate Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Four at Edwards AFB Site

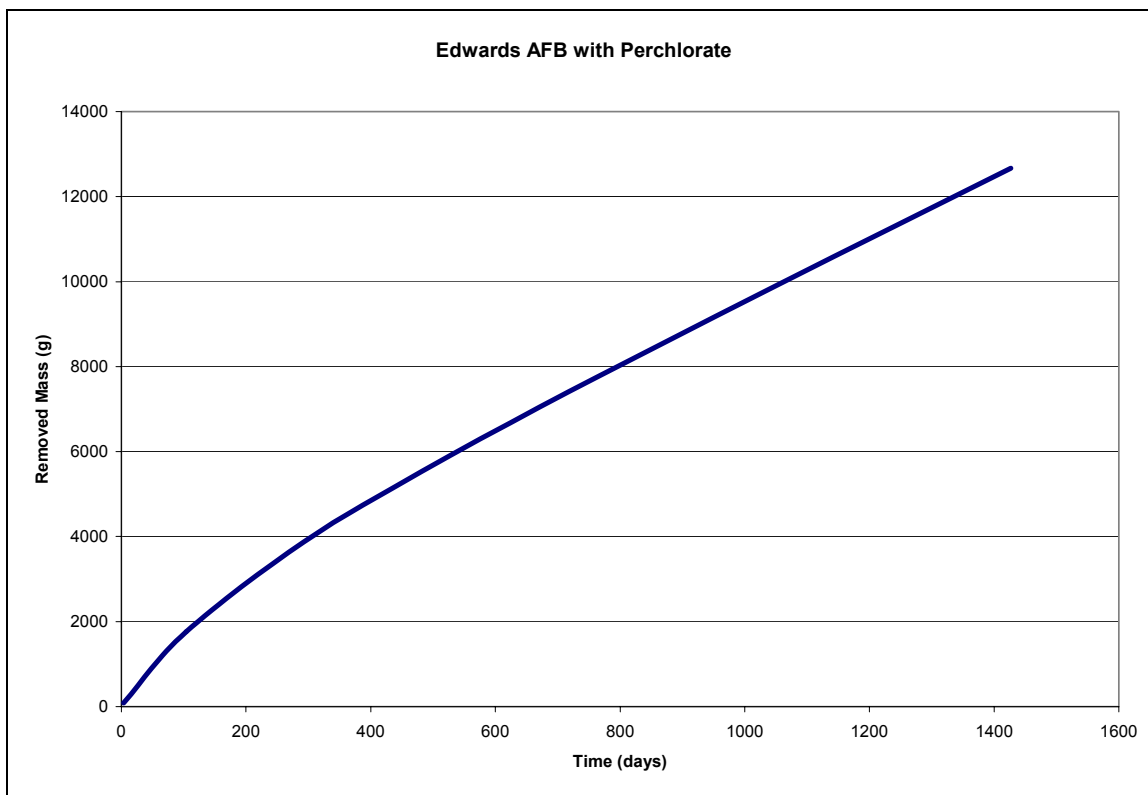


Figure 4-12: Cumulative Mass Destroyed Graph for Edwards AFB Site with Perchlorate

The clean-up standard chosen for evaluation of results of the nitrobenzene run, as reported in Chapter 2 and listed in Table 3-3, is  $18 \mu\text{g/L}$  or  $18\text{e-}06 \text{ g/L}$ . As shown in Figures 4-10 and 4-11, the concentration of nitrobenzene leaving the remediation area after 1,500 days is well above the clean-up standard, though as discussed in earlier sections, due to violation of our steady-state assumption, this does not indicate that the system is not able to eventually meet the requirement. A comparison of Figures 4-1, 4-2, and 4-3 with Figures 4-10, 4-11, and 4-12 shows very similar behavior for the two contaminants. However, because of the much higher initial concentration for perchlorate, as indicated in Table 3-3, the final concentrations and mass removals of perchlorate are much higher than those for TCE.

### 4.2.3 TCE REMEDIATION AT PLANT 44 SITE

The simulation for the Plant 44 Site involved TCE as the contaminant, with the source zone removed. The initial TCE concentration was set at 100 and 1000 mg/L as indicated in Figure 3-4. The concentration contours for layers two and four and the plot of mass destroyed over time for this model run after 1,500 days are given in Figures 4-13, 4-14, and 4-15, respectively.

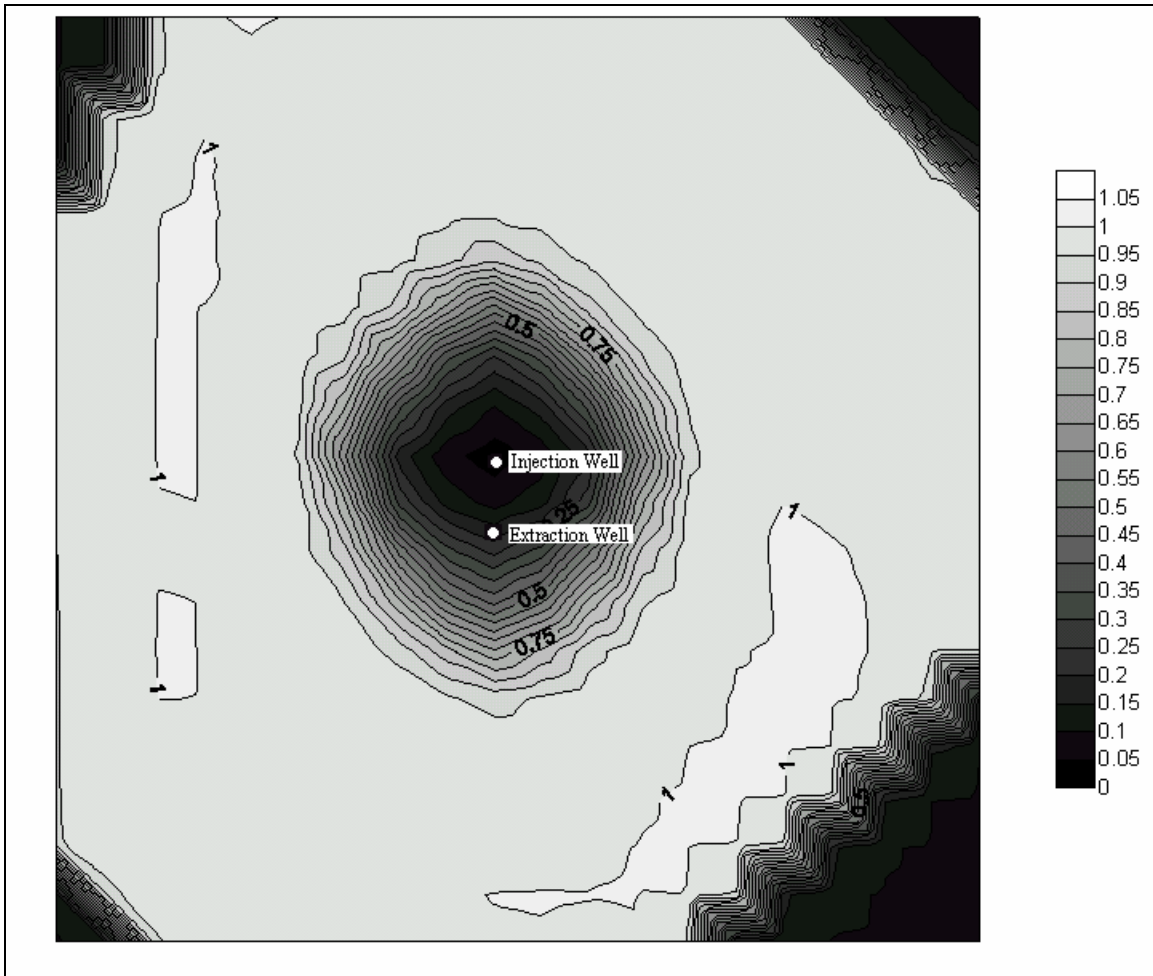


Figure 4-13: TCE Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Two at Plant 44 Site

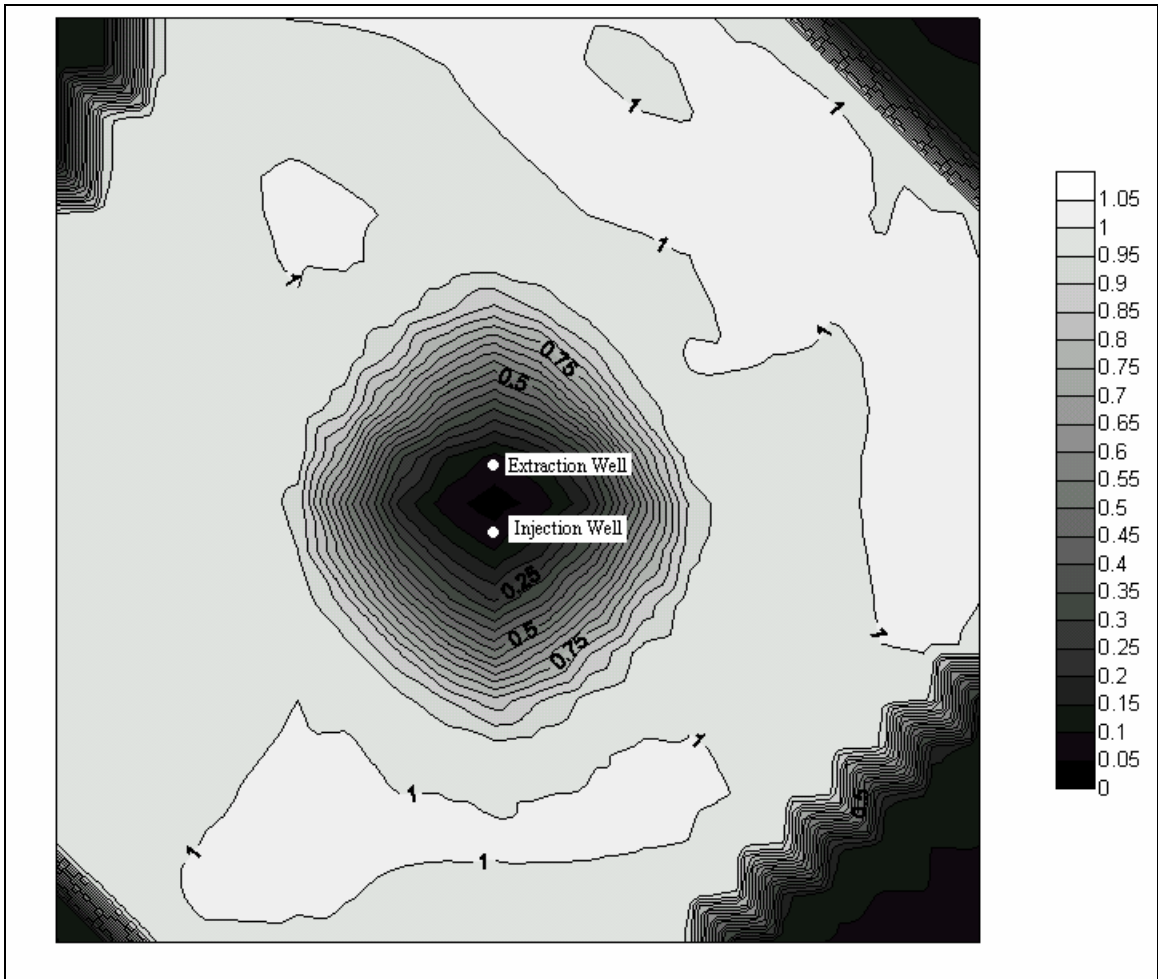


Figure 4-14: TCE Concentration Contours in g/L after 1,500 Days of HFTW Operation for Layer Four at Plant 44 Site

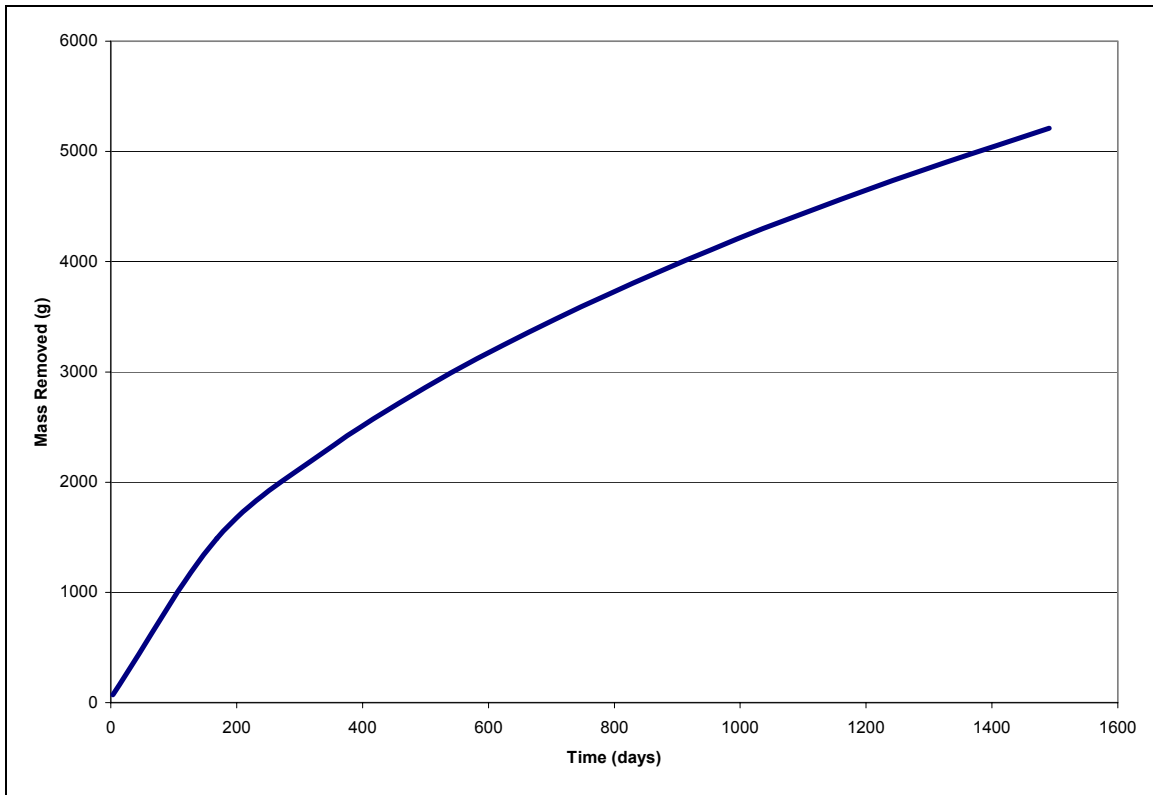


Figure 4-15: Cumulative Mass Destroyed Graph for Plant 44 Site

Recall the MCL for TCE  $5e-06$  g/L. As shown in Figures 4-13 and 4-14, although the system is effectively remediating the TCE in the area immediately around the wells, the concentration of TCE leaving the site boundary is significantly above the MCL in both layers. As discussed previously, it is unknown whether MCLs at the boundary will be attained once the system reaches steady-state. However, due to the slow movement of groundwater in Site 44, it will be many years before steady-state conditions are achieved.

This site's low hydraulic conductivity is the key factor hampering effective remediation of the area. Since the HFTWs in both scenarios are pumping at the same rate ( $14.4 \text{ m}^3/\text{d}$ ) for the same length of time (1500 days) the same amount of water will be cleaned up. The main



difference in the scenarios is due to the regional flow, which is less at Plant 44, so the zone of remediation is more radially symmetric around the treatment wells (since the influence of regional gradient on flow is relatively small compared to the influence of the treatment wells). Subsequently, the movement of treated groundwater to the boundary in the Plant 44 scenario is much slower than for the Edwards AFB scenario, so it will take many more years to achieve low contaminant concentrations at the boundary. In contrast, when comparing Figures 4-3 and 4-15, it is noted that much more TCE is destroyed at the Plant 44 site than at the Edwards AFB site in an equal amount of time. This is due to the different initial contaminant concentrations at the sites; the Plant 44 initial TCE concentrations were 2-3 orders of magnitude greater than the TCE concentrations at Edwards AFB.

## 5.0 CONCLUSIONS AND RECOMMENDATIONS

### 5.1 OVERVIEW

This thesis evaluated the potential of using an HFTW system with in-well Pd reactors to manage groundwater contaminants of concern at DoD and USAF installations. A numerical model was used to simulate system performance for treating a number of contaminants at two sites with very different hydrogeological characteristics.

### 5.2 CONCLUSIONS

**Numerical simulations of an HFTW system with in-well Pd catalytic reactors indicate the system has potential for remediating chlorinated hydrocarbons, such as TCE.** At both the Edwards AFB site in California and the Plant 44 Site in Arizona, TCE was removed to below the MCL near the treatment wells.

**In remediating other contaminants - specifically DBCP, nitrobenzene, and perchlorate – the system had varying effectiveness.** The concentration contour maps for each of these contaminants were similar to those for TCE. However, because of the varying initial concentrations, reaction rate constants, and clean-up requirements, the effectiveness of attaining cleanup goals varied with contaminant. In general, however, based on the fact that model simulations showed sub-MCL concentrations for all contaminants were attainable directly downgradient of the treatment system, it appears that given sufficient time, cleanup goals can be attained for all these contaminants of concern.



**Site conditions are a very important consideration when choosing to use an HFTW system.** The hydraulic conductivities at the two sites, Edwards AFB versus Plant 44, differed significantly; in fact, by two orders of magnitude. The significantly reduced conductivity at the Plant 44 site resulted in a low regional flow, which meant that the time to attain acceptable concentrations at the site boundary was considerably increased over the Edwards AFB site. Thus, hydrogeologic conditions are an important consideration when choosing and designing an HFTW remediation system.

### **5.3 RECOMMENDATIONS**

**Determine downgradient contaminant concentrations at steady state.** Specifically, the simulation run time should be extended to assure that steady state is achieved. Once a sufficient run time is modeled, it will be possible to determine if the system is capable of remediating the contaminated area to a level below the MCL or other level of regulatory concern.

**Compare model simulation to field data.** When this system is installed and operating at the Edwards AFB site, the simulation can be compared to actual system performance. This will allow researchers to evaluate the model, as well as to better understand system operation in the field.

**Study Pd-catalyzed reduction of contaminants of concern.** In the model used for this study, a number of assumptions were used to simulate Pd-catalyzed destruction of the various compounds (first-order kinetics, extrapolation of TCE rates to other compounds, etc). In

order for the technology to be implemented in the field to treat other contaminants of concern, the effectiveness of Pd-catalysis on these other contaminants should be investigated in the laboratory.

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## **VITA**

Captain Kerry J. Cadena was born in St.Petersburg, Florida. She grew up in Inverness, Florida where she graduated from Citrus High School in 1993. She then entered the University of Florida in Gainesville, Florida to commence her undergraduate studies. She graduated with a Bachelor of Science degree in Environmental Engineering and was commissioned as an Air Force officer on 1 April 1998. In August 2001, she entered the Graduate Engineering and Environmental Management program of the Graduate School of Engineering and Management, Air Force Institute of Technology.

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<b>14. ABSTRACT</b> Groundwater and soil contamination is a significant problem throughout the nation, with approximately 300,000 to 400,000 sites affected (National Research Council, 1994). Examples of groundwater contaminants of special interest to DoD and AF installations include fuel hydrocarbons, chlorinated hydrocarbons, and nitroaromatic compounds. Traditional remediation technologies, which include pump-and-treat, permeable reactive barriers, and natural attenuation, have numerous drawbacks associated with them. These drawbacks have prompted researchers to look for innovative contamination clean-up methods. The technology investigated in this thesis, recirculating horizontal flow treatment wells (HFTWs) with in-well palladium (Pd) catalyst reactors, offers the potential for destruction of groundwater contaminants commonly found at USAF and DoD installations at less expense, more safely and effectively, and without the need to pump contaminated water to the surface. In this study, a numerical model was used to simulate application of the remediation technology under different site conditions for a number of contaminants of interest. It was found that the HFTW system with in-well Pd catalyst reactors had potential to remediate groundwater contaminants of DoD interest. Based only on this modeling study, however, it was unclear whether the technology could reduce contaminant concentrations enough to meet regulatory standards downgradient of the treatment system. Further experimental study is recommended, both in the laboratory and in the field, to quantify the efficacy of the technology in treating various contaminants of concern.
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