Design of an In Situ Bioremediation Scheme of Chlorinated Solvents by Reductive Dehalogenation Sequenced by Cometabolic Oxidation

by

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B.S. Environmental Engineering
University of Florida, 1995

Submitted to the Department of Civil and Environmental Engineering in Partial Fulfillment of the Requirements for the Degree of

MASTER OF ENGINEERING
IN CIVIL AND ENVIRONMENTAL ENGINEERING

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June, 1996

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ABSTRACT

Bioremediation, or enhanced microbiological treatment, is one of the most promising technologies of the decade for the treatment of contaminated soil and groundwater. It is a scientifically intense technology incorporating many disciplines. Its application in situ has been very challenging because of the complexity involved in applying knowledge gained in a controlled environment (laboratory) to a diverse and heterogeneous one (field).

The control of the environmental conditions in the subsurface and the delivery of the necessary agents to create an environment conducive to biodegradation are major factors in the success of an in situ application.

An innovative in situ bioremediation scheme is proposed for the treatment of perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE). These contaminants have been detected in a groundwater plume at the Massachusetts Military Reservation, Cape Cod, Massachusetts. The proposed system combines reductive dechlorination (anaerobic process) with cometabolic oxidation (aerobic process) by methanotrophs. All necessary agents (methane, oxygen, and nutrients) are in the gas-phase and are delivered via horizontal wells. This eliminates the problem of liquid displacement which results in inadequate mixing often encountered in the field.

The biodegradation due to cometabolic oxidation was calculated to be 97 % for TCE and 100 % for DCE along the 200 ft wide zone of influence of the gas injection. The kinetic parameters used in the calculations were adapted from an in situ pilot test at another site. Therefore these values serve for estimation purposes only. It was estimated that 99% of the PCE can de reduced if given adequate residence time in the conditions that are conducive to the reductive dechlorination process.

The mass transfer limitations and the spatial heterogeneity of the transport, physical, chemical, and biological properties of the subsurface environment create conditions that cannot be predicted adequately by theoretical approaches. A pilot test is necessary to predict the system's efficacy and determine final design parameters.

Thesis Supervisor: Lynn W. Gelhar
Title: William E. Leonhard Professor, Civil and Environmental Engineering

ACKNOWLEDGMENTS

The past nine months have been an unforgettable ride. Exams, team-projects, assignments, deadlines, presentations; they have all made my MIT experience more fun and challenging than I could ever imagine. My thesis work has been the culmination point of this experience, and at the same time the most benefiting tool I received at MIT.

I would like to thank Professor Lynn Gelhar for his advice and guidance I very much needed throughout the semester. His insightful and critical way of thinking has been instrumental in the completion of my thesis. Most importantly, it has changed the way I approach problems and that is something that will benefit me for the rest of my life. I am very grateful to him.

I would also like to thank Professor Phil Gschwend for his teaching approach to answering all my questions. His enthusiastic way of teaching his Environmental Organic Chemistry class and his advice throughout the semester made my thesis work fun and interesting.

Thanks to Professor David Marks and Shawn Morrisey for making my Master of Engineering experience smoother and less stressful. Bruce Jacobs for his patience and interest in listening to all my questions and providing help whenever possible.

For their support and constructive criticism throughout this effort, my team members for the Master of Engineering project; namely, Crist Khachikian, Alberto Lázaro, Enrique López-Calva, Christine Picazo, and Donald Tillman. Special thanks to Alberto Lázaro for helping me recover a part of my thesis from what seemed to be an "unrecoverable error on disk" a few days before the due date. Mike Collins who provided the estimations for the reductive dechlorination part of the thesis.

Ed Pesce and his staff from the Air National Guard Installation Restoration Program for all their cooperation and willingness to provide us with data and help us in any way possible.

I want to thank my parents, Dimitrios and Alexandra, whose values and teaching have made me what I am today. Their moral support, although from an ocean away, was invaluable and indispensable.

This work is dedicated to the memory of my beloved cousin Panos (1973-1996).

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CHAPTER 1
INTRODUCTION

Groundwater and soil contamination with chlorinated solvents is a widespread problem in the US and many other industrialized nations. Chlorinated solvents are the most frequently observed groundwater contaminants in the United States. They are significant components of hazardous waste sites, landfill leachates, and are frequently found in military bases classified as Superfund sites. They are of major concern because of their high toxicity, persistence to natural biota, and high frequency of occurrence. This has created the need for the development of a cost-effective and efficient means of remediation.

Counter-current air-stripping and granular activated carbon (GAC) have been the most frequently used technologies for synthetic organic chemicals remediation. Neither of these technologies, however, eliminate the existence of the harmful chemicals; they simply relocate the chemicals from one medium to another. Bioremediation, a promising technology currently under development, combines low capital cost with low energy requirements while it renders dangerous contaminants into harmless end-products. This thesis focuses on the application of an in situ bioremediation scheme for the remediation of a plume contaminated with chlorinated solvents.

1.1 Problem Identification

The Cape Cod aquifer has been contaminated by various pollutants emanating from the Massachusetts Military Reservation (MMR). One such plume of contaminants, termed Chemical Spill 4 (CS-4), is the only one that so far is being contained. At present, a pump and treat system has been installed to prevent the advancement of the plume. Contaminated water is extracted at the toe of the plume to reduce the contaminant concentrations to federal maximum contaminant levels and then discharged back to the aquifer. However, this pump and treat system is an expensive interim remedial action. A final remedial plan must be formulated to completely clean up the groundwater.

1.2 Objectives

The CS-4 plume was assigned as a team project to six Master of Engineering students at the Department of Civil and Environmental Engineering at the Massachusetts Institute of Technology. The first objective of the team project was to understand the transport mechanisms of water and contaminants in the Cape Cod aquifer. The second objective was to design a final remediation scheme.

The objective of this thesis is to present the design of an innovative in situ bioremediation scheme and discuss the issues involved with its application at CS-4. A pilot scale study is proposed in order to determine the full scale design parameters as well as to determine the efficacy of this previously untested system. The remediation scheme proposed is a final remedial design.

1.3 Scope

The team project covers the technical aspects of the current situation of the CS-4 plume at the MMR site and describes new clean-up strategies based on the application of in situ bioremediation, a new pump and treat scheme, or a combination of the two. The results of the team project are shown in the appendix.

This thesis describes the design of an innovative in situ bioremediation scheme and the factors that must be considered in order for the application to be successful. Chapter 2 briefly describes the site. General geographical background information is provided as well as the history of the activities at MMR. These data are needed to understand the context and importance of the groundwater contamination. The current situation at the CS-4 site is presented, including an overview of the plume extent and a description of the existing interim remedial action.

Chapter 3 describes the technology of bioremediation. The factors that determine the success of its application are discussed. In situ bioremediation and the issues that must be addressed when scaling up a laboratory study to a field study are discussed.

In chapter 4 cometabolic oxidation is defined and its applications discussed. The microbiology of the microorganisms of interest (methanotrophs) is explained. Factors affecting the microbial growth of the methanotrophs and the transformation of the contaminants induced by them is discussed. The kinetic modeling equations of the microbiological processes are presented and discussed. The input parameters used in this design are presented and the methodology for determining the degradation is discussed.

In chapter 5 reductive dechlorination is briefly discussed. Its environmental significance and its application to the site of interest is presented.

In chapter 6 the in situ bioremediation scheme proposed is presented. The challenges associated with its application at CS-4 are discussed. The delivery of the desired agents is discussed and the different phases of the system identified and explained. The degradation of the contaminants is then calculated and the assumptions made are discussed. The overall system design incorporating all the phases is presented.

Chapter 7 summarizes the results and discusses issues that must be considered so a proper interpretation of the results is achieved.

CHAPTER 2

SITE DESCRIPTION

2.1 Location

Cape Cod is located in the southeastern most point of the Commonwealth of Massachusetts (Figure 2-1). It is surrounded by Cape Cod Bay on the north, Buzzards Bay on the west, Nantucket Sound to the south, and the Atlantic Ocean to the east. Cape Cod, a peninsula, is separated from the rest of Massachusetts by the man-made Cape Cod Canal.

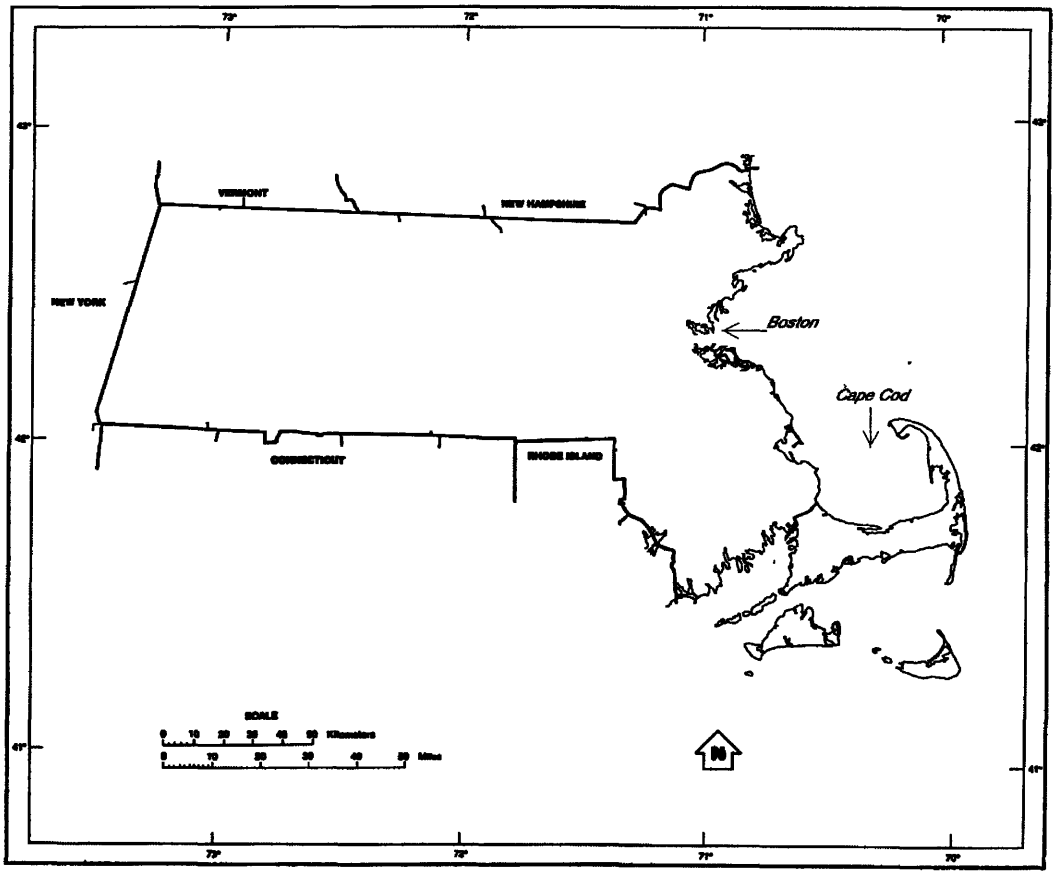

Figure 2-1 Map of the Commonwealth of Massachusetts

The MMR is situated in the northern part of western Cape Cod (Figure 2-2). Previously known as the Otis Air Force Base, the MMR occupies an area of approximately 22,000 acres (30 square miles).

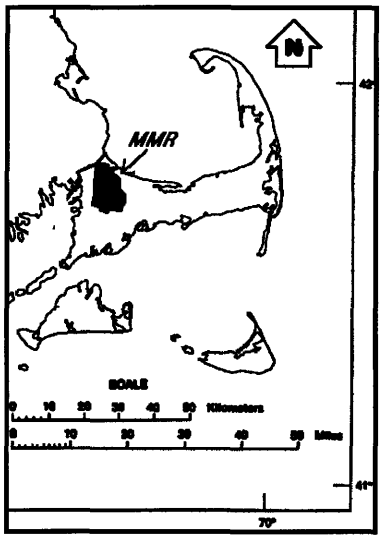

Figure 2-2. Location of MMR

2.2 Geopolitics and Demographics

Geopolitically, Cape Cod is located in Barnstable County, and is divided into 15 distinct municipalities (towns): all of these municipalities have their own individual form of government and community organizations. The reservation is bordered by four towns: to the west by Bourne, to the east by Sandwich, to the south by Falmouth, and to the southeast by Mashpee.

The population of Cape Cod fluctuates with the season. In 1990, U.S. Census Bureau (USCB) determined the number of year-round residents to be 186,605

(Massachusetts Executive Office of Environmental Affairs, 1994). It is estimated that the number of Cape residents triples from winter to summer, topping a half million with the influx of summer residents and visitors (Cape Cod Commission, 1996). The county's median age in 1990 was 39.5 years (Cape Cod Commission, 1996). Age distribution studies conducted by the USCB, concluded that 22% of the Cape's residents are aged 65 and over, the highest percentage of this age group in any county in Massachusetts (Cape Cod Commission, 1996). Population growth studies estimate the year-round population of Cape Cod to increase 23% by the year 2020 (Massachusetts Executive Office of Environmental Affairs, 1994).

2.3 General Physical Site Description

Cape Cod sediments are predominantly sands and gravels with a low percentage of silty soils. Left behind by the advancement of a glacier thousands of years ago, these deposits are generally well sorted but layered, and therefore heterogeneous in character. These sandy deposits allow a large portion of precipitation to seep beneath the surface into groundwater aquifers. This is the only form of recharge these aquifers obtain. The groundwater system of Cape Cod serves as the only source of drinking water for most residents.

2.4 Natural Resources

Cape Cod is characterized by its richness of natural resources. Ponds, rivers, wetlands and forests provide habitat to various species of flora and fauna. Many of the

Cape's ponds and coastal streams serve as spawning and feeding grounds for many species of fish. The Crane Wildlife Management Area, located south of the MMR in western Cape Cod, is home to many species of birds and animals. In addition, throughout the Cape there are seven Areas of Critical Environmental Concern (ACEC) as defined by the Commonwealth of Massachusetts. These were established as areas of highly significant environmental resources and protected because of their central importance to the welfare, safety, and pleasure of all citizens.

2.5 Land and Water Use

The majority of the land in Cape Cod is either covered by forests or "open land". Twenty-five percent of the land is residential, while only less than 1% of the land is used for agriculture or pasture (Cape Cod Commission, 1996).

Water covers over 4% of the surface area of Cape Cod. This water is distributed among wetlands, kettle hole ponds, cranberry bogs, and rivers. Nevertheless, all 15 communities meet their public supply needs with groundwater. Falmouth is the only municipality that uses some surface water (from the Long Pond Reservoir) as a drinking water source. Approximately 75% of the Cape's residents use water supplied through public works, while the remaining use private wells within their property.

Water demand in the Cape follows the same seasonal variations as population. Water work agencies are called to supply twice as much water during the summer months than during the off-season (September through May). The highest monthly average daily demand (ADD) in 1990 was in July when 34.98 mgd were used. The lowest monthly

ADD was in February with 14.03 mgd (Water Resources of Cape Cod, 1994). The towns of Falmouth and Yarmouth have the highest demand for water, with a combined percentage of almost 30% of the Cape's total water demand (Massachusetts Executive Office of Environmental Affairs, 1994).

Agriculture also constitutes a part of the water use in Cape Cod. Cranberry cultivation is an important part of the economy of the Cape and is a water intensive activity. The fishing industry also provides a boost to the Cape's economy. Tourism accounts for a substantial part of the Cape's economy and therefore the surface water quality is important.

2.6 MMR Setting and History

The MMR has been used for military purposes since 1911. From 1911 to 1935, the Massachusetts National Guard periodically camped, conducted maneuvers, and weapons training in the Shawme Crowell State Forest. In 1935, the Commonwealth of Massachusetts purchased the area and established permanent training facilities. Most of the activity at the MMR has occurred after 1935, including operations by the U.S. Army, U.S. Navy, U.S. Air Force, U.S. Coast Guard, Massachusetts Army National Guard, Air National Guard, and the Veterans Administration.

The majority of the activities consisted of mechanized army training and maneuvers as well as military aircraft operations. These operations inevitably included the maintenance and support of military vehicles and aircraft as well. The level of activity has greatly varied over the MMR operational years. The onset of World War II

and the demobilization period following the war (1940-1946) were the periods of most intensive army activity. The period from 1955 to 1973 saw the most intensive aircraft operations. Today, both army training and aircraft activity continue at the MMR, along with U.S. Coast Guard activities. However, the greatest potential for the release of contaminants into the environment was between 1940 and 1973 (E.C. Jordan, 1989a).

Wastes generated from these activities include oils, solvents, antifreeze, battery electrolytes, paint, waste fuels, transformers, and electrical equipment (E.C. Jordan, 1989b).

2.7 Current Situation

2.7.1 Interim Remedial Action and Objectives for Final Remedy

The existing remedial action was designed as an interim solution, with the objective of containing the plume against further migration. This is achieved by placing pumping wells at the plume toe and treating the extracted water (Figure 2-3).

In contrast, the final remedial action will address the overall, long-term objectives for the CS-4 Groundwater Operable Unit which are as follows (ABB ES, 1992b):

- Reduce the potential risk associated with ingestion of contaminated groundwater to acceptable levels.
- Protect uncontaminated groundwater and surface water for future use by minimizing the migration of contaminants.

- Reduce the time required for aquifer restoration.

In terms of treatment objectives, the target levels for the treatment of the water are defined through the established Maximum Contaminant Levels (MCL). These apply to

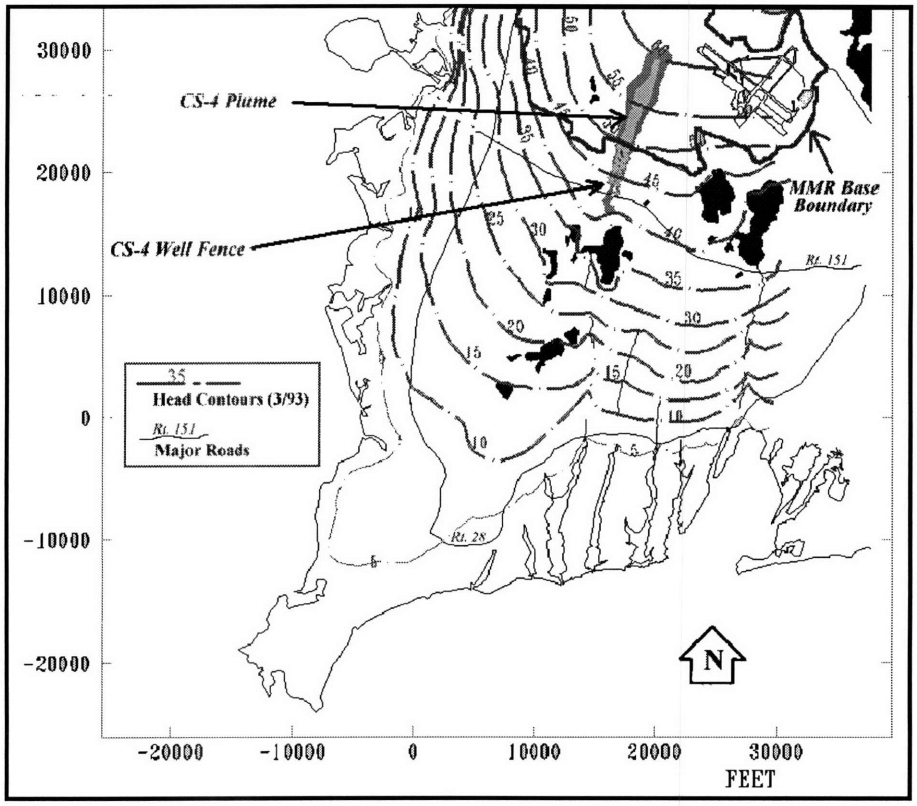

Figure 2-3 CS-4 plume and well-fence location

the contaminants of concern and are summarized in Table 2-1. Maximum measured concentrations, average concentrations within the plume, and an approximate frequency of detection are also shown.

Although the existing remedial action is interim, its clean-up goals have to be consistent with the long-term goals. Therefore, the above target levels are applicable to

the existing interim action.

Table 2-1 Contaminants of concern and treatment target level (ABB ES, 1992b).

Contaminant of concern	Maximum Concentration (ppb)	Average Concentration (ppb)	Frequency of detection	Target level (MCL) (ppb)
Tetrachloroethylene (PCE)	62	18	14/20	5
Trichloroethylene (TCE)	32	9.1	14/20	5
Total 1,2-Dichloroethylene (DCE)	26	1.1	11/20	70
1,1,2,2- Tetrachloroethane (TeCA)	24	6.8	1/20	2[a]

a No federal or Massachusetts limits exist. Therefore, a risk-based treatment level was proposed. This was calculated assuming a 1x10-5 risk level and using the USEPA risk guidance for human health exposure scenarios.

2.7.2 Existing Remedial Action

The currently operating remediation system consists of the following components:

- Extraction of the contaminated groundwater at the leading edge of the plume by 13 adjacent extraction wells.
- Transport of the extracted water to the treatment facility at the edge of the MMR area.
- Treatment of the water with a GAC system.
- Discharge of the treated water back into the aquifer to an infiltration gallery next to the treatment facility.

The treatment facility consists of two adsorber vessel in series filled with granular activated carbon (Model 7.5, Calgon Carbon Corporation). This system of two downflow,

fixed-bed adsorbers in series is one of the most simple and widely used designs for groundwater treatment applications (Stenzel et al., 1989). Two vessels in series assures that the carbon in the first vessel is completely exhausted before it is replaced, thus contributing to the overall carbon efficiency. The removed carbon is then transported off-site for reactivation.

2.7.3 Plume Location

CS-4 plume is located in the southern part of MMR moving southward (Figure 2-3). From field observations, the dimensions of the plume have been defined as 11,000 ft long, 800 ft wide, and 50 ft thick (E. C. Jordan, 1990).

2.7.4 Other Technologies Considered

Evaluating the technologies considered for the interim remedial system provides an understanding of the reasons for selecting the current pump and treat system. Of the 13 remedial technologies screened in the Focused Feasibility Study (E.C. Jordan, 1990), five were selected and retained for detailed analysis. For further evaluation, they were compared against the following nine criteria:

- overall protection of human health and the environment
- compliance with ARARs (Applicable or Relevant and Appropriate Requirement)
- long-term effectiveness and permanence
- reduction of mobility, toxicity, or volume through treatment
- short-term effectiveness

- implementability
- cost
- state acceptance
- community acceptance

The no action alternative served as a baseline for comparing various strategies (ABB ES, 1992a; E.C. Jordan Co., 1990). The selected carbon adsorption technology was evaluated against the following alternatives:

- air stripping followed by activated carbon
- UV oxidation
- spray aeration
- Otis Wastewater Treatment Plant

2.7.5 Performance of Current Remediation Scheme

Since the treatment facility started operating in November 1993, only minimal inflow concentrations of 0.5 ppb (ABB ES, 1996) have been detected and treated.

Numerous authors have raised serious concerns about the ability of existing pump and treat systems to restore contaminated groundwater to environmentally and health-based sound conditions (Mackay and Cherry, 1989; MacDonald and Kavanaugh, 1994). Other studies have shown that pump and treat in conjunction with other treatment technologies can restore aquifers effectively (Ahlfeld and Sawyer, 1990; Bartow and Davenport, 1995; Hoffman, 1993;). However, there is a consensus that pump and treat is an effective means of *controlling* the plume migration.

In conclusion, the interim CS-4 pump and treat system is an appropriate way to quickly respond to the plume migration. However, for the final CS-4 remedial system new ways of remediating the aquifer must be addressed. This thesis proposes an in situ bioremediation scheme as a final remedial action for the CS-4 plume.

CHAPTER 3
BIOREMEDIATION

"If we have a magical torch, it is biotechnology research", EPA director Reilly said in 1990 when asked what he thought of the future of Superfund (Civil Engineering News, 1990). Currently, most groundwater treatment technologies relocate the chemicals they treat from one phase (groundwater) to another (usually a solid). Bioremediation , or enhanced microbiological treatment, is one of the most promising remediation technologies of the decade because it has the potential to: (1) eliminate the existence of hazardous substances; (2) avoid costly chemical and physical treatment technologies; (3) operate in situ; and (4) combine low capital and low energy requirements (Sturman et al., 1995). Understanding the technology's abilities and limitations is essential to an engineer who wants to utilize this technology for hazardous waste remediation.

3.1 Definition

Bioremediation engineering is the application of biological process principles to the treatment of water or soil contaminated with a hazardous substance (Cookson, 1995). It is the process in which microorganisms, mainly bacteria, degrade organic chemicals to obtain the energy stored in the carbon-carbon bonds, as well as obtain carbon for growth. The biochemical reaction is reliant upon enzymes which act as catalysts. The enzymes are produced by the bacteria and the biochemical reaction takes place when the organic

substrate collides with the active site of the enzyme. Figure 3-1 illustrates how an enzyme reaction can be thought of as a lock and key. The products of the reaction are then released and the enzyme is available to facilitate another reaction.

The contaminants are transformed into simpler compounds (biotransformation) and in most cases, to inorganic species such as carbon dioxide and water (mineralization). The energy released by the reaction is used by the microorganisms to grow and reproduce. Only the reactions that are energetically favorable to an organism will take place.

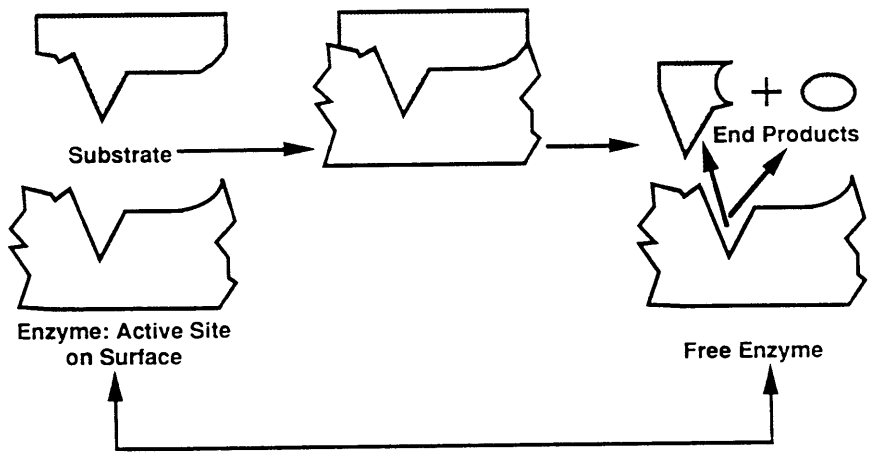

Figure 3-1 Enzyme reaction represented as a lock and key (Nyer, 1992).

3.2 Environmental Requirements

Several requirements are necessary for the biochemical reactions to take place. In order to optimize biodegradation, it is important to create an environment where all these factors are conducive to biodegradation and the limiting factor(s) are the contaminants.

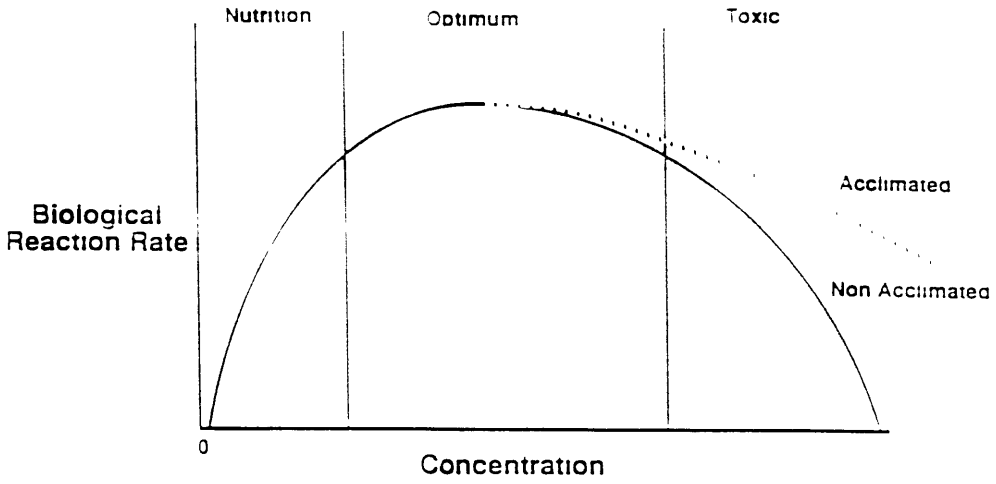

Figure 3-2 Leibig's law of the minimum (Nyer, 1992).

Figure 3-2 illustrates Leibig's law of the minimum which states that a process is limited by the factor at the lowest level. The factors affecting biochemical reactions are shown in Figure 3-3 in descending order of importance. Assuming that the targeted compound is biodegradable and available (not sorbed, mobile), the presence of the microorganism(s) with the capability to degrade the targeted compounds is of foremost importance. Generally, these microorganisms are indigenous to most sites since virtually all groundwater supports a population of viable bacteria (unless extremely toxic conditions exist). Bacteria have been found even at depths of 1800 ft (Thomas and Ward, 1992). Microorganisms grown in different environments are not acclimated to a particular environmental setting and therefore they are more likely to get outcompeted by the natural populations. The reason intrinsic bioremediation may not be taking place at a site is because one or more of the other requirements have not been satisfied. Microbial

numbers and their activity are generally higher in sandy transmissive sediments than in those with high clay content and low transmissivity (Thomas and Ward, 1992).

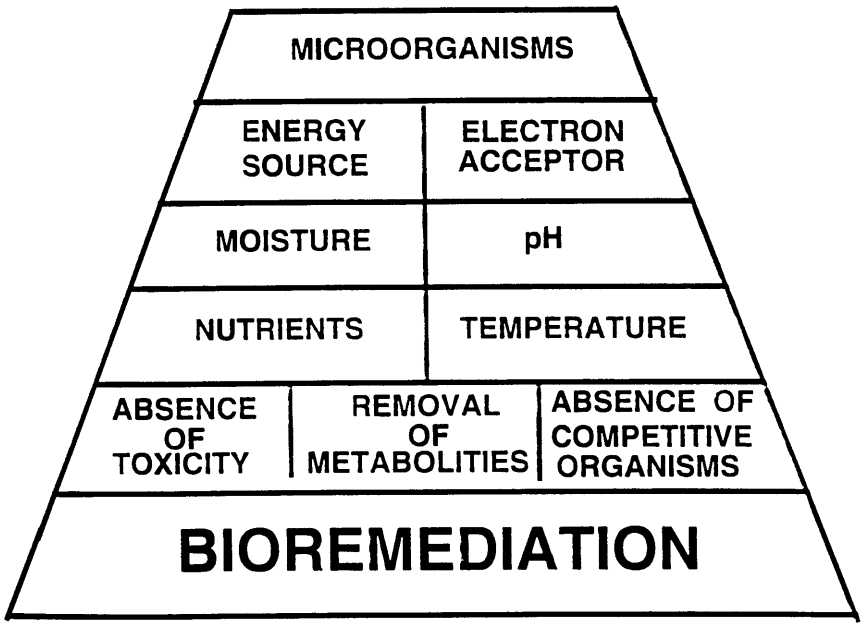

Figure 3-3 Bioremediation requirements (Cookson, 1995).

The microorganisms gain their energy through oxidation-reduction (redox) reactions. The presence, therefore, of a substrate that can be used as an energy source and carbon source and an appropriate electron acceptor-donor system are essential to the success of the biodegradation process (Cookson, 1995). The carbon is necessary for cellular growth and reproduction.

The environmental conditions (moisture and pH) must be appropriate for the reactions to take place. Adequate moisture content is essential for cellular movement. In groundwater remediation this factor is obviously not a concern. The pH must be optimal

in order for the microorganism to conduct cellular functions, cell membrane transport, and reaction equilibrium. Generally, pH 7 ± 2 is acceptable for most microorganisms (Cookson, 1995).

Nutrients are necessary for microbial growth and enzyme production. A simple expression of the chemical structure of a bacterial cell is $C_5H_7O_2N$ with trace amounts of other elements (phosphorus, iron, sulfur, etc.). The availability of these nutrients varies from site to site and must be addressed on a site specific basis. Temperature has a direct effect on the rate of degradation. The reaction rate obeys the Arrhenious relationship (Schwarzenbach et al., 1993). According to the Arrhenious relationship, the rate decreases by half for every 10°C. Therefore, rates obtained from laboratory studies (usually 20-25 °C) must always be adjusted (among other factors) for field temperatures (about 10°C for groundwater).

The absence of toxic substances is also essential to the degree of degradation of a contaminant. Toxic effects can also be induced by the build-up of toxic intermediates due to the lack of degradation of the metabolic products. Competition effects for the electron acceptor and donor, energy source, and nutrients can be posed by other microorganisms and competition between different compounds degradable by the same enzyme may ultimately "slow down" the desired reaction and lessen the efficacy of the remediation process.

3.3 In Situ Bioremediation

3.3.1 Definition

Compounds that are resistant to biodegradation and exist in the non-aqueous phase (NAPL) generally result in plumes that are large in aerial extent. Pump and treat methods that have been traditionally employed to remediate such plumes have proven to be ineffective in achieving final treatment levels while the long term treatment required for contaminants to desorb makes pump and treat a very expensive approach (Semprini, 1995).

In situ bioremediation is the utilization of microorganisms to degrade contaminants in their "original place" with minimal disturbance to the subsurface. In situ bioremediation provides a more effective and inexpensive approach because it has the potential to: (1) completely degrade the contaminants (2) decrease the treatment time; and (3) use the subsurface as a bioreactor eliminating the need to pump the water to the surface for treatment (Semprini et al., 1992b).

In order to apply a process (that has been proven to be effective in the laboratory) in situ, transport, physical, chemical, and biological processes of the subsurface must be considered. The degree of understanding of those processes will determine for the most part whether an in situ application will be successful in biodegrading the target compounds.

3.3.2 Engineering Scale-up

In situ bioremediation is a scientifically intense technology requiring knowledge from many disciplines (Cookson, 1995):

- biochemistry
- microbiology
- geochemistry
- hydrogeology
- water chemistry
- soil science

The complexity encountered in a subsurface environment complicates the application of a bioremediation process that has conclusively been proven in the laboratory scale. Therefore it is important to understand and account for the effect of scale-dependent variables such as mass transport mechanisms and limitations, spatial heterogeneities, variation in environmental conditions (pH, redox conditions, etc.), and the presence of many contaminants and species of microorganisms (Sturman et al., 1995). In addition, abiotic losses in the subsurface that cannot be duplicated in the laboratory, provide additional skepticism for the efficacy of an in situ bioremedation process.

Because of the complexities mentioned above, process design and operation of bioremediation projects are frequently undertaken without complete knowledge of the processes involved leading to uncertainty in the response of the system (Cookson, 1995). Thus, a successful in situ bioremediation scheme requires pilot testing.

The engineering challenge is to control the environmental conditions, and provide a uniform distribution of the added agents for an optimized degradation rate and complete mineralization of the target compounds. The engineering and control of the delivery systems and understanding the mixing processes occurring in the subsurface present to the engineer more challenge than understanding the biochemical process. Responsive control and a monitoring system is required to provide data for process optimization. The success of a large field application will highly depend on how the engineer can address those issues for the site of interest.

Typically, there are two approaches to in situ bioremediation. The first is to extract the contaminated water, add oxygen and nutrients, and reinject the water to the aquifer. The enriched water moves through the aquifer stimulating microbial growth and ultimately to contaminant biodegradation. The second approach is to inject water high in nutrients and oxygen (or hydrogen peroxide) and count on molecular diffusion and dispersion to mix the agents with the contaminated water in the subsurface. The enriched water then leads to microbial growth resulting in contaminant biodegradation.

When dealing with plumes of large aerial extent (and therefore large volumes of contaminated water), typical of chlorinated solvent contamination that took place several decades ago, both of the approaches mentioned above are flawed. The first approach is similar to pump and treat. Pumping large volumes of water out of the aquifer and then back in it would be time-consuming and labor-intensive, minimizing the cost effectiveness of the process. The second approach is non-realistic. Mixing due to molecular diffusion, advection and dispersion of oxygen and nutrients would not be

sufficient to overcome the displacement of the contaminated water by the added liquid. Therefore, biodegradation would be very minimal.

To overcome the problems mentioned above, agents of choice can be injected in the gas-phase. The gases move through the aquifer in discrete channels (Hayes, 1996) diffusing into the water on their way to the surface (carried by buoyancy). This effect creates a continuous source of the injected agents that affects an area equal to the size of the influence of the injected gases (biozone). The contaminated groundwater flows into the biozone and is remediated as it flows through it. This approach overcomes the displacement problem since the volume of water displaced by the gases is minimal.

CHAPTER 4
COMETABOLIC OXIDATION

Xenobiotic chemicals (i.e. foreign to natural biota) such as the chlorinated solvents of concern at CS-4 introduce a problem for the bacteria which cannot derive neither a source of carbon nor energy from their degradation. This is attributed to the higher oxidation state of carbon in the molecule due to the negatively charged chlorine. Organic compounds where carbon has a negative oxidation state (benzene, toluene, etc.) are more easily biodegradable and bioremediation of such compounds is well documented (Davis, 1994). Cometabolic oxidation provides a different approach to degrade the recalcitrant compounds and has been a major topic of research interest throughout the world. Cometabolism induced by methane-oxidizing bacteria has been studied extensively because these microorganisms are indigenous to most soil and water bodies (Chu and Alvarez-Cohen, 1996), and methane is a cheap and abundant gas capable of supporting a microbial population that can oxidize a wide range of common subsurface contaminants.

4.1 Definition

Cometabolism is defined as "the transformation of a non-growth substrate in the obligate presence of a growth substrate" (Grady, 1985). In other words, when an organic compound cannot serve as the primary substrate (i.e. the source of energy and carbon),

another compound can support the growth of the microorganisms that will degrade both compounds. Methane, propane, ethylene, propane, toluene, phenol, and other compounds have been documented to be capable of supporting microbial populations while inducing enzymes (oxygenases) that are fortuitously capable of oxidizing several chlorinated solvents (Sawyer, 1994).

4.2 Microbiology of methanotrophs

Methanotrophs (from "methane" and the Greek "trophia" meaning "to nourish") are microorganisms growing on methane. Methanotrophs are believed to be native to most aquifer systems. The enzyme enabling the methanotrophs to oxidize methane is the methane monooxygenase enzyme (MMO) which because of its relaxed specificity, it can oxidize many other compounds some of which are the very recalcitrant chlorinated ethenes and ethanes. The enzyme's relaxed specificity is also what makes the bacteria such an adaptable and prevalent organism in the subsurface.

The products of the oxidation of chlorinated ethenes are their respective epoxides which are unstable compounds quickly transforming non-enzymatically in aqueous solution to various products (formic acid, glyoxylic acid, etc.). The new products are subject to further degradation, mainly by heterotrophs, ultimately yielding carbon dioxide, water, and chloride (Semprini et al., 1992b).

4.3 Oxygen Demand

Cometabolic oxidation is an aerobic process. Most methanotrophs perform well

in low oxygen concentrations turning the system anaerobic if enough methane is present. The half-saturation coefficient (affinity coefficient) for oxygen varies from microbe to microbe. The oxidation of the contaminants is also an aerobic process and degradation will not take place if biomass is present and oxygen is not. This is important in cases where biomass grown above surface is injected to the subsurface to degrade the contaminants (to eliminate competitive inhibition discussed in section 4-4). This process requires the addition of oxygen if the aquifer is oxygen deficient.

4.4 Competitive Inhibition

Since methane and the chlorinated ethenes are oxidized by the same enzyme, they are competitive inhibitors of each other's transformation. The extent of the competitive inhibition effect is a function of their relative concentrations: the greater the methane concentration, the greater the inhibition effect.

This effect is also a function of the culture's characteristic half-saturation coefficient. Some researchers (Tompson et al., 1994) have pursued an approach they call the resting cell transformation according to which a bacterial population is injected into the aquifer in the absence of methane to eliminate this competitive effect. The bacterial population is active towards cometabolic oxidation but there is no methane to compete for the enzyme.

Since different methanotrophs have different affinities (half saturation coeffients) for methane, it is important to know which species is present at a site and be able to adjust the addition of agents accordingly. Therefore when designing a process

application, attention must be paid to maintain the methane concentration below inhibitory levels.

4.5 Toxicity Effects

A toxicity effect induced by transient intermediates appears when TCE concentrations exceed 0.1 mg/L (Chang and Alvarez-Cohen, 1995). This effect outweighs the cell decay coefficient and must be accounted for in order to represent the microbial process. The intermediates (probably a hydrolysis product of the TCE-epoxide) are damaging to the methanotrophic cell (Chang and Alvarez-Cohen, 1995). High TCE concentrations do not cause any toxicity to the methanotrophic cell unless any transformation takes place and the intermediates are produced.

This implies that in higher contaminant concentrations it may be necessary to: (1) increase the methane concentration to compensate for the cell losses due to toxicity; and (2) increase the oxygen concentration because of the increased oxygen demand induced by heterotrophs catabolizing dead methanotrophic biomass.

4.6 Model Simulations

Semprini et al. (Semprini et al. 1990, Semprini et al. 1991a) conducted a pilot scale study in a shallow confined aquifer at the Moffett Naval Air Station, California. Methane, oxygen, and various chlorinated aliphatics were mixed with groundwater pumped to the surface. The mix was then injected to the subsurface to stimulate methanotrophic growth. Comparisons of test results and model simulations (Semprini

and McCarty 1991b; 1992a) from that study consist the modeling basis of the design of the bioremediation scheme at CS-4.

The Moffett Field study has been particularly successful in the sense that a careful mass balance of each contaminant was kept, enabling the researchers to attribute the degradation of the contaminants to cometabolic oxidation as opposed to other abiotic losses. In addition, the contaminants were mixed above surface with oxygen and methane and eliminating that way any mixing problems that might have occurred in the subsurface.

4.6.1 Biomass Growth and Decay

The biomass stimulated is assumed to be attached to the subsurface solids creating an immobile shallow biofilm that is fully penetrated with substrate and does not have mass-transfer limitations (Rittmann and McCarty, 1980). This simplifies the model since no consideration for diffusion into the biofilm must be given. In addition, the assumption that the biomass is attached to the solids is supported be several researchers (Harvey et al., 1984; Semprini and McCarty, 1991b) and seems appropriate to be used in the design. Microbial growth and decay are assumed to be functions of the electron acceptor (oxygen) and the substrate provided which acts like the electron donor (methane in this case). It follows the modified Monod kinetics model adapted by Semprini and McCarty (1991b) shown here:

$$\frac{dX}{dt} = XksY\left(\frac{Cs}{Ks + Cs}\right)\left(\frac{Co_2}{Ko_2 + Co_2}\right) - bX\left(\frac{Co_2}{Ko_2 + Co_2}\right) \qquad (4\text{-}1)$$

where X is the biomass concentration (mg/L) on a pore volume basis; ks is the maximum utilization rate of the substrate (mg methane/mg cell-d); Y is the yield coefficient (mg cell/mg methane); Cs, and Co_2 are the substrate and oxygen concentrations (mg/L) respectively; Ks and Ko_2 are the half-saturation coefficients (mg/L) for the substrate and oxygen respectively; and b is the cell decay coefficient (d^{-1}). The steady-state biomass concentration is given by:

$$Xss = \frac{YCs}{b} \tag{4-2}$$

where Xss is the steady-state biomass concentration (mg/L). The model describing the methane utilization is not shown here as it is not used in the design. Methane concentration is assumed to be constant and not limiting in the biochemical reactions since it can be adjusted by taking the proper engineering measures.

4.6.2 Oxygen Consumption

The rate of utilization of oxygen is described by (Semprini and McCarty, 1991b):

$$\frac{dCo_2}{dt} = -ksFX\left(\frac{Cs}{Ks + Cs}\right)\left(\frac{Co_2}{Ko_2 + Co_2}\right) - dcfdbX\left(\frac{Co_2}{Ko_2 + Co_2}\right) \tag{4-3}$$

where F is the stoichiometric ratio of oxygen to the substrate for biomass synthesis (mg oxygen/mg methane); dc is the cell decay oxygen demand (mg oxygen/mg cells) posed by the respiration of heterotrophs and fd is the fraction of the biomass that is biodegradable.

4.6.3 Cometabolic Oxidation

The competitive inhibition effect (section 4.4) must be incorporated in the model describing the cometabolic transformation of the contaminant since it can influence the rate of degradation of the contaminant. Oxygen must also be present for the degradation of the contaminant so a term is included to account for its effect. The following model describes the degradation process of cometabolic oxidation adapted by Semprini and McCarty (1991b):

$$\frac{dCc}{dt} = -Xkc\left[\frac{Cc}{Kc\left(1+\frac{Cs}{Ks}\right)+Cc}\right]\left(\frac{Co_2}{Ko_2+Co_2}\right) \tag{4-4}$$

where C_c is the contaminant concentration (mg/L); k_c is the maximum utilization rate of the contaminant (mg contaminant/mg cell-d); and K_c is the contaminant half-saturation coefficient (mg/L) of the contaminant.

The effect of sorption to the availability of the contaminants for degradation is excluded from this model because the retardation factors for the site were low (Khachikian, 1996).

4.6.4 Input Parameters

The parameters that will be used in the modeling equations described above have been determined experimentally both in the field and in the lab by "best fit" techniques. They were derived by matching the field or lab observations to the modeling equations

simulating the process at the Moffett Field study (Semprini and McCarty, 1991b; 1992a).

It is important to note that extrapolating values from one site and use them in another only serves only as an estimation. Site-specific tests should be conducted in order to determine the actual parameters. For example, k_c has been found to vary by three orders of magnitude (Henry and Grbic'-Galic', 1994), depending on under what conditions the study was conducted (the low value is for field studies). The significant difference from laboratory to field studies arises from the subsurface complexity and heterogeneity as expected (section 3.3).

The parameters used in the different models are shown in Tables 4-1 to 4-3.

Table 4-1 Microbial growth model input parameters (Semprini and McCarty, 1991b)

	CH_4
Y (mg/mg)	0.5
k_s (mg/mg-d)	2.0
K_s (mg/L)	1.0
K_{O_2} (mg/L)	1.0
b (d^{-1})	0.10

Looking at Table 4-1 it is evident that the K_s is relatively low (the range given by Henry and Grbic'-Galic'(1994) was 0.016-2.56 mg/L), indicating high affinity of the native methanotrophs for methane. On the contrary, the relatively high value of K_{O_2} (the range given by Henry and Grbic'-Galic'(1994) was 4.5×10^{-3}-0.54 mg/L) indicates that the methanotrophs did not have a high affinity for oxygen.

Table 4-2 Oxygen consumption model input parameters

(Semprini and McCarty., 1991b)

	O_2
F	2.4
f_d	0.8
dc (mg/mg)	1.42

Table 4-3 Cometabolic oxidation model input parameters

(Semprini and McCarty, 1992a)

	TCE	c-DCE	t-DCE	VC
k_c (g/g-d)	0.01	0.05	1.0	1.0
K_c (mg/L)	1.0	1.0	1.0	1.0

Looking at Table 4-3, it is evident that the native microorganisms present at the Moffett Field have a relatively low K_c value (the range given by Henry and Grbic'-Galic' (1994) for TCE was 0.52-18.85 mg/L). This indicates that they have a high affinity for the contaminants and therefore competitive inhibition effects are less pronounced. The utilization rate of the contaminant decreases with increasing degree of chlorination as expected.

It is important to note that Semprini and McCarty (1991b) found that the utilization rate of methane by the microbes increased with time. This may be due to adaptation of the indigenous population to the new conditions. Therefore, short-term studies may give conservative estimates of the actual treatment potential.

4.6.5 Determination of Degradation

The right hand side of equation 4-4 can be simplified by neglecting the value of C_c (the contaminant concentrations are in the order of 0.01-0.06 mg/L at CS-4) in the denominator since it is at least an order of magnitude smaller than the other term in the denominator. The right hand side of equation 4-4 then provides the first-order degradation constant, k_{deg} which can be calculated by using values from Tables 4-1 and 4-3. The first-order degradation constant can be used to calculate the degree of biodegradation in the area influenced by the injection of the methane and air (where their concentrations can be considered constant) using:

$$\frac{Cc}{Cc_o} = e^{-k_{deg} t} \qquad (4\text{-}5)$$

The residence time (d) each contaminant "spends" in the biozone is denoted by t and it is calculated using:

$$t = \frac{x}{vs} \qquad (4\text{-}6)$$

where x is the longitudinal distance (ft)of the biozone, and vs is the seepage velocity (ft/day) of the groundwater. The retardation effect of sorption does not affect the residence time since only state-state conditions are considered.

It is apparent from equation 4-5 that in cases where the microbiological factors are not favorable (k_{deg} is low), increasing the residence time can provide additional degradation.

CHAPTER 5
REDUCTIVE DECHLORINATION

The electronegative character of chlorine substituent groups makes the chlorinated compounds more oxidized than the corresponding non-substituted compounds. The higher oxidation state of carbon in chlorinated compounds, therefore, makes those compounds less susceptible to oxidative reactions but more susceptible to reductive reactions. This chapter describes reductive dechlorination of chlorinated organic compounds.

5.1 Definition

Reductive dechlorination is the process in which a chlorine substituent is replaced by a hydrogen atom (Montgomery et al., 1994). This is a strictly anaerobic (oxygen deficient) process since in the presence of oxygen, it (oxygen) will be the primary recipient of electrons instead of the contaminants. The electron donor is the primary organic substrate.

Within a family of chlorinated compounds, the most highly substituted compound has the highest redox potential and is therefore the most favorable electron acceptor (Montgomery et al., 1994). In the ethylene family, for example, the redox potential is as following: PCE>TCE> DCE> VC.

5.2 Environmental Significance

The rate of anaerobic degradation is usually lower than aerobic degradation. The control of the redox reactions involved in reductive dehalogenation require an understanding of the redox conditions present in the water and the availability of electron acceptors and donors.

In order for reductive dechlorination to take place , a sufficiently high ratio of electron donor to electron acceptor must exist. Therefore, this process is favorable in waters with low E_h (high presence of electrons). Methanogenic bacteria have been documented to be the microorganisms involved in reductive dechlorination.

In this process the carbon achieves a lower oxidation state becoming more susceptible to oxidative reactions. Therefore, an anaerobic reductive dechlorination process followed by an oxidative process could ultimately mineralize the targeted contaminants.

CHAPTER 6
PROCESS DESIGN

In the design of any bioremediation scheme, the feasibility of delivery of the necessary substrates must be considered. An innovative in situ bioremediation scheme combining reductive dechlorination and cometabolic oxidation in separate phases is proposed to treat the contaminants of concern at CS-4. In this design, a series of horizontal wells are utilized to deliver the gaseous agents in order to stimulate microbial degradation in the biozone. The system is a passive system in the sense that the contaminants get biodegraded as the plume moves through the biozone. The design consists of three phases. Each phase has a distinct objective and each must accomplish its goal in order for the bioremediation scheme to be successful.

6.1 Application at CS-4

The challenge with CS-4 is that the plume contains PCE and TeCA which cannot be cometabolically oxidized like TCE and DCE. Therefore reductive dechlorination must be utilized in order to degrade PCE. The two processes, however, are fundamentally different since one (cometabolic oxidation) is aerobic and the other one (reductive dechlorination) anaerobic.

To promote cometabolic oxidation, a growth substrate, oxygen, and nutrients must be added. The process requires the addition of oxygen (despite the fact that the aquifer at

CS-4 is aerobic) because a steady-state biomass exerts an oxygen demand exceeding what can be provided by the aquifer. Fortunately, the contaminant concentrations are too low (<0.1 mg/L) to pose a toxicity effect to the biomass growth.

Since PCE can only be removed anaerobically and the aquifer at CS-4 is aerobic, turning an aquifer anaerobic is a challenge because it must be "polluted" with some form of a biochemical oxygen demand (BOD). In addition, reductive dechlorination is a process that requires long residence times (Collins, 1996). Therefore, a continuous BOD must be applied in order to consume the oxygen carried by advection into the anaerobic zone.

Reductive dechlorination also requires that organic matter is present so there is an electron donor for the biochemical reaction to take place. The aquifer at CS-4 has very low organic carbon concentrations (Khachikian, 1996). Therefore provisions must be made in the design so the anaerobic phase is not electron deficient.

The reductive dechlorination process, if incomplete, transforms PCE into less chlorinated ethenes like TCE, DCE, and VC. All of these ethenes are cometabolically oxidized, so a reductive dechlorination process sequenced by cometabolic oxidation can account for the degradation of all the contaminants.

The high aquifer transmissivity at CS-4 is favorable for transport and distribution of the added agents. The relatively deep plume (the bottom of the plume is at 130 ft at the toe) (Lázaro, 1996) requires that the added agents are injected at a depth of about 150 ft below the water table. Injection at that depth increases the mass transfer of the added gaseous agents since their concentration in the gas-phase will be higher (than if

closer to the water table where hydrostatic pressure is less) because they are under pressure (about 5 atm). On the other hand, the depth of the plume makes monitoring and well drilling more expensive.

6.2 Conceptual Design

The conceptual design of the bioremediation process consists of three phases. Phases 1 and 2 take place in biozone I as shown in Figure 6-1. Phase 3 takes place in Biozone II.

Phase 1 has the objective of creating a steady-state biomass by stimulating methanotrophic growth. This is an aerobic phase and requires the injection of methane, oxygen, and nutrients to the aquifer. The biomass provides the organic matter required for reductive dechlorination.

Once the required biomass is created, the injection of air is stopped and phase 2 begins. The injection of methane and nutrients is continued, however, to exert a BOD to the aquifer. This assures that the aquifer is anaerobic, a prerequisite for reductive dechlorination. Phase 2 continues until the biomass created in phase 1 is depleted.

Phase 3 is the aerobic cometabolic phase in which air, methane, and nutrients are continuously injected into the aquifer to stimulate a biomass capable of oxidizing the contaminants of concern. A different biozone is necessary for phase 3 since it occurs simultaneously with phase 2.

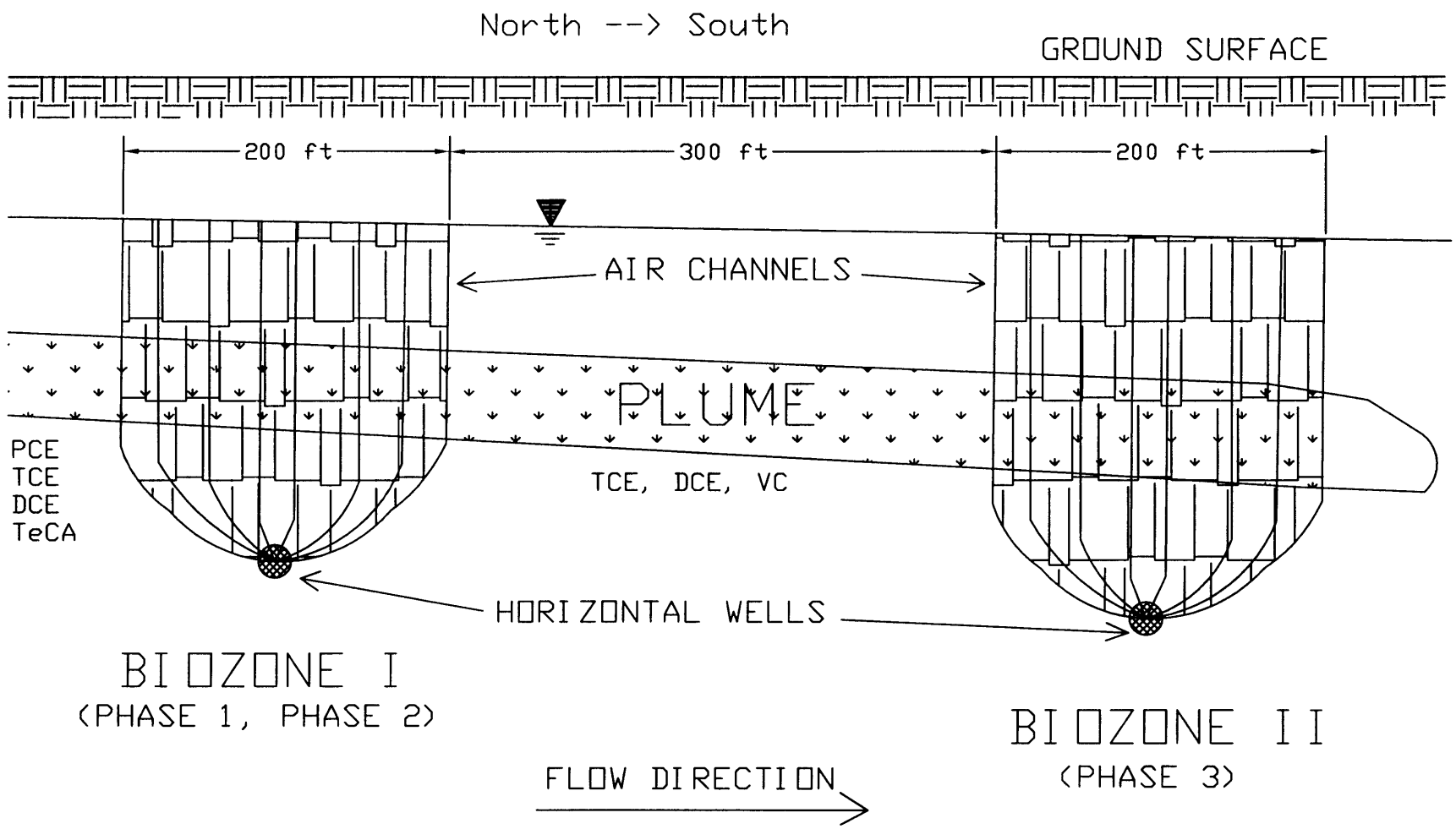

Figure 6-1 North-South Cross Section

6.3 In Situ Delivery

As discussed in chapter 3, the agents added to the subsurface must be in the gas-phase to overcome liquid displacement problems. Therefore, only agents with boiling points below ambient temperature were considered for injection.

6.3.1 Horizontal Drilling Technology

Horizontal drilling technology has been adapted from oil recovery and utility installation industries to applications of groundwater and soil remediation. Horizontal drilling has several advantages over vertical ones: (1) a horizontal well can extend along a wide plume or follow an elongated plume. Thus, one horizontal well can replace up to 10 vertical wells resulting in substantial savings; (2) horizontal wells can reach inaccessible areas without disrupting surface activities; and (3) they can generate less waste soil (Parmentier and Klemovich, 1996).

Given that the average width of the CS-4 plume was calculated to be 1180 ft (Lázaro, 1996), injection of the desired agents by vertical wells would be very expensive and labor-intensive. Horizontal wells with a length of over 500 ft have been constructed and operated successfully in the past, so two to three horizontal wells can cover the width of the plume (Parmentier and Klemovich, 1996).

Hayes (1996) reports that a 200 ft wide zone of influence by the injected gases is a conservative value given the hydrogeology of Cape Cod. Lazaro (1996) reports that the seepage velocity at CS-4 is 0.8 ft/d. Therefore, the time a contaminant takes to travel

through the biozone created by a single well is 250 days according to equation 4-6. If additional residence time is required for any process to be completed, one or more horizontal wells can be installed in-series.

6.3.2 Substrate Delivery

Methane is a gas at ambient temperatures (boiling point is -164°C). Its solubility is low (6670 ppm at 25°C) making the Henry's constant relatively high (660 Latm/mol at 25°C) (Schwarzenbach et al., 1993). The methane aqueous concentration (i.e. the flux of methane into the water) is a function of the diffusivity and film thickness of methane in the gas-phase and in the water, and the concentration of methane in the gas-phase. Therefore the methane aqueous concentration can be increased by increasing the methane concentration in the gas-phase (assuming the diffusivity and film thickness are constant).

Four percent methane (by volume) in air was injected into the saturated zone at a TCE-contaminated site at the Savannah River Department of Energy Site. Its objective was to assess the performance of the cometabolic in situ transformation of TCE by injection of a substrate (methane), nutrients, and oxygen through horizontal wells along the width of the plume (Travis and Rosenberg 1994, Brockman et al. 1995). Although methane concentrations were not reported, increased microbial counts indicate that four percent methane was sufficient to sustain a healthy and active methanotrophic population.

Hayes (1996) calculated that a methane aqueous concentration of 0.5 mg/L can be achieved by injecting four percent methane in air at a neighboring plume at the MMR. The explosive limit of methane is 5 % but higher fractions of methane can be injected if

the proper engineering measures are taken. Thus, aqueous concentrations of methane are considered controllable in the field simply by adjusting the fraction of methane in the gas mix. A methane concentration of 1 mg/L is assumed to be feasible and this value is used for all calculations.

6.3.3 Nutrient Delivery

Nutrients play a very important role in the growth of the microorganisms. Chu and Alvarez-Cohen (1996) report that certain methane-oxidizing microorganisms have been found to be capable of fixing molecular nitrogen (N_2) for cell uptake. The delivery of N_2 is done with the delivery of air (since atmospheric air has about 78% N_2). This is very important for subsurface environments low in nitrate (which microorganisms readily uptake) since the injection of air could meet the microbe demand for both oxygen and nitrogen.

Brockman et al. (1995) report that the injection of nitrous oxide (0.07% by volume) and triethyl phosphate (0.007% by volume) along with methane (4% by volume) and air resulted in an increase (than methane and air alone) of one to three orders of magnitude in the methanotroph most probable number (MPN) index. The use of these gas-phase nutrients enabled the operators of the site to mix in the nutrients with either the methane or the air creating a homogeneous mix. The methanotrophic growth following the nutrient injection showed that the microorganisms were nutrient deficient.

In the Moffett Field Study, high nitrate (25 mg/L) and phosphorus (0.1 mg/L) levels were present so no additional nutrients were added.

At Cape Cod, levels of nitrate and phosphorus vary from place to place. It is assumed that the nutrients will not be a limiting factor in the stimulation of the methanotrophs. Nitrogen needs can be met by the delivery of the air which contains molecular nitrogen. If there is a nutrient deficiency, it can be overcome by injecting nitrous oxide and triethyl phosphate as it was done at the Savannah River Site. Both molecular nitrogen and nitrous oxide (Brockman et al., 1995) are not readily assimilated by most microorganisms so the nutrients would travel some distance before they are uptaken by the cell.

6.3.4 Oxygen Delivery

Oxygen concentrations at Cape Cod have been reported to be in the 5-10 mg/L range (obtained electronically from USGS). This, however, is not sufficient to meet the demands of a steady-state biomass concentration required in this design. Therefore air must be added. Considering the depth of the injection point, an oxygen concentration of 10 mg/L seems achievable in the field and this value is assumed in the design.

6.3.5 Clogging

Clogging of the aquifer pores and injection wells is a potential operating problem. Clogging can occur due to excessive biological growth (biofouling), and chemical clogging (precipitation of metals). Both phenomena are hard to predict and action is only necessary when clogging appears to be a problem.

Uncontrolled clogging of the aquifer pores in the biozone results in a decrease of

the aquifer permeability. This causes the aquifer water to move around the biozone (through the more permeable areas) ultimately resulting in minimal treatment.

Clogging of the injection well occurs when excessive biological growth occurs in the vicinity of the well where the concentrations of the added agents are in their highest concentrations. When this occurs, no more agents can be added to the aquifer resulting in failure of the system. To overcome well clogging, if this occurs, it is necessary that the agents added are not all injected simultaneously. A pulse injection must be utilized to eliminate optimum conditions for biological growth near the well. Pulsing at the right frequency will ensure that the agents will have a uniform distribution at some distance away from the well due to hydrodynamic dispersion.

Chemical clogging can be a serious problem with this design considering the change of redox states from reducing to oxidizing. The reducing conditions may cause mobilization of metals such as iron (the reduced form of iron, Fe(II), is more mobile than Fe(III)) which may precipitate out when the aquifer conditions become oxidizing. The aquifer sediments at the MMR contain high levels of Fe (III) in crystalline and amorphous mineral forms (Barber et al., 1992) which may be mobilized after the oxygen and nitrate have been depleted.

6.4 Phase 1

The objective of phase 1 is primarily to stimulate microbial growth and create a steady-state biomass concentration, and secondarily to biodegrade a portion of the contaminants. Methanotrophic growth is stimulated by the injection of methane, air, and

nutrients. Biomass grows exponentially as described by Monod kinetics until it reaches a steady-state (equation 4-1). Once a steady-state biomass concentration is achieved, the injection of air is stopped. The methane and nutrients continue to be injected to assure that the oxygen transported into the biozone by advection will be consumed. In the process of creating biomass, a portion of the TCE and the DCE is degraded by cometabolic oxidation.

6.4.1 Biomass Calculations

Using equation 4-2, the steady-state biomass concentration was calculated to be 5.0 mg/L. In order to calculate the time required to reach the steady-state methanotrophic biomass concentration, equation 4-1 is integrated yielding the following equation:

$$\ln\frac{Xss}{Xo} = \left[ksY\left(\frac{Cs}{Ks + Cs}\right)\left(\frac{Co_2}{Ko_2 + Co_2}\right) - b\left(\frac{Co_2}{Ko_2 + Co_2}\right)\right]\Delta t \qquad (6\text{-}1)$$

Assuming an initial methanotrophic biomass concentration (Xo) of 1 mg/L and using values from table 4-1, Δt was calculated to be 4.42 days. The time calculated above is a very important parameter because it determines the duration of phase 1 (i.e. the injection of methane, air, and nutrients).

6.4.2 Contaminant Degradation

As methanotrophic biomass is created, cometabolic oxidation of the contaminants is taking place. Since the process is strictly aerobic and injection of air only lasts for about 5 days, only a small fraction of the contaminants is expected to biodegrade in this

phase. In addition, biomass concentration in this phase is low and this directly (according to equation 4-4) affects the degree of biodegradation.

6.5 Phase 2

Phase II is the time allowed for reductive dechlorination to take place. Reductive dechlorination requires anaerobic conditions and therefore the injection of air is stopped. The injection of methane and nutrients is continued in order to exert a BOD to the aquifer that carries oxygen into the biozone. Phase 2, consequently, has two sub-areas of different activities: area A and area B. Area A is in the upgradient part of biozone I where oxygen carried into the biozone with the water is consumed by methanotrophs. Area B is the rest of the area in biozone I. Area B is anaerobic since all of the oxygen gets consumed in area A. Area B has a biomass of 5 mg/L (from phase 1) which does not decay because there is no oxygen present. This biomass is the organic matter that is used as the electron donor in the reductive dechlorination process.

6.5.1 Oxygen Consumption

In order to calculate the distance into the biozone where the oxygen gets consumed, equation 4-3 is integrated yielding the following equation:

$$Ko_2 \ln \frac{(Co_2)t}{(Co_2)o} + (Co_2)t - (Co_2)o = \left[-ksFX\left(\frac{Cs}{Ks + Cs}\right) - dcfdbX \right]\Delta t \qquad (6\text{-}2)$$

The concentration of oxygen where the system is considered anaerobic ($(Co_2)t$) is taken to be 0.01 mg/L. The initial oxygen concentration ($(Co_2)o$)is 10 mg/L which is how

much oxygen is present at the moment the injection of air is shut off. Using values from Tables 4-1 and 4-2, Δt was calculated to be about 1.3 days, so it is evident that in the absence of injected oxygen and in the presence of a steady-state biomass and adequate substrate the aquifer turns anaerobic very fast (within just about 1 ft into the biozone).

In terms of cometabolic oxidation, insignificant amounts of contaminants are expected to degrade in such a short period of time.

6.5.2 Anaerobic Phase

The rest of the biozone is anaerobic and has a biomass of 5 mg/L. Collins (1996) estimated that 5 mg/L of biomass is a rough estimation of the organic matter required to be present as the electron donor. The electron acceptor, of course, are the contaminants. Since the oxygen is consumed in less than two days, the anaerobic residence time is approximately 248 days. The degradation occurring in this phase can only be assumed since kinetic studies have not been performed in this topic. Collins postulated that a degradation of 99% of PCE is possible based on similar conditions at different sites (Collins, 1996). The degree of the degradation is a function of the residence time (provided adequate amounts of electron donor are present). Therefore, additional biozones may be necessary to increase the residence time of the contaminants. Each horizontal well can increase the residence time by 250 days per well.

TeCA will also be subject to reductive dechlorination but its degradation cannot be quantified since no previous studies have been conducted.

It is important to note, however, that despite the lack of oxygen other chemicals

may pose competition effects to the contaminants for accepting the electrons. In the absence of oxygen and nitrate, Fe (III) can potentially provide a large reservoir of electron acceptor and it can pose competition to the contaminants which are the targeted electron acceptors in the reductive dechlorination process.

6.6 Phase 3

Phase 3 takes place in biozone B. Biozone B is placed downstream at a distance where no interference with biozone A is possible. In phase III, methane and air are injected into the subsurface with the sole purpose of cometabolically oxidizing the remaining chlorinated ethenes (those not biodegraded in phase I as well as the ones produced during phase II).

The injection is continuous, therefore a steady-state biomass is maintained. Using equation 4-4, the first-order degradation coefficient k_{deg} can be calculated. The k_c however, used in this design is half the value used by Semprini and McCarty (1991b) shown in table 4-3. The adjustment is made according to the Arrhenious equation (roughly half the rate for every 10°C decrease) to account for the lower water temperature at the Cape which is reported to be 10°C. The water temperature at the Moffett Field Study was reported to be 18°C. Although the reported temperature at the Moffett Field study is questionable, (it should be closer to 10°C), using a k_c value in this design half of the one reported provides some cushion of safety.

The values used in the calculations and the resulting normalized concentrations of TCE, t-DCE, c-DCE, and VC are shown in table 6-1. VC is included in this calculation

as it is expected to be a by-product of the reductive dechlorination process. It is not known which isomer of DCE is present at CS-4 so degradations for both isomers were calculated.

Table 6-1 Values used in the calculations and resulting normalized concentrations.

	TCE	c-DCE	t-DCE	VC
X_{ss} (mg/L)	5.0	5.0	5.0	5.0
k_c (g/g-d)	0.005	0.025	0.5	0.5
C_s (mg/L)	1.0	1.0	1.0	1.0
C_{O_2} (mg/L)	10.0	10.0	10.0	10.0
k_{deg} (d^{-1})	0.014	0.068	1.36.	1.36
x (ft)	200	200	200	200
C_c / C_{c_o}	0.03	0	0	0

Figure 6-2 illustrates the degradation of the contaminants within the biozone as a function of distance. It is apparent that almost complete degradation for all the contaminants is expected to take place. Given the concentrations of the contaminants at the site (Table 2-1), the biodegradation would be capable of meeting MCLs for all the contaminants subject to cometabolic oxidation.

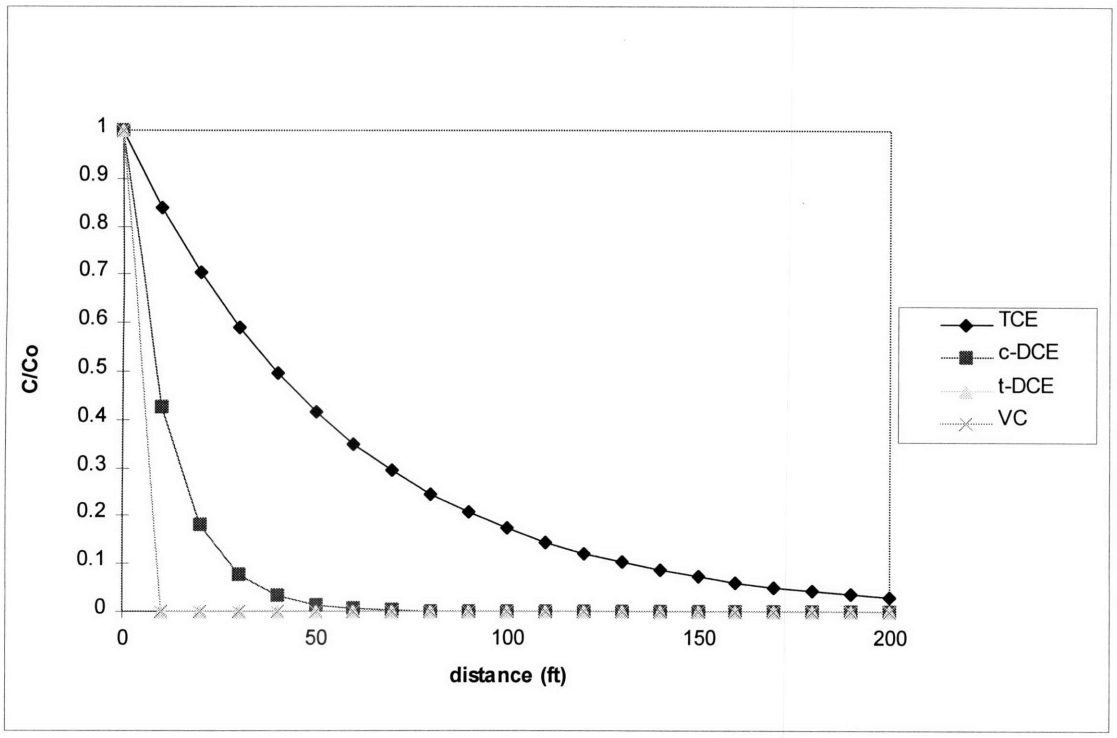

Figure 6-2 Degradation of the contaminants as a function of distance for C_s =1.0 mg/L and C_{O_2}=10 mg/L.

To show the sensitivity of the system to the concentrations of methane and oxygen, the same process is shown for a methane concentration of 0.5 mg/L and an oxygen concentration of 5 mg/L. In this case, a different set of data is calculated as shown in Table 6-2. Figure 6-3 illustrates the degradation of the contaminants as a function of distance within the biozone.

Table 6-2 Values used in the calculations and resulting normalized concentrations.

	TCE	c-DCE	t-DCE	VC
X_{ss} (mg/L)	2.5	2.5	2.5	2.5
k_c (g/g-d)	0.005	0.025	0.5	0.5
C_s (mg/L)	0.5	0.5	0.5	0.5
C_{O_2} (mg/L)	5.0	5.0	5.0	5.0
k_{deg} (d^{-1})	0.0078	0.039	0.78	0.78
x (ft)	200	200	200	200
C_c / C_{c_o}	0.14	0	0	0

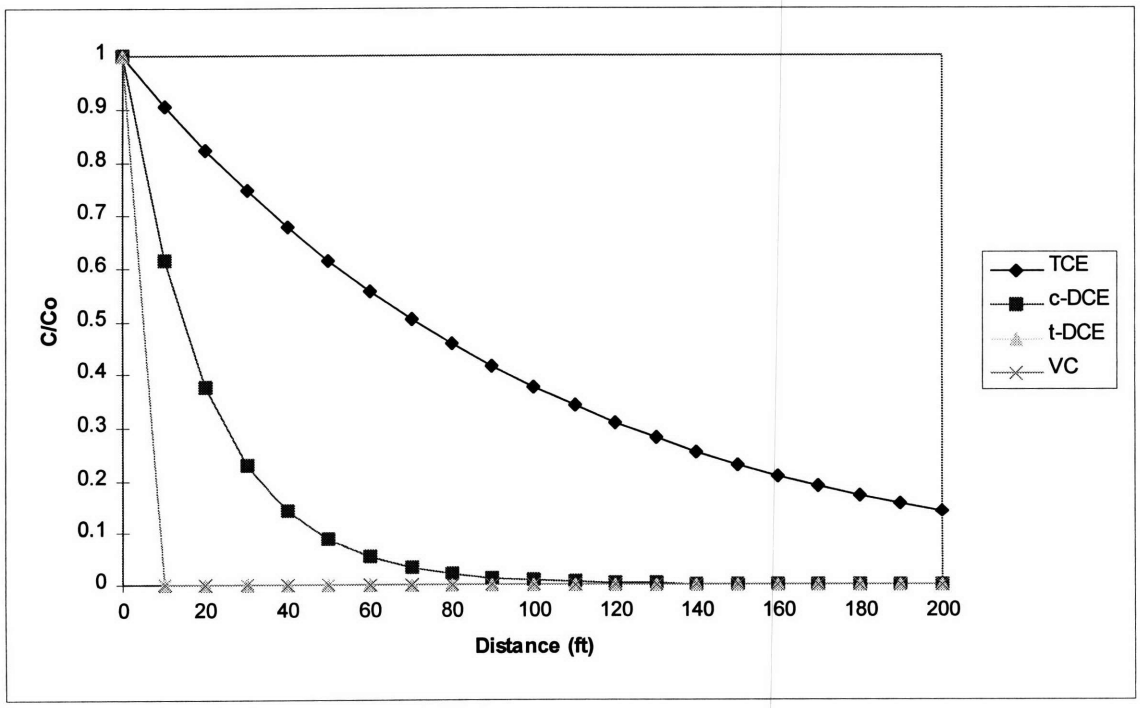

Figure 6-3 Degradation of the contaminants as a function of distance for C_s =0.5 mg/L and C_{O_2}=5 mg/L.

The only difference noted is the decrease in the degradation of TCE which is the least degradable of the group.

6.7 System Design

A preliminary design consists of one horizontal well per biozone. In biozone I, the residence time in the anaerobic phase is about 250 days. It is uncertain whether this is enough time for reductive dechlorination to take place. Additional wells may be added, if deemed necessary, which can provide an additional 250 days of residence time per well.

In biozone II, one horizontal well will be sufficient to degrade 97 % of the TCE, and 100 % of DCE and VC. A distance of 300 ft between the two biozones is sufficient to allow for decay of suspended solids (dead methanotrophic biomass) carried from biozone I. Build up of suspended solids in biozone II where high microbial activity occurs may result in clogging of the aquifer pores.

6.8 Pilot Test

In order to determine whether in situ bioremediation is a feasible option, a detailed investigation of the site characteristics that determine biotic and abiotic losses and a verification of the effectiveness of in situ bioremediation through microbiological assays must be conducted. The design proposed is an innovative and previously untested scheme. It is imperative that a pilot test is conducted to: (1) determine the efficacy of the process, and (2) evaluate the design parameters (number of wells required, gas flow rates, methane composition, etc.) of a full scale application. Only after a pilot test is conducted

the costs (capital and operational) can be estimated.

A pilot test should be conducted with the objective to resemble field conditions as closely as possible. Although testing closer to the water table is advantageous because of easier and more efficient monitoring, it may not be representative of conditions at depth. The primary reason is that microbial populations and oxygen concentrations vary with depth (decrease as you go deeper). Redox conditions also may vary (become reducing with depth). The other parameter affected is the aqueous concentration of the added agents. The mass transfer of the gases into the water increases with depth, therefore lower concentrations should be expected closer to the water table (where hydrostatic pressure is less).

Because of the different transforming abilities of methanotrophic bacteria, it is important to identify the characteristics of the indigenous microorganisms of the site of interest. Laboratory assays using material from the site of interest are recommended by the Committee on In Situ Bioremediation (National Research Council, 1993). Dolan and McCarty (1995) suggest that laboratory soil-column microcosms can determine the site potential for in situ bioremediation. The site potential, however, can only be determined by a field test because it is a function of many other parameters that simply cannot be duplicated in a lab setting.

CHAPTER 7
CONCLUSION

An innovative in situ bioremediation scheme combining reductive dechlorination and cometabolic oxidation in separate phases is proposed to treat the contaminants of concern at CS-4. The design utilizes a series of horizontal wells to deliver the gaseous agents in order to stimulate microbial degradation. This delivery of gases creates areas (biozones) where optimal conditions for reductive dechlorination and cometabolic oxidation exist. The contaminants get degraded as they are carried through the biozones by advection.

7.1 Summary and Discussion

The design consists of three phases. Phases 1 and 2 take place in biozone I. Phase 1 has the objective of creating a steady-state biomass (required for phase 2) by stimulating methanotrophic growth. This is an aerobic phase and requires the injection of methane, oxygen, and nutrients to the aquifer. Using kinetic parameters from a pilot test utilizing methanotrophs for the cometabolic transformation of chlorinated ethenes (Semprini and McCarty, 1991b; 1992a), it was calculated that about five days are required to achieve the desired steady-state biomass concentration of 5 mg/L. The model assumes an aqueous methane concentration of 1.0 mg/L and an oxygen concentration of 10.0 mg/L.

The biomass created provides the organic matter required for reductive dechlorination. After the five days, the injection of air is stopped and phase 2 begins. The injection of methane and nutrients is continued, however, to exert a BOD to the aquifer. It was calculated that the oxygen carried into the biozone by advection will be consumed by the BOD mentioned above in less than 2 days. This assures that the aquifer is anaerobic, a prerequisite for reductive dechlorination. Under these conditions, and provided that sufficient residence time is allowed, 99 % of PCE can be biodegraded. Phase 2 continues until the biomass created in phase 1 is depleted. The time it takes for the biomass to be depleted has to be determined experimentally since little is known about the kinetics of reductive dechlorination.

Phase 3 is the aerobic cometabolic phase in which air, methane, and nutrients are continuously injected into the aquifer to stimulate a biomass capable of oxidizing the contaminants of concern. Phase 3 takes place in a biozone located downgradient of biozone I. It was calculated that a 97 % degradation of TCE and a 100 % degradation of c-DCE, t-DCE, and VC can be achieved if the methane and oxygen concentrations are 1.0 and 10.0 mg/L respectively. More wells can be added to extend the biozones and allow additional residence time for the contaminants to be degraded if deemed necessary.

The results presented by this design are optimistic. A 97 % removal of TCE and 100 % removal of c-DCE, t-DCE, and VC can be achieved at CS-4. The conditions required (1.0 mg/L methane aqueous concentration and 10.0 mg/L of oxygen concentration) are assumed to be achievable in the field through proper engineering measures. The results indicate that in situ bioremediation is a potential final remedial

solution for CS-4.

All kinetic parameters used in this design have been adapted from a pilot test at another site. A contaminated site the size of CS-4 is not expected to have the uniformity of a well-characterized pilot test setting at another site. Field conditions are complex and hard to control. Preferential flow paths due to permeability variation causes areas of high and low biodegradation. Factors affecting the in situ biodegradation of contaminants vary from site to site and caution must be given in the interpretation of the results obtained in this design.

7.2 Future Work

The main assumption made in this design is that the distribution of methane and oxygen is uniform throughout the biozone. This has a great influence to the efficacy of the scheme proposed in this thesis. A better understanding of the distribution of the gas channels in the subsurface is necessary.

The spatial heterogeneity ultimately affects the degradation that will take place. Representing the process with "lumped" parameters may not be representative of the process taking place. A better understanding of the spatial variability of the degradation process is necessary.

Reductive dechlorination is still a process under laboratory research. Several assumptions were made to reach the estimation done in this thesis. Further research is needed in order to better predict performance of field applications as well as to determine

parameters that influence this process.

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APPENDIX

PROJECT RESULTS

EXECUTIVE SUMMARY

This report covers the technical aspects of the current situation of the Chemical Spill 4 (CS-4) groundwater plume at the Massachusetts Military Reservation (MMR) and proposes a final remedial design.

The aquifer underlying the MMR is contaminated by various pollutants forming a plume. The CS-4 plume is currently contained using a pump and treat system. The contaminants of concern detected in CS-4 are perchloroethylene (PCE), trichloroethylene (TCE), 1,2-dichloroethylene (DCE), and 1,1,2,2-tetrachloroethane (PCA). Granular activated carbon (GAC) is used to treat the extracted groundwater which is reinjected to the aquifer after treatment. This system was designed as an interim remedial action to quickly respond to the plume migrating off site. A final remedial design must be formulated.

In order to propose a final remedial system for CS-4, the following aspects are examined in depth: (1) an extensive site characterization, (2) the development of a computer model to simulate flow and contaminant transport, (3) the evaluation of the feasibility of bioremediation and its design, (4) the examination of the current

aboveground treatment system and possibilities of its enhancement; and (5) an evaluation of the risk associated with these remedial strategies.

Site characterization was based on previous studies of the area. Equilibrium sorption, however, was tested in the laboratory since this factor may affect the fate and transport of the contaminants. A three-dimensional model was constructed from the results of the site characterization. The model was used to simulate flow and transport under natural conditions and to predict effective capture curves for the extraction of the contaminated water. An innovative in situ bioremediation system consisted of an anaerobic zone sequenced by an aerobic zone was designed. The removal due to biodegradation was calculated. Optimization of the currently operating treatment system was conducted by evaluating economic benefits of combining the existing GAC system with zero-valent iron technology. Risk assessment was performed considering EPA acceptable range of carcinogenic and non-carcinogenic risk.

Results

a) Site Characterization

On a regional scale, the geology of western Cape Cod is composed of two glacial moraines deposited along the western and northern edges and a broad outwash plain between the two moraines. The outwash is composed of poorly sorted fine to coarse grained sands, and its thickness varies from approximately 175 ft to 325 ft. Precipitation is the sole source of recharge to the aquifer. Values of recharge are between 18 in/yr and

23 in/yr. A value of 380 ft/day has been accepted as a representative value of average horizontal hydraulic conductivity of the outwash sands. Effective porosity is estimated to be about 0.39 and the average hydraulic gradient is 0.0014.

The groundwater contains high values of dissolved oxygen (5-10 mg/L), and has a pH between 5 and 7. The average water temperature is about 10°C. The average concentrations of the main contaminants in CS-4 are 18 ppb, 9.1 ppb, 1.1 ppb and 6.8 ppb for PCE, TCE, DCE and PCA respectively. Previous field observations suggested that the plume is 11,000 ft long, 800 ft wide and 50 ft thick.

The organic carbon content in the sediments is very low (in general, less than 0.01 %). For this low organic content, the degree of sorption of the contaminants is relatively small. The depth-averaged retardation coefficients are 1.04, 1.1 and 1.25 for DCE, TCE and PCE, respectively. For the more strongly sorbing PCE, the retarded longitudinal macrodispersivity increases by a factor of 2.1 relative to a non-sorbing solute. For the least sorptive compound (DCE), the velocity variances introduced by sorption are small as reflected by a small increase in the longitudinal macrodispersivity (factor of 1.2).

b) Groundwater Model

The groundwater flow model showed great sensitivity to the properties of the glacial moraine. The calibrated model (based on head distributions and particle tracking) has an average hydraulic conductivity of 221.6 ft/day, a hydraulic gradient of 0.0014, a seepage velocity of 0.8 ft/day, and a recharge of 19 in/yr.

Contaminant Transport Model:

Simulating a continuous input of the contaminants, the plume resulting from the simulations had greater dimensions than the plume defined by field observations. Average dimensions were 1,180 ft for the width, 40 ft for the height, and 12,660 ft for the length.

The no action alternative for remediation was simulated. According to the model, the total time it took for all the contaminants to enter the nearest pond was between 80 to 85 years. On the other hand, the total time for clean-up using the existing system was approximately 70 years.

Simulation of Pumping Schemes:

Simulations using the current 13-well fence indicated that for a plume defined according to the existing field observations the currently operating pumping scheme is appropriate. The flexibility of the current well fence was tested using a plume 50% larger (in cross-sectional area) that was captured by increasing the overall pumping rate by 78%. Results of different pumping schemes showed that similar capture curves can be obtained with the existing pumping scenario, and with a pumping system of seven wells located 120 ft apart and extracting water at an overall rate of 140 gpm. This seven-well option may be a better option, since presumably, operation and maintenance cost would be reduced.

c) Aboveground Treatment Alternative

The combination of the existing GAC with the zero-valent iron technology can be an effective means to reduce long-term treatment costs. This can be achieved by installing aboveground reactor vessels filled with zero-valent iron which treat the extracted water before it flows through the GAC. For scenarios in which concentrations of the plume are assumed to be high (maximum concentrations), overall treatment savings up to $0.2 million were estimated. For scenarios with low concentrations, no considerable savings can be expected

d) Risk Assessment

Worst case scenarios using pump and treat result in a carcinogenic risk of 1.4×10^{-6}. Using bioremediation results in a carcinogenic risk of 2.6×10^{-6}. The no action alternative results in a carcinogenic risk of 10^{-4}.

Conclusion

This project was undertaken to fully understand the transport mechanisms of groundwater and contaminants in the western Cape Cod aquifer, and to develop a final remediation scheme for the CS-4 plume. The following conclusions are drawn:

- Site characterization must be improved in order to provide a clearer understanding of the contamination problem. The representation of the aquifer conditions with the computer model was limited because of insufficient data.

- Total clean-up times using the current interim remedial scheme are very long and cost intensive. Development of a final remediation method which decreases clean-up times and decreases costs is necessary.
- Using only seven of the 13 existing wells produces the same results as the current operation. Reexamination of the current pumping scheme would reduce operation and maintenance costs. It is recommended that this new scheme be examined as an alternative to the existing operation.
- The anaerobic/aerobic in situ bioremediation scheme proposed demonstrates that it has the potential to completely degrade PCE, TCE, and DCE. A pilot test is needed to demonstrate the efficacy of this technology and to determine the final design parameters.
- By combining the existing GAC with the emerging zero-valent iron technology a reduction in overall treatment costs can be achieved for certain scenarios. A bench-scale study should be conducted to verify the results.

Risk calculations indicate that the CS-4 plume must be remediated to comply with regulations. The remediation strategies reduce the risks to acceptable levels. From a risk standpoint, the preferred strategy is a combination of bioremediation and pump and treat.

1 SITE CHARACTERIZATION

1.1 Geology

The geology of western Cape Cod is composed predominantly of glacial sediments deposited during the Wisconsin Period (7,000 to 85,000 years ago) (E.C. Jordan, 1989b). The three predominant geologic formations of the western Cape are: (1) the Sandwich Moraine (SM), (2) the Buzzards Bay Moraine (BBM), and (3) the Mashpee Pitted Plain (MPP) (E.C. Jordan, 1989b). The two moraines were deposited by the glacier along the northern and western edges of western Cape Cod. Between the two moraines lies a broad outwash plain (the MPP) which is composed of well sorted, fine to coarse-grained sands. At the base of the unconsolidated sediments (below the MPP), fine grained, glaciolacustrine sediment, and basal till are present.

Both the outwash and moraines have relatively uniform characteristics at the regional scale, even though they contain some local variability. The sediments are stratified and thus the hydraulic conductivities are anisotropic. The MPP is more permeable and has a more uniform grain size distribution than the moraines (E.C. Jordan, 1989b).

The total thickness of the unconsolidated sediments (i.e., moraine, outwash, lacustrine, and basal till) is estimated to increase from approximately 175 ft near the Cape Cod Canal in the northwest to approximately 325 ft in its thickest portion in the BBM; it then decreases to 250 ft near Nantucket Sound in south. The thickness of the MPP

outwash sediments ranges from approximately 225 ft near the moraines, to approximately 100 ft near shore of Nantucket Sound (E.C. Jordan, 1989a).

1.2 Hydrology

Cape Cod's temperate climate produces an average annual precipitation of about 48 in, widely distributed throughout the year (Masterson and Barlow, 1994). High permeability sands and low topographic gradient, minimize the potential for runoff and erosion, and thus recharge values have been reported in the range of 17 to 23 inches/year (LeBlanc, 1986). Consequently, about half of the water that precipitates recharges the aquifer. This creates a high probability of contaminant transport from the surface to the groundwater.

Beneath western Cape Cod lies a single groundwater system (from the Cape Cod Canal to Barnstable and Hyannis) which the U.S. Environmental Protection Agency (EPA) has designated as a sole source aquifer (E.C. Jordan, 1990). This aquifer is unconfined and its only form of natural recharge is by infiltration from precipitation. The highest point of the water table (the top of the groundwater mound) is located beneath the northern portion of the MMR. In general, groundwater flows radially outward from this mound and ultimately discharges to the ocean.

Kettle hole ponds, depressions of the land surface below the water table, are common on the MPP. These ponds influence the groundwater flow on a local scale. Streams, wetlands and cranberry bogs serve as drainage for some of these ponds and as

areas of groundwater discharge, and thus comprise the rest of the hydrology of the western Cape.

1.3 Hydrogeology

The geology and hydrology of western Cape Cod define the hydrogeologic characteristics of the aquifer. General information on the geology and hydrology of Cape Cod can be found in the works by Oldale (1982), Guswa and LeBlanc (1985), LeBlanc et al. (1986), and Oldale and Barlow (1987). This section summarizes the data on the major aquifer properties measured throughout the area. Variability of these values may be due not only to natural heterogeneities of the soil, but also to differences in measuring techniques and data analysis (E.C. Jordan, 1989a).

1.3.1 Hydraulic Conductivity

Throughout the western Cape, there appears to be a general trend of decreasing conductivity from north to south and from the surface to the bedrock. The conductivity of the western Cape has been studied extensively. Geologic variability within the outwash suggests that some variability in hydraulic conductivity is likely. Nonetheless, the maximum and minimum values reported are probably biased by the analytical method or exhibit a small-scale geologic heterogeneity. A value of 380 ft/d (obtained from the Ashumet Valley pump tests and corroborated by the tracer test south of the MMR) has been accepted as a representative value of the average hydraulic conductivity of the MPP outwash sands (E.C. Jordan, 1989a).

1.3.2 Anisotropy Ratio

The anisotropy ratio (ratio of horizontal to vertical hydraulic conductivities, K_h/K_v) has been studied along with some of the hydraulic conductivity tests. Values of anisotropy ratio for different studies are reported in Table B-1. Typical anisotropy values range from 10:1 to 3:1.

1.3.3 Porosity

Measured values of porosity range from 0.20 to 0.42. Effective porosity of the outwash is estimated from a tracer test (Garabedian et al., 1988; LeBlanc et al., 1991) to be about 0.39.

1.3.4 Hydraulic Gradient

The hydraulic gradient will be affected by the variations in water table elevations. These typically fluctuate about three ft because of seasonal variations in precipitation and recharge. During the period of a tracer test (22 months), the hydraulic gradient in the study area (Ashumet Valley) varied in magnitude from 0.0014 to 0.0020. Vertical hydraulic gradients measured during this test were negligible except near the ponds (LeBlanc et al., 1991).

1.4 Chemistry of the Water

The properties of the chemicals of particular interest to the bioremediation design are shown in Table 1-1 (E.C. Jordan, 1990). The dissolved oxygen (DO) values vary

with depth. The values reported are for the depths of interest (depth < 100 ft below water table). The concentration of metals is also of particular interest since high concentrations can have a detrimental or toxic effect to microbial growth. The concentration of metals tested for at CS-4 are negligible.

Table 1-1. Groundwater properties[a]

Property	Value
Dissolved oxygen (mg/L)	5.0-10.0
Nitrate (mg/L)	0-1.8
pH	5-7
Temperature	10° C

[a] Obtained from E.C. Jordan (1990)

1.5 Equilibrium Sorption

Sorption of contaminants by aquifer solid matrices significantly affects their fate and transport. The bioavailability of contaminants can be reduced considerably because of sorptive uptake. Also, remediation times can be prolonged substantially because of a continuous feeding of contaminants to the aquifer by the sorbed species. Another effect of sorption is that it may alter the dispersive behavior of contaminants (i.e., enhancement of longitudinal dispersivity).

One way to quantify all of these effects is to use equilibrium sorption distribution coefficients to calculated retardation factors. Laboratory batch tests are setup to determine distribution coeffecients. These are used to validate the use of equilibrium

relationships to extract retardation factors. Once this relationship is shown, retardation factors were calculated which were then used to assess the behavior of contaminants.

2 FLOW MODELING UNDER NATURAL CONDITIONS

2.1 Description of the Model

A three-dimensional model was constructed using the finite-element modeling code DynSystem (Camp Dresser & McKee, Inc, 1992). More than 100 wells are located in the area of concern. Data of hydraulic head and contaminant concentrations from the wells were used to construct input files to the model.

The model includes an area of approximately 50 mi^2 on the western Cape. The thickness of the modeled region was non-uniform, defined by ground surface and bedrock elevations. The horizontal boundaries were defined by two no-flow boundaries and the ocean. Johns Pond, Ashumet Pond and Childs River were included in the model as fixed head boundary conditions. Coonamessett Pond is the most important surface water body within the modeled area because of its vicinity to the end of the CS-4 plume region.

2.2 Model Recalibration Using Particle Tracking

The calibrated hydrologic flow model was used as the basis for the simulation of contaminant transport in the aquifer. After the first particle run, however, it was evident that the model was not fully calibrated. Even though the heads agreed with the observations, particles went too deep into the aquifer and did not match the field observations. Thus, the model was recalibrated paying special attention to anisotropy ratios, recharge, and the Buzzards Bay Moraine conductivity; (i.e. factors which

considerably affected the transport of particles). Table 2-1 summarizes the hydraulic parameters in the final calibrated model.

Table 2-1 Hydrologic parameters of flow model resulting from the final particle tracking calibration

Parameter	Value
Average Hydraulic Conductivity	221.6 ft/day
Hydraulic Gradient	0.0014
Seepage Velocity	0.8 ft/day
Anisotropy Ratio	10:1 and 12.5:1
Recharge	19 in/yr
Head Mean Difference (calc. - obs.)	0.24 ft
Head Standard Deviation	1.61 ft

3 CONTAMINANT TRANSPORT MODELING

3.1 Description

A particle tracking code was used to simulate the movement of particles from the source for a specified amount of time. Particle locations were recorded at the end of each simulation and concentrations were calculated based on particle weight and number of particles per unit volume. A more detailed description of some aspects and outcomes of the transport model is discussed next.

3.1.1 Source

A thorough description of the source, its location, dimensions, and input loadings are essential for a reliable model. E.C. Jordan (1989b) provides a thorough description of what is believed to be the CS-4 plume source.

The transport model focuses on the solvents PCE, TCE and DCE. Due to limitations in the program code, they were modeled as one contaminant. Thus, concentration outputs files included the sum of PCE, TCE, and DCE concentrations. The source loading was calibrated to match the field values. Consequently, the calculated concentrations are compared to the observed values at different well locations.

The source was modeled as a continuous source input. From groundwater velocity data, it was determined that the contamination must have started at least 15 years ago. The source loading was modeled as seven 5 year intervals, from 1960 to 1993 (Figure 3-1).

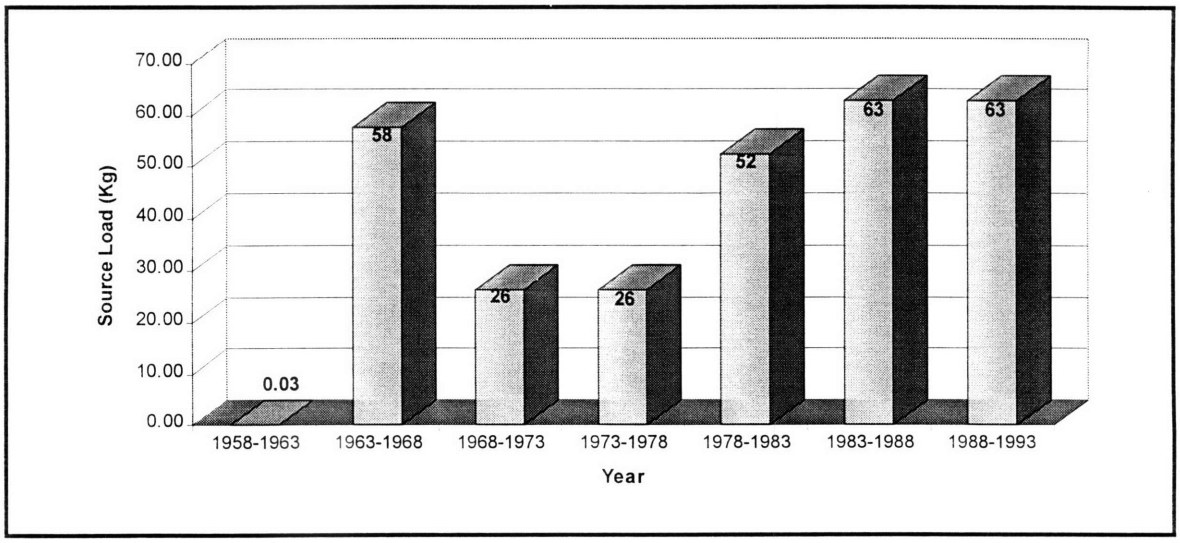


Figure 3-1 Source Loadings for the CS-4 Model

3.1.2 Dispersivity

Garabedian et al. (1988) calculated dispersivities using the data obtained during the Ashumet Valley tracer test. The method of spatial moments was used to interpret the data; which was regarded by Gelhar et al. (1992) as having a high degree of reliability. Values of dispersivity obtained by Garabedian et al. (1988) are summarized in Table 3-1 below.

Table 3-1 Dispersivity values of the Ashumet Valley *Tracer Test (*Garabedian et al.*, 1988)*

Dispersivity	Value
Longitudinal (A_0)	3.15 ft
Transverse, horizontal (A_{22})	0.59 ft
Transverse, vertical (A_{33})	0.005 ft

It must be noted that these values, which are generally well accepted in the literature for the site, were obtained for a source with different dimensions as the CS-4 site. The displacement of the CS-4 plume is larger than that of bromide used in the tracer test experiment. Consequently, the overall test scale of the CS-4 site is larger, and the macrodispersivity should be modified (Gelhar, 1993). In addition, Rajaram and Gelhar (1995) concluded that dispersivities for transport over large scales are significantly influenced by the source dimensions. The authors define a relative dispersivity which is appropriate for characterizing the dilution and spreading at individual heterogeneous aquifers. Using their two scale exponential model, the relative longitudinal dispersivity (A_0^r) is estimated to be 66 ft (Gelhar, 1996).

Transverse dispersivities are not affected, since their variability is not due to this phenomenon but to temporal variations of the hydraulic gradient's direction. This is a topic that is undergoing current research, and it is therefore beyond the scope of this work.

3.2 Transport Model Results

The code's capabilities allow concentration contours to be delineated. From this information the general size and shape of the contaminant plume was evaluated. The figures below (Figures 3-2 to 3-4) show the graphical output of the model.

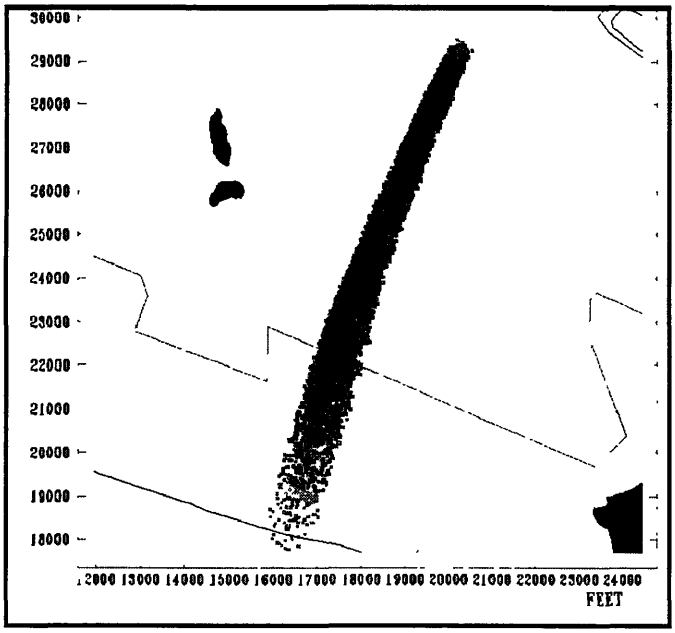


Figure 3-2 Distribution of Particles in the CS-4 Plume Simulation

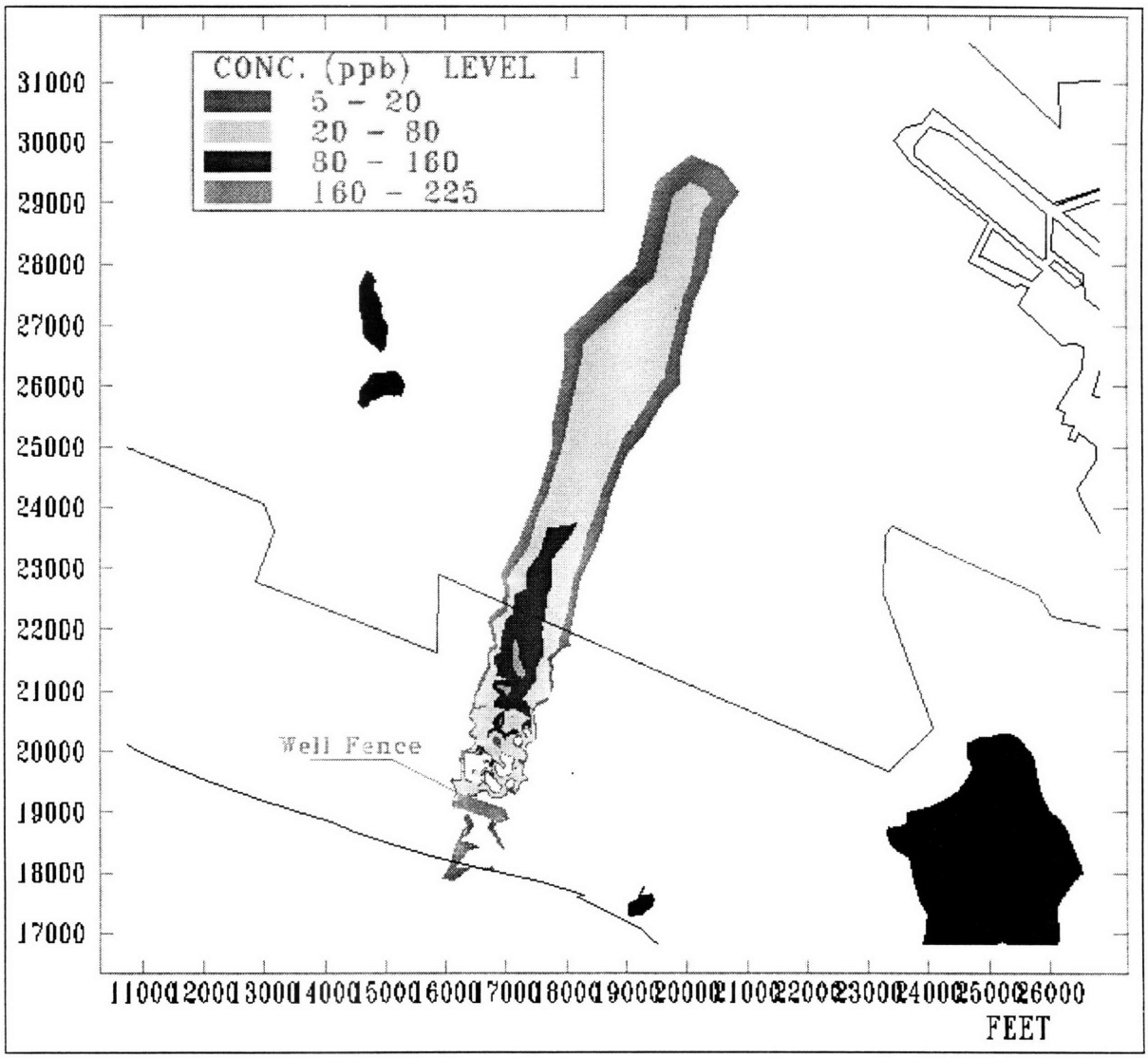


Figure 3-3 Plan View of Maximum Concentration Contours

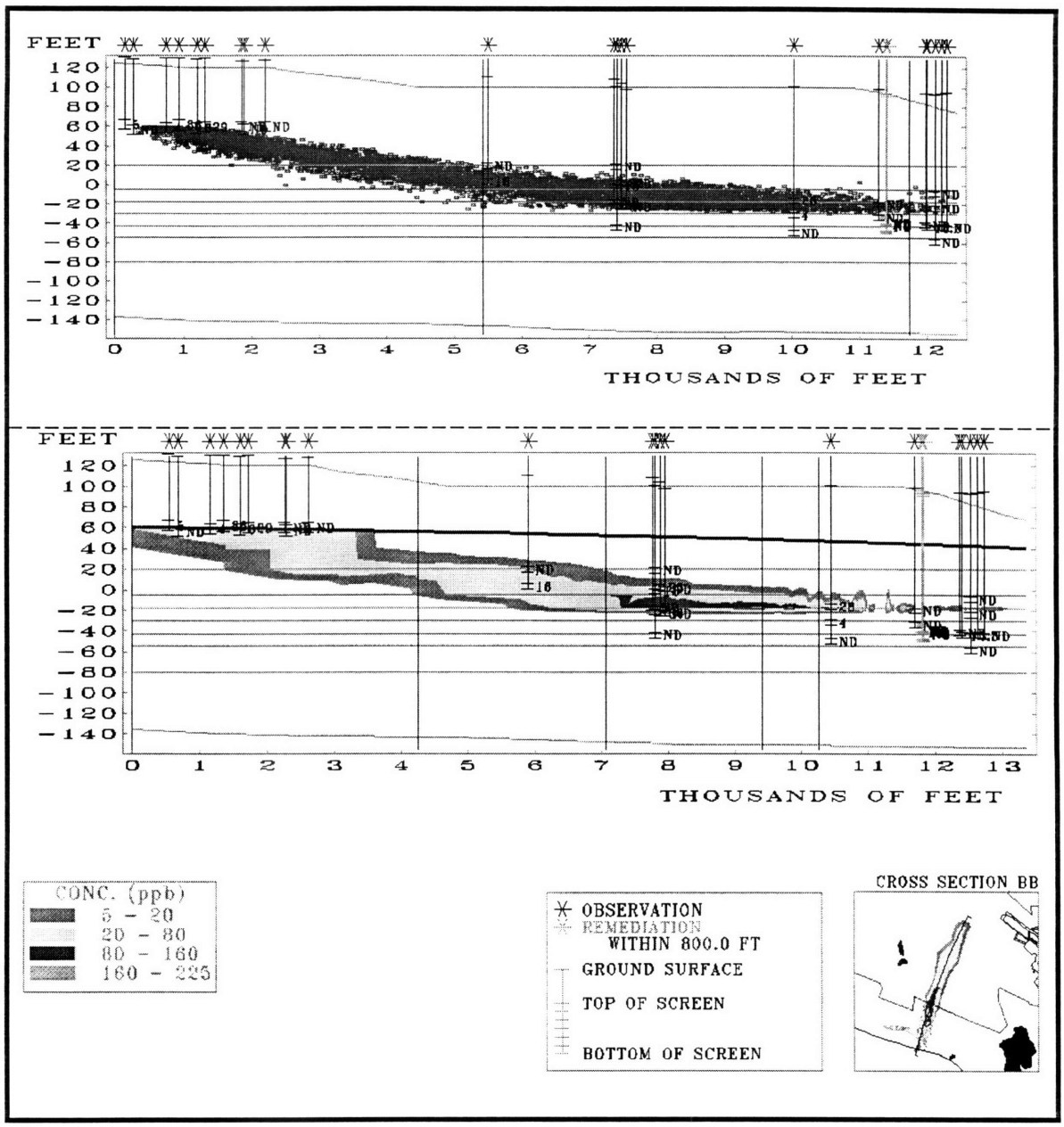


Figure 3-4 North-South Cross Section of CS-4 Plume Showing Particle Distribution (top), Concentration Contours (bottom)

Table 3-2 Dimension of Modeled Plume

Parameter	Value
Length	3,840 m (12,600 ft)
Maximum Width	640 m (2,100 ft)*
Average Width	360 m (1,180 ft)
Maximum Height	17 m (55 ft)
Average Height	12 m (40 ft)

* Maximum width is probably overestimated due to grid resolution

In general. the dimensions of the modeled plume (Table 3-2) are greater than the ones reported by ABB Environmental Services Inc.(1992b). This result does not necessarily invalidate either plume interpretation. The plume defined by ABB Environmental Services Inc. (1992a) was developed from interpretation of the field observations. This simulation used field observations and site characterization data, applied to a calibrated natural conditions model of the Cape Cod aquifer, and thus probably produces a more appropriate representation of the real plume. Nevertheless, there are many assumptions that are made and factors that come in when a computer model is constructed. Some of these, such as source dimensions and location, recharge, hydraulic conductivity distribution, and amount of data available may ultimately be the sources of discrepancy between the modeled solution and the real plume. This suggests that site characterization should be improved in order to obtain a better understanding of the subsurface conditions.

3.3 Transport Simulations

The CS-4 plume model described above was used to simulate two different remediation alternatives. These simulations attempted to forecast the clean-up times for the alternatives examined.

The first simulation was the no option alternative and therefore modeled the natural flushing of contaminants. The total time it took for all the particles to enter Coonamesett Pond was between 80 to 85 years. Thus, the model suggests that if the well fence had not been operating, the aquifer under the MMR would be "clean" approximately by the year 2075. Once the particles reached the pond, concentrations dropped notably, possibly due to dilution effects. This model could be used as the basis for further studies on surface water impacts.

The second simulation attempted to replicate the current pump and treat scheme used at the MMR. Thirteen extraction wells at the toe of the plume pump at a total rate of 140 gpm. The purpose of the simulation was to predict the time it would take to operate the pump and treat system continuously until concentrations reach acceptable levels. This occurred approximately 70 years after the simulation run started. This strongly suggests that a more economically efficient final remediation scheme should be put in place. It is interesting to note however, that some particles escaped the well fence and ultimately ended up in Coonamessett Pond. This is most probably be due to the fact the well fence is designed for an 800 ft (244 m) wide plume. López-Calva (1996) presents pumping schemes for the well fence in question.

4 EQUILIBRIUM SORPTION RESULTS

The sand samples used in this study were obtained from the USGS Well S315 (Figure 4.1)

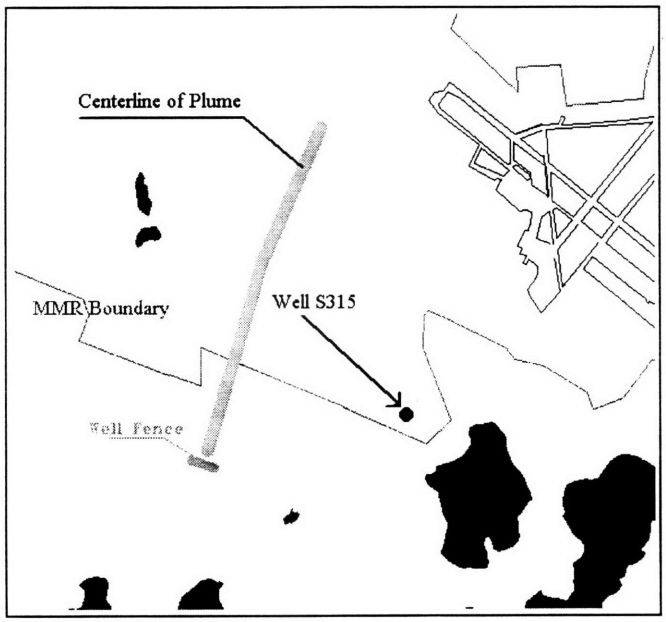


Figure 4-1 Location of Well S315 relative to the centerline of the CS-4 plume, the base boundary and the current location of the extraction well fence.

The organic carbon content (f_{oc}) of the sands used in this study are listed in Table 4-1. The f_{oc} is the part of the solid matrix primarily responsible for sorption.

Table 4-1. Sand Identification including laboratory measured f_{oc}s and hydraulic conductivities, K. Samples were obtained from Well S315

Sand ID	Sand Depth (ft)	f_{oc} ($\pm\sigma$), (%)	K, cm/s
S315-5	18-20	0.0433 (0.0015)	0.012
S315-13	58-60	0.0098 (0.0005)	0.041
S315-2	73-75	0.0058 (0.0013)	0.100
S315-14	78-80	0.0048 (0.0008)	0.060
S315-9	88-90	0.0076 (0.0011)	0.037

Using these f_{oc} values, equilibrium distribution coefficients are calculated (Table 4-2). The f_{om} values listed in Table 4-2 are assumed to be twice the measured f_{oc} values (Schwarzenbach et al., 1993). Phase partitioning is assumed as the predominant mechanism controlling sorption.

Table 4-2 K_d' values calculated from the linear equilibrium sorption equation $K_d'=K_{om}f_{om}$.

	K_d' (L/kg)			
Sample ID	f_{om}, %	DCE	TCE	PCE
S315-5	0.0866	0.026	0.063	0.158
S315-13	0.0196	0.006	0.014	0.036
S315-2	0.0116	0.004	0.008	0.021
S315-14	0.0096	0.003	0.007	0.017
S315-9	0.0152	0.005	0.011	0.028

4.1 Implications of Distribution Coefficients

The depth-averaged retardation factors calculated for the contaminants of interest were calculated (Table 4-3). Appendix A describes retardation factors in more detail.

Table 4-3 Effective retardation factors

Compound	R_{eff}
DCE	1.04
TCE	1.10
PCE	1.25

The longitudinal macrodispersivity is a key factor in the modeling and understanding of plume transport. The value for the longitudinal macrodispersivity for a conservative substance at Cape Cod is estimated to be 66 ft. However, for sorbing solutes, an adjustment to this value has to be made. The net effect of sorption is to retard the transport (i.e. the velocity) of the contaminants in the aquifer. Variability of sorption can produce an enhanced longitudinal macrodispersivity (Garabedian et al., 1987); this effect is more important when the sorption coefficient and hydraulic conductivity are negatively correlated (Figure 4-2).

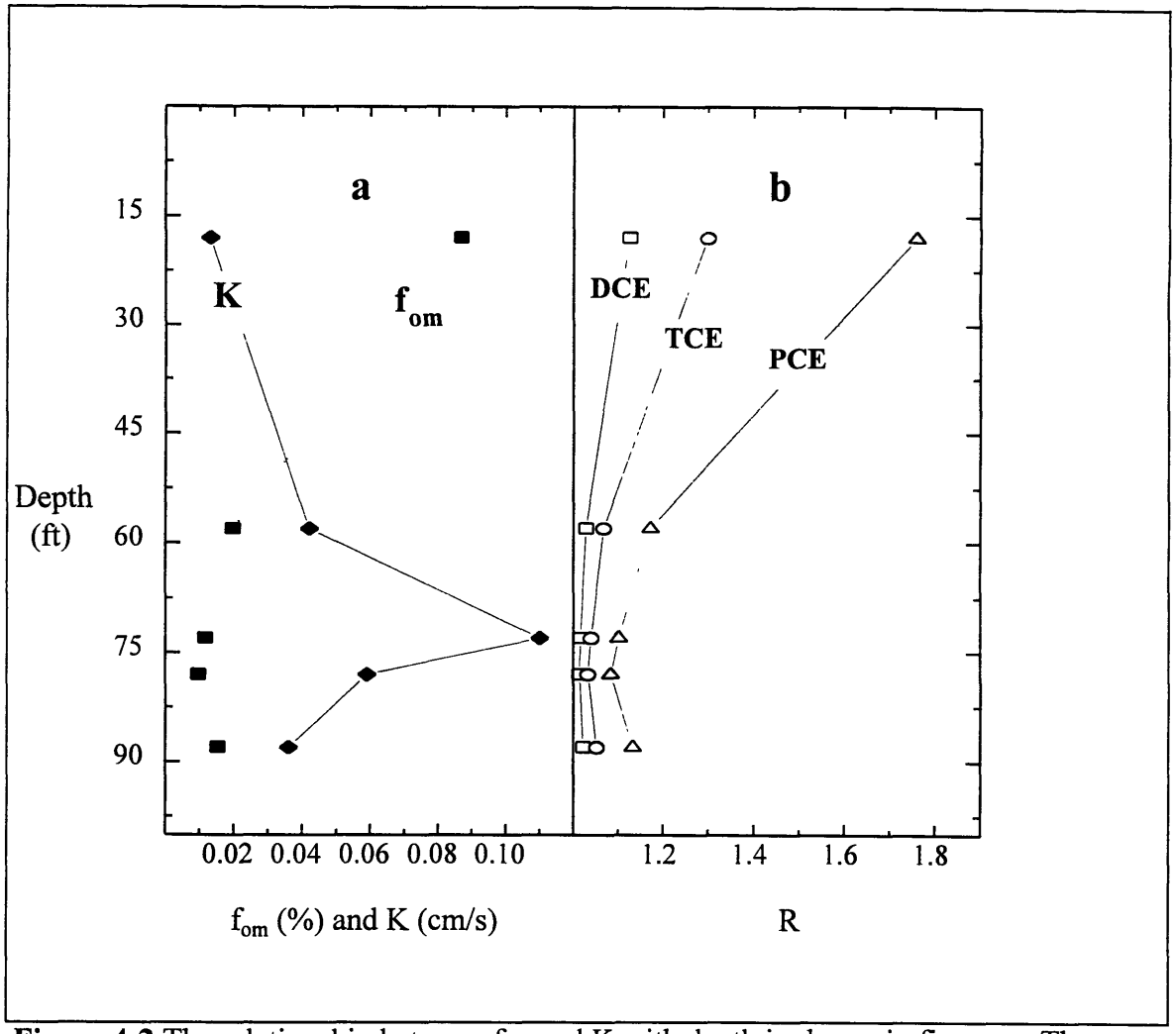


Figure 4-2 The relationship between f_{om} and K with depth is shown in figure a. The experimentally determined retardation factors are shown in figure b. As expected, the f_{om} and K, and the R and K are inversely related.

The values of the retarded longitudinal macrodispersivity, A_{11}, are included in Table 4-4. For the more strongly sorbing PCE, the retarded longitudinal macrodispersivity, A_{11}, increases by a factor of 2.1 relative to the non-retarded value. This is an important consideration in the modeling or understanding of the transport of this compound. For the least sorptive compound (DCE), the velocity variances

introduced by sorption are small as reflected by a small increase in the longitudinal macrodispersivity (factor of 1.2).

Table 4-4 Values of the retarded longitudinal macrodispersivity, A_{11} from Khachikian (1996).

Compound	A_{11} (m)
DCE	23.5
TCE	28.7
PCE	41.3

The retarded longitudinal macrodispersivity, in effect, quantifies the extent of a mixing zone in front of the leading edge of a contaminant plume. While the bulk of the mass of the contamination may be held back (i.e., retarded), some will disperse ahead of the conceived contaminant plume, resulting in early breakthrough times.

Macrodispersivity is a phenomenon that is currently under research. The effects are scale dependent and, thus, presents a certain challenge to the investigator. More research is needed to fully understand this phenomenon and to be able to quantify it.

5 MODELING PUMPING SCHEMES FOR REMEDIATION

An aquifer test was carried out by E. C. Jordan (1990) and results are reported in the feasibility study for CS-4 area. This aquifer test was simulated using the model, in order to calibrate it under pumping conditions.

5.1 Pumping Schemes for Remediation

The first step in the design of a pump and treat system is to determine the quantity of groundwater that will need to be pumped from the aquifer. This contaminated water discharge for CS-4 was estimated to be 60 gpm. The minimum overall pumping rate of any remedial system simulated needs to consider this discharge as its minimum pumping rate.

5.1.1 Analysis of the Capture Zones Under Different Pumping Schemes

The particles which reach the well fence in the middle of pumping wells may or may not be captured, depending on the distribution of hydraulic head. Points of greater head value are formed at the midpoint between the pumping. This factor was important in the geometry for the capture zones as described below.

The results from the simulation of six wells non-uniformly spaced indicate that this option was less effective than the equally-spaced option. However, an efficient capture curve can be achieved with a proper combination of pumping

5.1.2 Flexibility of the current well fence

The existing well fence was simulated first. A particle tracking simulation using 13 wells, pumping a total flow rate of 140 gpm (530 L/min), located 60 ft apart, as in the existing well fence, was run.

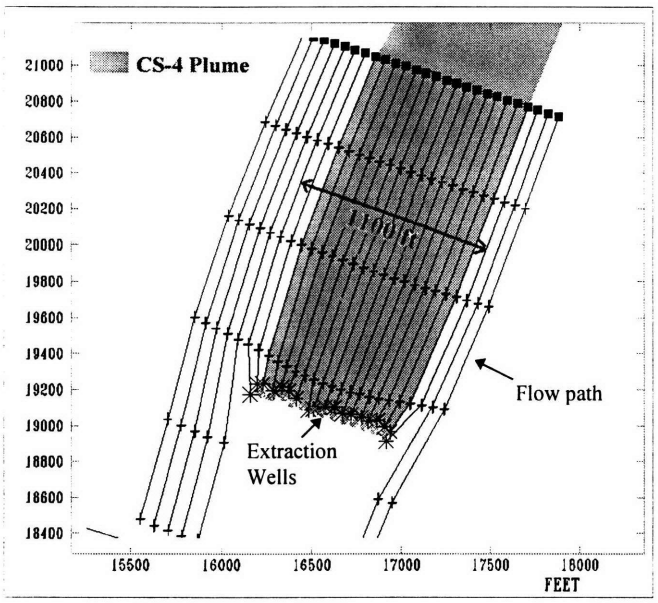


Figure 5-1 Capture curve simulation of the IRP well fence.

The pumping rate and the number and spacing of wells in the existing well fence can be considered adequate (Figure 5-1). In the horizontal view, a capture curve about 1,100 ft wide is observed. However, this horizontal view of the capture zone does not give information about the three-dimensional geometry. In order to obtain this information, a cross-sectional particle tracking was run. The particles were introduced into the modeled aquifer 1,500 ft upgradient of the well fence. The simulation was run

and the starting points of the particles were plotted. The plot of the starting points is only a cross-section of the aquifer showing where the particles were at the beginning of a simulation. A second plot was made on top of the first one, showing only the starting points of the particles that, as a result of the pumping, were removed from the aquifer. In Figure 5-2 a cross-sectional particle tracking for the simulation of the IRP well fence is shown. The larger dots can be interpreted as the cross-sectional area of the capture zone, 1,500 ft upgradient of the well fence.

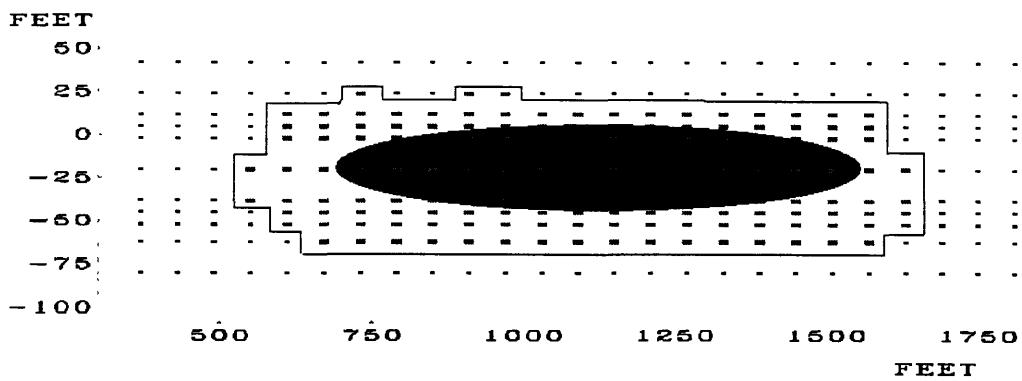


Figure 5-2 Cross-sectional areas of the capture curve 1,500 ft upgradient of the 13-well system (IRP well fence).The capture curve is represented by the larger dots.

From the analysis of the cross-sectional area of the capture zone (Figure 5-2), the vertical and horizontal effects of the pumping scheme were sufficient for the capture of the plume. The capture zone was calculated to be approximately 250 ft wider and 25 ft thicker than the CS-4 plume. The area of the ellipse formed by the plume is 31,400 ft^2. The area of the ellipse formed by the capture zone is about 64,800 ft^2. The cross-section

of the capture zone is two times bigger than the cross-section area of the plume. This guarantee the removal of all contaminated water.

The simulated plume described be the model, is wider than the plume reported by E.C. Jordan (1990). The flexibility of the 13 well containment system, in terms of its response to different field conditions such as a wider plume was tested. In order to do this, simulations using the current well fence but increasing the pumping rate were made and the extent of the resulting capture zones were analyzed. Results indicate that pumping an overall discharge of 220 gpm, 13 wells will capture a plume about 50% bigger (in cross-sectional area) than that reported by E.C. Jordan (1990). However, if the plume is located deeper in the aquifer, the increase in pumping rate will not be effective, since the lower limit of the capture zone does not go deeper even for a pumping rate 75% larger than the original pumping rate. Placing the well screens deeper into the aquifer is a more effective way to contain a deeper plume than increasing the pumping rate. The 220 gpm pumping rate, however, would not be enough to capture a plume with the dimensions of that simulated in this study. Higher pumping rates would be needed. A better solution for the containment of a plume with the dimensions of the modeled one, would be the placement of new wells to increase the length of the well fence.

5.1.3 Prediction of an Alternative Pumping Scheme

After the analysis of the current well fence of 13 wells, and the response of the aquifer to different pumping scenarios, the option of an alternative containment system was addressed. The different simulation runs for this purpose are presented in Table 5-1.

Table 5-1 Simulations to predict an alternative effective capture zone for CS-4 plume. Simulations were run according to the dimensions of the plume reported by E. C. Jordan (1989).

Number of wells	Wells operating	Pumping rate (gpm)	Individual pumping rate (gpm)	Distance between wells (ft)
8	13, 11, 10, 8, 7, 5, 3, 1	140	20 in the outside wells, and 16.7 at the rest of the wells	102
8	13, 11. 10. 8. 7, 5, 3, 1	140	17.5	102
7	13, 11, 9, 7, 5, 3, 1	140	20	120
5	13, 10, 7, 4, 1	140	28	180

All simulations were run with schemes of equally-spaced wells. since in the six-well simulation it was clear that an option of non-equally spaced wells presents disadvantages compared with the uniformly-spaced options. The results in the cross-section capture zone generated by eight wells were very similar in terms of the shape of the capture zone and almost identical in terms of cross-sectional area, which is of about 64,800 ft^2.

Since fewer wells for a fixed pumping rate (140 gpm) may imply reduction in the operation and maintenance costs. the simulation of seven wells was performed. The resulting capture zone cross-section is illustrated in Figure 5-3 (while in Figure 5-2, the capture zone resulting from the existing well fence is presented).

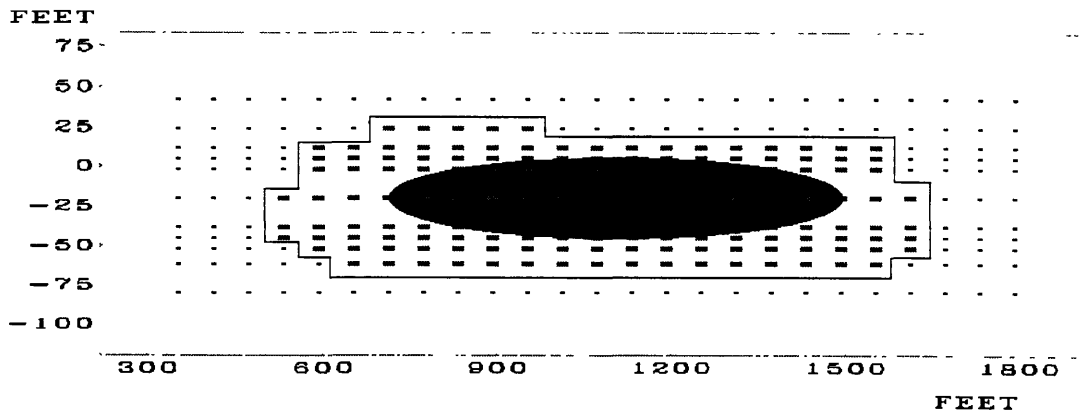


Figure 5-3 Cross-sectional areas of the capture curve 1,500 ft upgradient of the 7-well system, pumping a total of 140 gpm. The capture curve is represented by the larger dots.

The area of the seven-well pumping strategy was also approximately 64,800 ft^2, which is the same as the 13 well and the previous eight well simulations. The seven well option is preferred over the eight-well option because both produced the same results, and in the eight-well system the wells had to be relocated. This relocation of wells would imply costs, not needed for the seven-well scheme.

For the simulation of five wells, pumping 140 gpm was not enough to contain the plume. Pumping rate had to be increased to offset the effect of well spacing. An increase of more than 40 % in pumping rate gave a capture zone of approximately 79,000 ft^2, which was greater than the one obtained from the other schemes. This capture curve, however was not effective in containing all the contaminants. No further simulations with five wells were run, since the greater capture zone from the five-well simulation implies the capture of a larger proportion of clean water, which makes this option less effective.

From the results of this study, no significant changes for the existing well fence and the seven-well alternative were observed. The seven-well alternative consists of wells located 120 ft apart, which is twice the distance between the wells in the current well fence. The pumping rate for each individual well was increased, although the overall pumping rate remained constant. The results show that the negative effect of increasing distance between wells was offset by the positive effect of increasing individual pumping rates.

In conclusion, the seven-well system may be a better option for the containment of CS-4. The operation and maintenance cost would be reduced and the capture of CS-4 plume would still be attained.

6 ABOVEGROUND TREATMENT ALTERNATIVE

Treatment of extracted groundwater by GAC is a proven and reliable technology (Stenzel et al., 1989). However, one of the disadvantages is that the operation and maintenance costs are relatively high. Principal cost contributions are due to the periodical exchange and reactivation of the exhausted carbon, when no more organic compounds can be adsorbed to it. Especially since successful pump and treat remediation requires operation of the system over a long period of time (for CS-4 estimated 70 to 75 years), this procedure results in considerable high costs.

It has been shown that the use of zero-valent iron is highly effective in promoting the breakdown of halogenated organic compounds in aqueous solution (Gillham, 1995). It was examined whether this emerging zero-valent iron technology could be combined cost-effectively with the existing GAC (Figure 6-1). And whether this combination would be a feasible implementation at the CS-4 site.

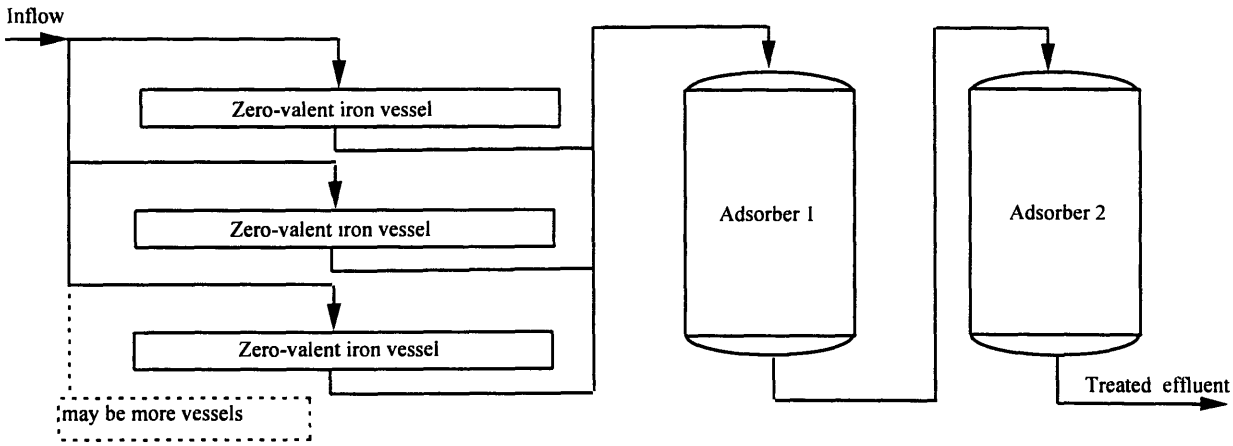


Figure 6-1 Combination of Zero-Valent Iron with GAC (not to scale)

The basic concept is to pass the contaminated water through vessels filled with granular zero-valent iron before passing it through the GAC. The contact of the VOCs with the iron surface results in reductive dechlorination and thus destruction of the contaminants. Since this technology is innovative and only very little data regarding the efficiency and implementability is available, the GAC is added to the system as a polishing and safety unit. As a result of degrading the contaminants before they enter the GAC columns, the carbon does not get exhausted and therefore carbon reactivation costs can be reduced. Assuming the innovative zero-valent iron technology is feasible, a comparison between investment and savings indicates the worth of the concept.

6.1 Scenarios of inflow concentration

The size of the treatment facility depends on two major parameters: volumetric flowrate of water and the range of inflow concentrations of contaminants to be treated.

Since only about 20 samples determine the range of contaminant concentrations, there is a large uncertainty regarding the actual contaminant concentrations. Furthermore, the proposed bioremediation system has never been tested in the field and therefore its efficacy as a treatment scheme is uncertain. In order to understand the behavior of the treatment system with respect to different inflow concentrations, the following calculations were made for four different scenarios. The four scenarios are thus defined as follows and summarized in Table 6-1:

Scenario 1: Assuming the maximum concentrations in the influent and bioremediation was not capable to diminish plume concentrations This scenario represents the worst case.

Scenario 2: Assuming average concentrations prevailed throughout the whole plume, and no reduction by bioremediation.

Scenario 3: Assuming that bioremediation reduced plume concentration, which were initially taken as maximum concentration.

Scenario 4: Assuming that bioremediation reduced plume concentrations, which were initially taken as average concentration.

Table 6-1 Four scenarios for influent concentrations

Contaminant of concern	Scenario 1: max conc. no bioremediation (ppb)	Scenario 2: average conc. no bioremediation (ppb)	Scenario 3: max. conc. with bioremediation (ppb)	Scenario 4: average conc. with bioremediation (ppb)
PCE	62	18	0	0
TCE	32	9.1	0	0
1,2-DCE	26	1.1	0	0
1,1,2,2-TeCA	24	6.8	24	6.8

6.2 Combination of abiotic dehalogenation and GAC

The net savings depend on the influent concentrations (Table 6-2). For high concentrations (scenario 1), considerable savings can be expected, while at lower inflow concentrations (scenario 2) the costs are higher than the savings. Scenarios 3 and 4 are not considered important so they are not included Table 6-2.

Table 6-2 Net savings of the combination of GAC and zero-valent iron

Scenario	Costs: Installation of zero-valent iron system (million $)	Savings: Present worth of carbon exchange cost (million $)	Net savings (million $)
Scenario 1	0.4	0.6	0.2
Scenario 2	0.2	0.3	0.1

The results do not allow firm conclusions but require appropriate interpretation. Some assumptions made for the calculations are the following: steady inflow concentration, multi-component adsorption prediction, half-lives of the reductive dechlorination process, build-up of by-products, cost of the iron technology (vessels, construction etc.) and project lifetime. Therefore, the net savings should be seen as an order of magnitude estimate.

6.3 Conclusions

The results indicate that the combination of GAC with zero-valent iron could be feasible and result in a more economic aboveground treatment than the existing one. Furthermore, in the near future the iron process is expected to progress significantly (Gillham, 1995). In order to better determine the effectiveness of this system, more data is required. A better estimation of the actual plume contamination and bench-scale or pilot testing of the zero-valent iron technology for the CS-4 site specific parameters are needed.

7 RISK

7.1 Introduction

There are numerous risks involved in any groundwater contamination or cleanup. Risk assessment is the identification and quantification of these risks and it is an objective scientific evaluation of the expected adverse health effects of exposure to potentially hazardous substances. Risk assessment consists of hazard identification, dose-response assessment, exposure assessment, and risk characterization. The data generated by a risk assessment is useful in determining the level of cleanup of a particular site, and in selecting the best remedial strategy for that site.

In the CS-4 plume, four hazardous substances are identified as primary contaminants in the groundwater: PCE, TCE, DCE and TeCA. Both carcinogenic and non-carcinogenic health effects are associated with these chemicals.

Risk calculations for carcinogens yield the probability of excess lifetime cancer from the exposure to the particular chemical. The cancer slope factor is needed for this calculation. This factor can be derived from dose-response relationships of the specific chemical. It represents the carcinogenic potency for the chemical. Carcinogenic risk can be calculated as follows (LaGrega, 1994):

$$Risk = CDI \times SF$$

where CDI is the chronic daily intake (mg/kg-day) and SF is the carcinogen slope factor (kg-day/mg). The acceptable range of carcinogenic risk (as set by EPA) is between 10^{-4} and 10^{-6} probability of excess lifetime cancer. However, the EPA uses a risk of 10^{-6}

as a point of departure: risk above this level is acceptable only under extenuating circumstances.

Non-carcinogenic risk is quantified by a hazard index (HI). The hazard index is the ratio of the intake to the reference dose. Unlike carcinogens, non-carcinogens do not produce adverse health effects below a specific dose, or threshold. This dose or threshold is referred to as the reference dose. Non-carcinogenic risk is measured relative to this reference dose. A hazard index greater than 1.0 thus indicates that there is a possibility of adverse health effects. The hazard index, quantitatively, is (LaGrega, 1994):

$$HI = CDI \,/\, RfD$$

where RfD is reference dose (mg/kg-day) and CDI has been defined previously. The major pathways of human exposure to the contaminants are through direct ingestion of contaminated water, and through inhalation of vapors (volatilized during showering, etc.). The chronic daily intake (CDI) of the contaminants may be calculated directly from groundwater concentrations for the ingestion pathway. However, the concentration of inhaled vapor must be calculated via a "shower model", and the model of Foster and Chrostowski (1979) is used for this purpose.

7.2 Results

In the bioremediation scheme two cases are presented because the amount of TeCA that is degraded cannot be estimated due to lack of data. Two cases are then applicable: one wherein all TeCA is degraded, and one where all the TeCA remains in the

groundwater. TeCA is more likely to be degraded, and a pilot study will be useful to determine the level of TeCA degradation. Table 7-1 shows the resulting concentrations.

Table 7-1 Contaminant levels after cleanup through bioremediation

	μg/L	PCE	TCE	DCE	TeCA
Case 1	Maximum	0.6	1	0	0
	Average	0.2	0.3	0	0
Case 2	Maximum	0.6	1	0	24
	Average	0.2	0.3	0	6.8

In the case where TeCA may not be subject to bioremediation, as mentioned above, a pump and treat system is necessary to remove the TeCA. In this case the resulting contaminant concentrations are tabulated below (Table 7-2).

Table 7-2 Contaminant levels after cleanup through bioremediation and pump and treat.

μg/L	PCE	TCE	DCE	TeCA
Maximum	5	5	0	2
Average	5	5	0	2

Table 7-3 summarizes the risks associated with the different treatment schemes. The data contained in the table can be viewed graphically in Figures 7-1 and 7-2. Both the table and the graph show that, following EPA guidelines, the plume must be

remediated. Since it is possible to almost completely remove all contaminants from the groundwater, the best case for all remediation strategies involves no risk.

Table 7-3 Risks associated with remediation schemes.

	Carcinogenic Risk		Non-carcinogenic Risk	
	Maximum	**Average**	**Maximum**	**Average**
no action	1.6×10^{-4}	4.5×10^{-5}	3.7×10^{-1}	9.2×10^{-2}
pump and treat	1.4×10^{-5}	1.4×10^{-5}	9.5×10^{-2}	3.8×10^{-2}
bioremediation (1)	3.1×10^{-7}	8.9×10^{-8}	5.7×10^{-3}	1.6×10^{-3}
bioremediation (2)	1.5×10^{-4}	4.2×10^{-5}	5.7×10^{-3}	4.5×10^{-3}
combination (bio 2)	1.3×10^{-5}	1.3×10^{-5}	5.7×10^{-3}	1.6×10^{-3}

Figure 7-1 Carcinogenic risk

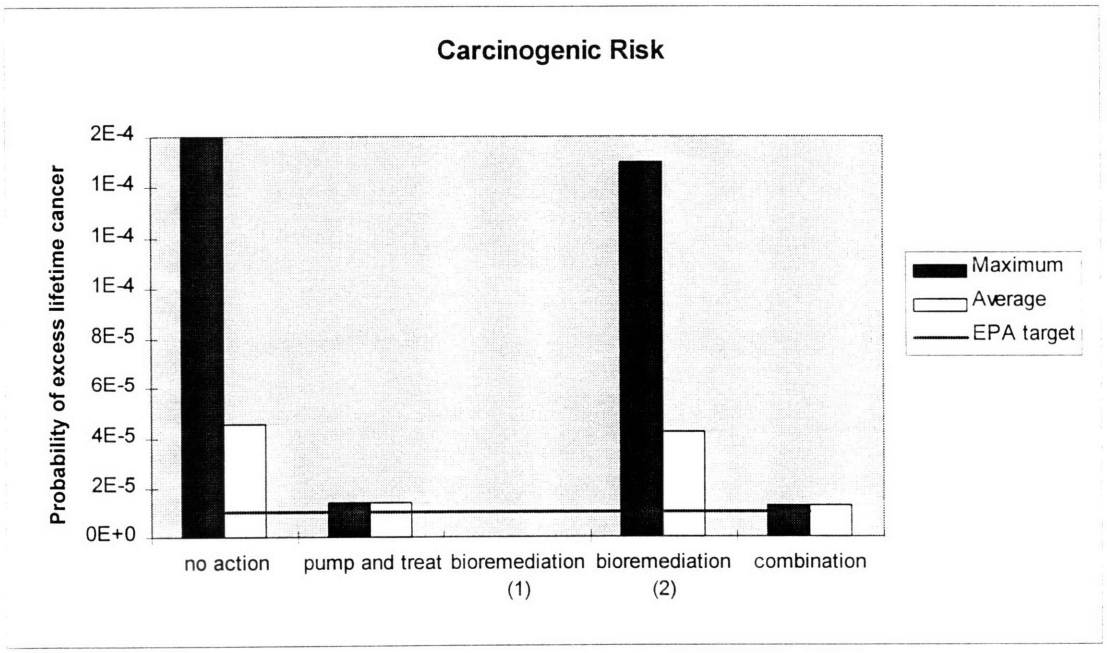
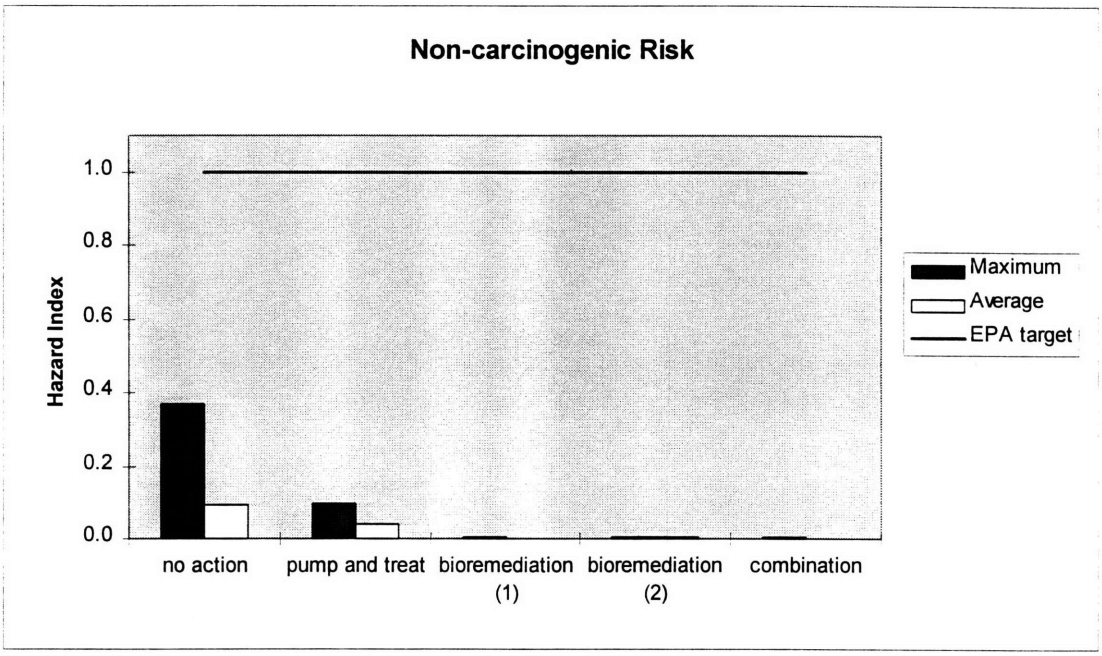


Figure 7-2 Non-carcinogenic risk.



7.3 Discussion

The process of calculating risk involves the use of approximations and conservative assumptions. Thus the risks calculated are generally estimates. Keeping in mind that the primary purpose of risk assessment in this project is the comparison of alternative remediation strategies, these values then become meaningful. All the uncertainties inherent in the calculations apply to each remediation scenario, and therefore the risks can be compared across remediation strategies. The assessment can also show which of the contaminants poses the greatest risk.

It is apparent that simply allowing the plume to proceed unabated can result in unacceptable risk, at least from a regulatory standpoint. In addition, the calculated risks

do not take into account any potential ecological risk if groundwater contaminants are discharged into surface waters such as Coonamessett Pond.

From Figure 7-1 it can be seen that all calculated non-carcinogenic risks are well below the Hazard Index limit of 1.0, and do not seem to pose a threat to human health. Carcinogenic risks, however, vary up to two orders of magnitude from case to case. Figure 7-2 shows that in contrast to non-carcinogenic risks, carcinogenic risks for the no action alternative are above the limit. The various treatment schemes yield risks within acceptable range, except for the bioremediation case where TeCA is assumed to resist degradation. In this case a pump and treat system is necessary to remove TeCA.

From a risk point of view, any of the alternatives which reduce the risk to permissible levels is acceptable. Therefore the pump and treat system, the bioremediation scheme (assuming satisfactory TeCA degradation), and a combination of the two are acceptable. However, the one which realistically yields the lowest risk, namely the combination, is the recommended one. The bioremediation scheme which assumed complete TeCA removal results in the lowest calculated risk, but if this is true then addition of pump and treat system will lower the risk even more. Aside from the lowered risk, the pump and treat system serves as a back-up to the bioremediation, especially during the start-up period. The combination assures the satisfactory removal of the groundwater contaminants.

It should be noted that the incremental risk of developing cancer is minute compared to the background cancer risk of 0.25. Aside from this, the likelihood that a well will be installed in the vicinity of the plume is small. Despite this, the public

perception is that this level of increased threat of cancer is unacceptable, and therefore the water must be cleaned up and the threat removed.

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