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Human Health Risk Assessment of Chemical Spill 4 at the Massachusetts Military Reservation

by

Christine Pilar L. Picazo

B.S., Chemical Engineering
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Submitted to the Department of Civil and Environmental Engineering
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Signature of Author: _____
Department of Civil and Environmental Engineering
May 20, 1996

Certified by: _____
David H. Marks
James Mason Crafts Professor of Civil and Environmental Engineering
Thesis Supervisor

Accepted by: _____
Joseph M. Sussman
Chairman, Departmental Committee on Graduate Studies

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Abstract

This thesis compares the risks associated with remedial alternatives for the Chemical Spill 4 groundwater contamination at the Massachusetts Military Reservation (MMR). The assessment is limited to the human health effects of the four primary contaminants detected in the groundwater at CS-4. There are four steps in making a risk assessment:
1. Hazard identification - identifies chemicals that cause adverse health effects.
2. Exposure assessment - estimates the quantities of the chemicals received by individuals.
3. Toxicity assessment - estimates the relationship between the dose received and the individual's response to the chemical.
4. Risk characterization - quantifies "risk", or the probability that an adverse effect will occur.

The four primary contaminants of concern at CS-4 are tetrachloroethylene (PCE), trichloroethylene (TCE), 1,2-dichloroethylene (DCE), and 1,1,2,2-tetrachloroethane (TeCA). These contaminants produce both carcinogenic and non-carcinogenic effects. Potentially exposed population include any future residents of the area overlying the contaminant plume. These individuals may be exposed either by direct ingestion of the contaminated water or by inhalation of volatilized contaminants.

Risk characterization is first done for the no action alternative, i.e., simply allowing the plume to flow unabated. The risks for two other treatment alternatives are evaluated. These treatment systems are a pump and treat system at the toe of the plume and a bioremediation scheme. For all cases the non-carcinogenic risks fall well below the regulatory limit. Carcinogenic risks, on the other hand, vary. Those for the no action alternative are above the regulatory limit; this means that no remediation is unacceptable. Carcinogenic risk for the different treatment schemes fall within range of the regulatory limit (making a reasonable assumption for the bioremediation case which can be tested and verified by a pilot study). The pump and treat system can also act as a back up system in conjuction with bioremediation, in case the bioremediation fails to remove the contaminants as expected. A pilot study should first be conducted to verify the applicability of bioremediation to the contaminated site.

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1. Introduction

The Cape Cod aquifer is 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 advance of the plume. Contaminated water is extracted at the toe of the plume and treated to reduce the contaminant concentrations to federal maximum contaminant levels and is 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. One tool helpful in selecting this final remedial strategy is a risk assessment.

In any groundwater contamination or cleanup, a number of risks are involved. Risk assessment is the identification and quantification of these risks. It is a "systematic process for describing and quantifying the risks associated with hazardous substances, processes, action, or events" (Covello and Merkhofer, 1993) . 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 have been identified as primary contaminants in the groundwater--tetrachloroethylene (PCE), trichloroethylene (TCE), 1,2-dichloroethylene (DCE), and 1,1,2,2-tetrachloroethane (TCA). Both carcinogenic and non-carcinogenic health effects are associated with these chemicals. Interim remedial action to contain the plume is underway; however, a final remedial action to clean up the groundwater has not been implemented. Although the pump and treat system is not a final treatment system, it can also be used to fully remediate the plume. An alternative to simply pumping and treating the groundwater is to employ bioremediation. While bioremediation is at present not a "tested" technology, it can substantially reduce the remediation time and therefore lower costs.

This thesis attempts to assess and compare the risks associated with the four detected groundwater contaminants under different remedial systems. The first, which will be used as a base case, is the no-action alternative. The second is the pump and treat system. Although a risk

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assessment has already been done for the present pump and treat system, the risks associated with this system will again be evaluated, as well as the risks associated with an alternative pump and treat system with a different pumping scheme and a different treatment technology. Lastly, the risks associated with the proposed bioremediation scheme is presented.

This thesis deals with human health risks, as this is the primary adverse effect of the contaminants in this particular plume, and risk estimates are presented as point values rather than as distributions. Data for this risk assessment is based on data previously gathered by the Installation Restoration Program at the MMR, and relies heavily on the results of the CS-4 group project which aims to determine a final remediation scheme for the CS-4 plume (Khachikian et al, 1996). Certain portions of this thesis are also adapted from the group project.

2. Site Description

2.1 Location

Cape Cod is located in the southeasternmost 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.
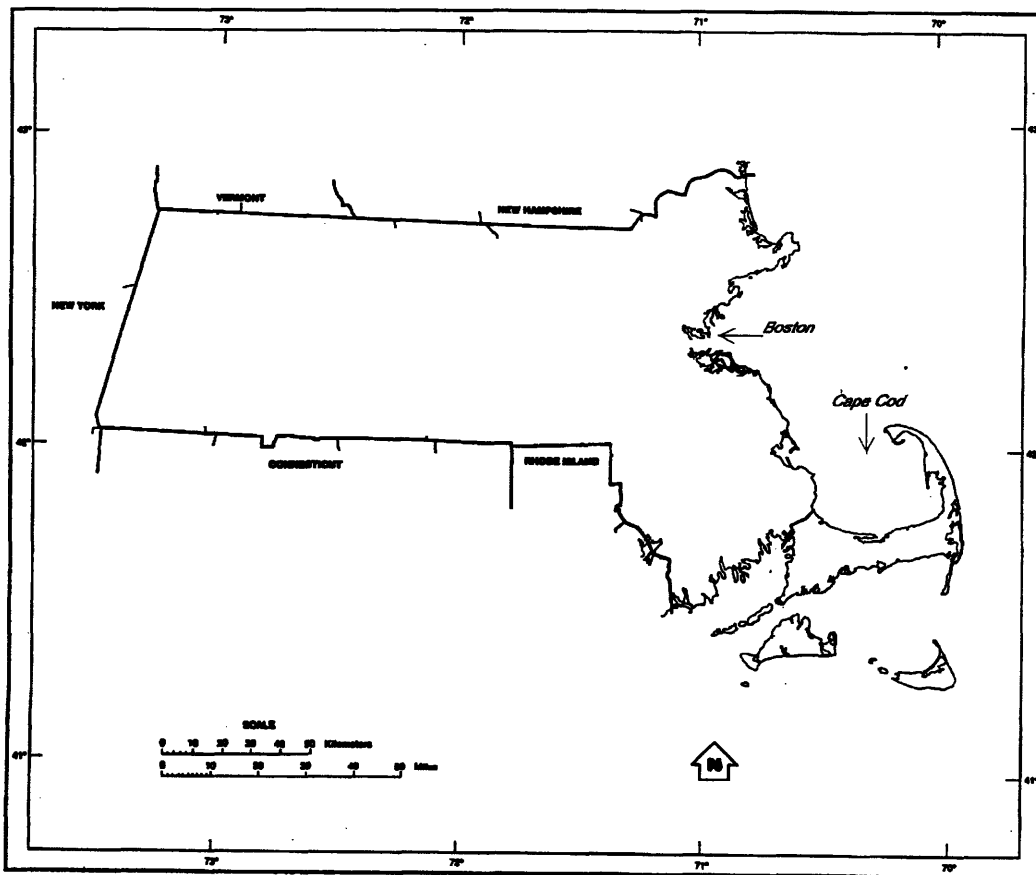
Figure 2-1. Map of the Commonwealth of Massachusetts

The MMR is situated in the northern part of western Cape Cod (Figure 2-1). Previously known as the Otis Air Force Base, the MMR occupies an area of approximately 22,000 acres (30 square miles).
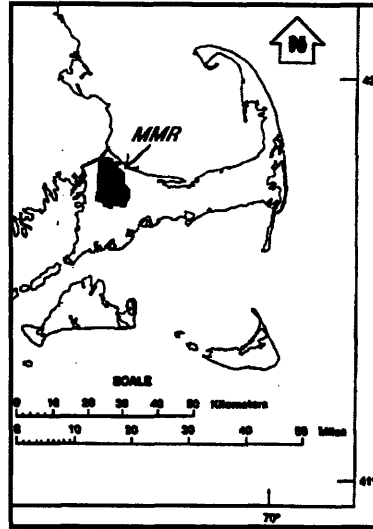
Figure 2-2. Location of MMR

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 MMR is bordered by four towns: Bourne to the west, Sandwich to the east, Falmouth to the south, and Mashpee to the southeast.

The population of Cape Cod fluctuates with the season. In 1990, the 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 conclude 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).

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2.3 General Physical Site Description

Cape Cod sediments are predominantly sands and gravel 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 receive. 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 a variety 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 covered by forests or is "open land". Twenty-five percent of the land is residential, and 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. Individual towns develop and maintain separate municipal water supply systems. Falmouth is the only municipality that uses some surface water (from the Long Pond Reservoir) as a source of drinking water. 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 variation 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 (Massachusetts Executive Office of Environmental Affairs, 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, and 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 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. 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,

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1989a). Wastes generated from these activities may 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 (see Figure 2-3).
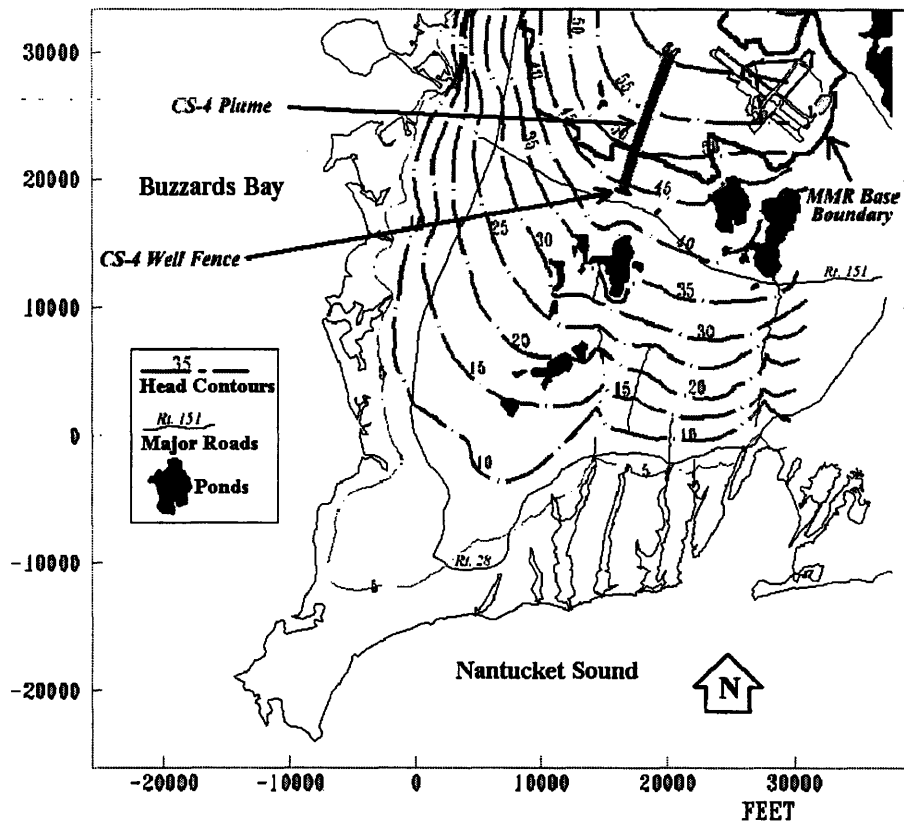
Figure 2-3. CS-4 plume and well-fence location

In contrast, a 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 treated water are defined through the established Maximum Contaminant Levels (MCL). These apply to the contaminants of concern and are presented in Table 2-1. Maximum measured concentrations, average concentrations within the plume, and an approximate frequency of detection are also shown.

Table 2-1. *Contaminants of concern concentrations and treatment target levels (adapted from 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 1×10^{-5} risk level and using the USEPA risk guidance for human health exposure scenarios.

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 also applicable to the existing interim action.

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.

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The treatment facility consists of two adsorber vessel in series filled with granular activated carbon. This system of two downflow, fixed-bed adsorbers in series is one of the most simple and widely utilized design 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 transported off-site for reactivation.

2.7.3 Plume Location

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

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 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
- use of the Otis Wastewater Treatment Plant

From these alternatives, GAC was selected as the most appropriate.

2.7.5 Performance of Current Remediation Scheme

The current treatment facility started operating in November 1993. Since then, only minimal inflow concentrations of 0.5 ppb have been detected and treated (ABB ES, 1996), possibly because more than the anticipated amount of clean water is being pumped.

Numerous authors have raised serious concerns about the ability of existing pump and treat to restore contaminated groundwater to sound environmental and health-based standards (Mackay and Cherry, 1989; Travis and Doty 1990; 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 seems to be an appropriate way to quickly respond to the plume migration. However, for the final CS-4 remedial system new methods of remediating the aquifer must be addressed.

3. Risk Assessment

3.1 Risk Assessment Methodology

Risk assessment involves using scientific principles to calculate quantitative estimates of risk. The United States Environmental Protection Agency (EPA) has set general guidelines in making a risk assessment to help achieve both quality and consistency. Quantitative risk assessment, according to the guidelines, consists of four steps or stages: (1) hazard identification, (2) exposure assessment, (3) toxicity assessment, and (4) risk characterization.

3.1.1 Hazard Identification

This stage of the process determines which of the chemicals detected at a contaminated site pose a threat to humans or to ecology. It is not unusual to detect as many as a hundred different chemicals at a site, and for manageability these must be narrowed down to those that represent the majority of the risk posed by the site. It is sometimes appropriate to select a group of chemicals which are representative indicators or surrogates for the entire group found at the site. Information regarding the chemicals of concern is gathered and the chemicals' contribution to the overall risk is evaluated.

For carcinogens, for example, information regarding the chemicals' physical and chemical properties, routes and patterns of exposure, structure/activity relationships, metabolic and pharmacokinetic data, influence of other toxicological effects, and short- and long-term tests are evaluated. The chemical is then classified according to the following scheme:

- Group A - human carcinogen
- Group B - probable human carcinogen
- Group C - possible human carcinogen
- Group D - not classifiable as to human carcinogenicity
- Group E - evidence of noncarcinogenicity towards humans

Other contaminant effects such as mutagenicity are also taken into consideration.

For mixtures of chemicals, the risks for each are first calculated and the sum total is found by simple addition. The chemicals are generally according to the specific organ they affect, i.e., pollutants which affect the lungs are separated from those that affect the liver.

3.1.2 Exposure Assessment

To fully characterize exposure to a set of contaminants, the source, the exposure pathway, the exposed population, the exposure concentrations, and the intake doses must be evaluated.

a. Exposure Pathway

The environmental pathway from source to receptor generally includes a release mechanism, such as a spill or leaching, and a medium through which the contaminants are transported. The transport medium is usually the soil, air, surface water or groundwater, or a combination of these. Computer models are used to predict the direction and speed with which the contaminants advance. Other mechanisms may act to slow, transform or otherwise affect the amount or velocity of contaminants. Such mechanisms, for example sorption or biodegradation, should also be taken into account. These mechanisms also affect the contaminant concentrations at the point of exposure.

b. Exposed Population

Populations or sub-populations which may be exposed are identified. These groups are usually within the vicinity of the source and are along a specific environmental pathway. Different populations are exposed to the contaminants in different ways. Thus several scenarios may be developed; commonly used scenarios are the worker scenario, trespasser scenario, residential use scenario, recreational use scenario, and a construction scenario. Each scenario is characterized by different degrees of exposure.

c. Exposure Concentration

Exposure concentration is the amount or dosage that an individual may be exposed to. There are three types of doses: (1) administered dose, (2) intake dose, (3) target dose. The dose used in quantifying risk should be the one consistent with that used in the dose-response relationship for the given chemical. Dose-response relationships describe the response of an individual to varying different doses of a chemical. Usually dose-response relationships are

reported using either the intake dose or the target dose. The target dose is the concentration that reaches the specific organ affected by the chemical. This concentration will depend on factors such as the absorption, distribution, metabolism, and excretion of the chemical.

The intake dose an individual is exposed to is the amount absorbed by the body. The scenario determines the intake. It may be calculated by the following equation:

$$I = \frac{(C \times CR \times EF \times ED)}{(BW \times AT)}$$

where I =   intake (mg/kg of body weight-day)
       C =   concentration at exposure point (mg/L)
      CR =   contact rate (L/day)
      EF =   frequency (day/year)
      ED =   exposure duration (year)
      BW =   body weight (kg)
      AT =   averaging time (days)

The constants of the equation differ for each exposure scenario. For instance, body weight depends on whether an adult or a child is being considered.

Another parameter that comes into play when computing the intake dose is a relative absorption factor. This factor is used to account for both (1) the absorption efficiency of the chemical via the particular route and medium of exposure and (2) the absorption efficiency for the route and medium of exposure in the experimental study on which the toxicity (dose-response) information is based. The intake is multiplied by the absorption factor to get the final intake dose.

3.1.3 Toxicity Assessment

The toxicity assessment generally aims to quantify the degree of harm that a chemical can bring about. For this purpose, most chemicals are classified as either carcinogenic or non-carcinogenic. Toxicity is quantified using a dose-response relationship; carcinogens and non-carcinogens produce toxic responses in different ways and therefore give rise to different types of dose-response relationships. Some chemicals may exhibit both carcinogenic and non-carcinogenic effects.

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a. Carcinogens

A carcinogen induces the malignant, uncontrolled growth of cells. Dose-response relationships for carcinogens are characterized by a slope factor (SF). SF is the slope when the probability of developing cancer is plotted against dose.

These slope factors are generally found through laboratory animal studies wherein the animals are exposed to high concentrations at short intervals. However, human exposure to carcinogens in the real world usually occur at low concentrations over prolonged periods of time. The exact mechanism for developing cancer is not known, making it difficult to extrapolate the high concentration lab data to lower concentrations. However, literature shows that the general belief is that there is no safe level of exposure to a carcinogen, i.e., any exposure is harmful. This results in a dose-response relationship for carcinogens which shows no harmful effect only at zero exposure.

b. Non-Carcinogens

In contrast to carcinogens, non-carcinogens exhibit a threshold dose, i.e, a dose below which there is no adverse health effect. This level is called the reference dose (RfD), and varies between chemicals.

3.1.4 Risk Characterization

This stage integrates the results from the previous stages and estimates risk quantitatively. The quantified risk is the incremental risk brought about by exposure to the chemicals of concern, and does not include background risk. At times the incremental risk may be very small compared to background risk. For instance, the background risk for cancer (the probability of developing cancer) is 0.25 (or 25%), while acceptable incremental risk is in the order of about 10^{-4}.

a. Carcinogens

Risk calculations for carcinogens yield the probability of excess lifetime cancer from the exposure to the particular chemical. Carcinogenic risk is calculated by multiplying the cancer slope factor (SF), which represents the carcinogenic potency of the chemical, by the intake dose (CDI or I):

$$Risk = CDI \times SF$$

where CDI = chronic daily intake (mg/kg-day)
SF = carcinogen slope factor (kg-day/mg)

The acceptable range of carcinogenic risk as set by the EPA is between 10^{-4} and 10^{-6} probability of excess lifetime cancer. For the state of Massachusetts the acceptable level has been set at 10^{-5}.

b. Non-Carcinogens

Non-carcinogenic risk is quantified by a hazard index (HI). The hazard index is the ratio of the intake (CDI or I) to the reference dose (RfD). Since harmful effects are induced above, but not below, the reference dose, a hazard index greater than 1.0 indicates that there is a possibility of adverse health effects. The hazard index, quantitatively, is:

$$HI = CDI \: / \: RfD$$

where CDI = chronic daily intake (mg/kg-day)
RfD = reference dose (mg/kg-day)

3.2 Limitations, Uncertainties, Assumptions

Inherent in risk calculations are certain uncertainties, generally due to lack of data or knowledge regarding a particular aspect of the risk assessment.

In calculating risk, an important quantity is the concentration that individuals may be exposed to. To determine this, contaminant concentrations are measured both at the source and in the transport medium. However, this data is usually limited. In the case of contaminated groundwater only a limited number of wells can be drilled to obtain samples that can be analyzed, which limits data.

To predict the path and the resulting future concentrations of the contaminants computer models are used to simulate the fate and transport of the chemicals. Models cannot provide exact predictions although they generally are good representations of reality. In modeling groundwater, for example, soil characteristics such as hydraulic conductivity and dispersivity are approximated from results of field tests.

At times the contaminant concentration at the exposure point cannot be directly measured (such as inhalation of vapors that volatilize from showers), and mathematical models are used to calculate these values.

When analyzing exposure to population, certain assumptions must be made regarding the characteristics of the given population. Average values of body weight, amount of water ingested, amount of time exposed to the chemical are used. For example, it is usually assumed that exposure to a carcinogen lasts for 30 years.

Perhaps the greatest uncertainty is in obtaining dose-response data. One source of dose-response data is from human epidemiological studies. These studies involve analysis of the response of humans who have been exposed to the chemical of interest. These studies, however, are few, and generally involve workers who have been exposed to chemicals before these chemicals were suspected of causing adverse health effects. The effects manifest themselves years after exposure, and the conditions under which these people are exposed to the chemical are not controlled. Other factors which may or may not affect an individual's response to the chemical cannot be screened out. Smoking, for example, may aggravate human response to certain substances. Aside from this, the people under study may be exposed to the chemical in several ways. This makes it difficult to measure the actual dose received.

Dose-response data is also obtained from laboratory animal studies involving rats and mice. In contrast to epidemiological studies, animal studies have the advantage of controlled conditions. Both the dose and the frequency of dose can be regulated. The pathway by which the animal absorbs the particular chemical (ingestion, inhalation, dermal absorption) can also be controlled, since different absorption mechanisms can lead to different responses.

However, animal studies also have their disadvantages. Firstly, a large enough number of animals must be tested to be able to obtain a statistically significant result Next, to achieve results within a reasonable amount of time and to be able to detect a statistically significant increase in incidence of cancer, the animals are exposed to high doses for a short period of time.

Thus the observed effects are acute, and the chronic effects must be extrapolated from the high-dose data. For carcinogens it is generally accepted that there is no threshold dose, i.e., that no adverse effect results only when there is no exposure. An safety factor of ten is usually included to account for any uncertainties in making this extrapolation. After the effects on

animals has been established, this must then be converted to dose-response data for humans. The two most commonly used methods for this are the use of either body weight or surface area as a basis for conversion. The relationship between human response and animal response is not precisely known. Another tenfold safety factor is included when converting from animal to human response. Furthermore, another 10-fold factor may be used to account for sensitive members of the population. In total a 100- to 1000-fold factor is added.

When a humans are exposed to a mixture of contaminants the total risk to exposure to the mixture is taken simply as the summation of the individual components of risk. Again, the actual mechanism by which individuals are affected and interactions produced by the mixture is not always known.

Due to the uncertainties discussed above, risk assessment is by nature conservative. It is designed to be protective of human health, taking into consideration sensitive subsets of the population. Upper bound estimates are used. Note that if upper bound estimates are used at every step of the calculation, the entire assessment becomes too conservative and does not anymore reflect the actual risk to humans.

4. Hazard Identification

The primary contaminants detected in the groundwater of the CS-4 plume are volatile organic compounds (VOC's): tetrachloroethylene (PCE), trichloroethylene (TCE), 1,2-dichloroethylene (DCE), and 1,1,2,2-tetrachloroethane (TeCA). Contaminant concentration range from non-detect to values above their allowed maximum concentration levels (see Table 2-1).

4.1 Tetrachloroethylene

Tetrachloroethylene (PCE) is a liquid used in dry cleaning, in the production of textiles, as a degreaser, to synthesize certain fluorocarbons, and as a building material for other chemicals. PCE is not soluble in water, and mostly enters the environment by evaporation into the air. It is not easily degraded, and therefore can persist in groundwater for a long period of time.

Humans absorb PCE into the blood through the lungs. Studies show that dermal absorption of PCE is less important than inhalation or direct ingestion. Tetrachloroethylene apparently accumulates in human tissue, particularly fatty tissue, and is metabolized by humans only to a limited extent.

Acute and chronic effects from exposure to PCE include central nervous system depression, fatty infiltration of the liver and kidney with indications of tissue damage, upper respiratory tract irritation, liver damage, headache, dizziness, and drowsiness. High concentrations of PCE vapor (>1,000 ppm) can induce collapse, loss of consciousness, and death.

In the long term, tetrachloroethylene may cause cancer in humans, as well as damage to a developing fetus.

4.2 Trichloroethylene

Trichloroethylene (TCE) is a man-made, colorless, sweet-smelling liquid used as a solvent for extraction of greases, oils, fats waxes and tars. It is also used in the textile industry to scour various fabrics and for waterless dying and finishing. TCE is used with adhesives,

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lubricants, paints, varnishes, paint strippers, pesticides, and cold metal cleaners as a general solvent.

Inhalation of trichloroethylene by humans is followed by rapid absorption. Ingestion of TCE can cause poisoning, as the chemical is readily absobed across the gastrointestinal mucosa. TCE is also quickly absorbed through the skin. Unlike PCE, there is evidence that TCE is metabolized to a large extent in humans.

Inhaled trichloroethylene primarily attacks the nervous system. TCE was once used as a surgical anesthetic, so its effects are generally well known, such as adverse effects on complex reaction time, immediate memory, and perception at 100 ppm. Acute health effects include irritation of the skin, eyes, nose, throat, and lungs. Exposure may cause lightheadedness, dizziness, visual disturbances, nausea and vomiting. High levels of exposure can lead to unconsciousness and death.

While trichloroethylene is considered a possible human carcinogen, studies indicate that inhaled TCE does not result in an increased incidence of cancer. Effects of ingested TCE include childhood leukemia, cardiac arrhythmias, and immunological abnormalities. Some studies suggest that TCE has genotoxic effects such as sister chromatid exchange, chromosomal aberrations, single-strand breaks and gene mutations. However, other studies have produced contradicting results. Other long term effects from exposure to TCE include skin allergy, blistering and roughening, liver and kidney damage, and possible paralysis of the facial nerves and of the fingers from repeated exposure.

4.3 1,2-Dichloroethylene

Dichloroethylene (DCE) is a colorless, flammable liquid most commonly used in the production of solvents and in chemical mixtures. DCE, when released into groundwater, may dissolve in the water, where it has a half life of about 13 to 48 weeks.

There is little reliable data on dichloroethylene. It is reported that humans absorb 72-75% of inhaled trans-1,2-dichloroethylene. Mild burning of the eyes has been reported after acute inhalation exposure, and acute exposure in rats resulted in pathological lesions in the heart, liver and lungs.

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DCE as yet has not been tested for carcinogenicity. The cis-isomer of DCE has been classified by EPA under Group D (not classifiable as to human carcinogenicity) while its trans-isomer has not been classified due to lack of data.

4.4 1,1,2,2-Tetrachloroethane

1,1,2,2-Tetrachloroethane (TeCA) is a sickly sweet-smelling liquid that is either pale yellow or colorless. It is used in the production of other chemicals, insecticides, paints, rust removers and varnishes.

Absorption of TeCA occurs through inhalation or by passing through the skin. High exposure can result in unconsciousness and death, and short-term exposure can damage the liver and the kidneys enough to cause death. Lower concentrations of TeCA can lead to dizziness, drowsiness, poor appetite, nausea, weakness, and irritation to the eyes, skin, nose, mouth and throat.

Tetrachloroethane is a possible human carcinogen since it induces liver cancer in animals. There is limited evidence that it causes structural or functional defects in the developing fetus or embryo in animals, and possibly also in humans. Other long term effects are possible damage to the liver, kidneys, nerves, and blood-forming organs.

5. Exposure Assessment

Wastes and spills over the years at the CS-4 site has resulted in both soil and groundwater contamination. Chemicals that leach from the soil into the groundwater serve as an additional source of groundwater contamination. The contaminated soil was recently remediated, leaving the groundwater as the remaining source for potential human exposure to the contaminants.

The CS-4 site is located in the West Truck Motor Pool within the MMR. The plume is traveling approximately southwest of the source. South of the West Truck Motor Pool is the MMR Water Supply Well B. Use of this well as a source of potable water has been suspended since 1962 due to phenol contamination, but the well water is now used to irrigate the golf course at MMR. It would probably be best to suspend this practice.

5.1 Potentially Exposed Population

Population that can be potentially exposed to the contaminants in the groundwater are those living downgradient of the plume. The nearest residents are located in Falmouth, Massachusetts, about 1,500 feet downgradient of the suspected leading edge of the plume. The plume may also contaminate one of Falmouth's town water supply wells (about 3,000 feet downgradient), and may potentially reach Coonamessett Pond (Lazaro, 1996). Groundwater migration towards these possible receptors is uncertain because other bodies of water as well as pumping of the town well greatly influences groundwater flow. Moreover, the plume is presently being contained at its leading edge, and no further plume migration can be assumed.

At present there are no residents living in the area directly above the plume and therefore there are no domestic wells that tap into the contaminated portion of the groundwater. However, a future residential exposure scenario based on long-term repetitive exposure is used to make conservative risk estimates. The factors necessary for this exposure scenario are presented in Table 5-1.

Table 5-1. Future use onsite/offsite, Massachusetts Military Reservation

Parameters	Values
Age	Adult
Body Weight	70 kg
Frequency of Ingestion	350 days/yr
Frequency of Showering	2.9 days/yr
Exposure Duration	30 yrs
Averaging Time	70 yrs (carcinogens) 30 yrs (non-carcinogens)
Daily Water Ingestion Rate	2 L/day
Daily Indoor Air Inhalation Rate	15 m3/day

ABB ES, 1992a

Note that a frequency of showering of 2.9 days/yr is equivalent to about one 12-minute shower per day

5.2 Exposure Pathways

Exposure to the groundwater contaminants can occur via two major pathways: direct ingestion and inhalation. Direct ingestion is the most common route of exposure. Inhalation of the contaminant vapors can occur because the contaminants of concern can easily volatilize while the groundwater is used for showering or other domestic purposes. Absorption through the skin is also a potential pathway, but due to the low absorptivity of the contaminants, this pathway is insignificant compared to the other two (ABB ES, 1992a).

5.3 Exposure Quantification

The sands of the Cape Cod aquifer contain only minute amounts of organic matter, which makes biodegradation of the contaminants unlikely. Furthermore, sorption onto the soil does not significantly slow the advance of the plume, nor does it affect the contaminant concentrations (Khachikian, 1996). Therefore, it can be assumed that the concentrations ingested are equal to those present in the groundwater. A table containing the maximum and average concentrations detected in the groundwater (Table 4-1) can be found in the section on Hazard Identification (page 8).

The inhaled concentration is calculated for the inhalation pathway using the Foster and Chrostowski shower model (ABB ES, 1992a). Again, the concentrations calculated are based on the assumption that contaminant concentrations present in the shower water are the same as those detected in the groundwater.

Exposure quantification is expressed as the amount of contaminant intake. This can be calculated using the following equation:

$$I = \frac{(C \times CR \times EF \times ED)}{(BW \times AT)}$$

where I = intake (mg/kg of body weight-day)
         C = concentration at exposure point (mg/L)
         CR = contact rate (L/day)
         EF = frequency (day/year)
         ED = exposure duration (year)
         BW = body weight (kg)
         AT = averaging time (days)

For the direct ingestion pathway, C is the concentration of the contaminant in the water. For the showering pathway, additional calculations must be made using the Foster and Chrostowski model. The following equations will be used:

$$C(voc) = \tfrac{S}{R} \times (e^{RD_s} - 1) \times e^{-Rt}$$

where $C(voc)$ = concentration of VOCs in bathroom ($\mu g/m^3$)
        S = VOC generation rate ($\mu g/m^3$-min)
        R = air exchange rate (min^{-1})
        D_s = duration of shower (min)
        t = time at which concentration is being calculated (min)

$$S = \frac{C_{wd} \times FR}{SV}$$

where C_{wd} = concentration in water droplet ($\mu g/L$)
        FR = flow rate in shower (L/min)
        SV = shower volume (m^3)

$$C_{wd} = C_{wo} \times \left[1 - e^{\left(\frac{-K_{al} \times t_s}{60 \times d}\right)} \right]$$

where C_{wo} = concentration in groundwater ($\mu g/L$)
        K_{al} = temperature correction of the mass transfer coefficient, K_L (cm/hr)
        t_s = shower water droplet free-fall time (sec)
        d = droplet diameter (mm)

$$K_{al} = K_L \times \left[\frac{T_1 \times u_s}{T_s \times u_1} \right]^{-0.5}$$

where T_1 = reference temperature (K)

u_s = viscosity of water at shower temperature (cp)

T_s = emperature of water shower (K)

u_1 = viscosity of water at reference temperature (cp)

$$K_L(voc) = \frac{1}{\dfrac{1}{k_l(voc)} + \dfrac{RT}{H \times k_g(voc)}}$$

where $k_l(voc)$ = chemical-specific liquid mass-transfer coefficient (cm/hr)

$k_g(voc)$ = chemical-specific gas mass-transfer coefficient (cm/hr)

RT = molecular gas constant (R) x temperature (T) (atm-m^3/mole)

H = Henry's Law Constant (atm-m^3/mole)

$$k_l(voc) = k_l(CO_2) \times \left[\frac{44}{MW(voc)} \right]^{-0.5}$$

$$k_g(voc) = k_g(H_2O) \times \left[\frac{18}{MW(voc)} \right]^{-0.5}$$

where $k_l(voc)$ = liquid mass-transfer coefficient for carbon dioxide (cm/hr)

$k_g(voc)$ = gas mass-transfer coefficient for water (cm/hr)

MW (voc) = molecular weight of VOC

In order to utilize the Foster and Chrostowski model, several assumptions are adapted from ABB ES, 1992a. First is that the bathroom volume SV = 12 m^3 and that the air in the bathroom is well-mixed. Most homes have an air exchange rate between 0.5 and 2 per hour (0.0083 to 0.03 per minute) and the air exchange rate R is assumed to be equal to 0.03/min, corresponding to about 0.4 m^3 /min. Another assumption is that the concentrations in the bathroom are at their maximum, which in reality are only experienced at the end of the shower.

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Apart from these assumptions, some parameters have to be calculated/found from tables. These parameters are the mass transfer coefficients for carbon dioxide and water, and the viscosities of water at different temperatures. The mass transfer coefficients can be calculated using correlations, while the values of viscosity can be read off nomographs (Perry's, 19 73).

Table 5-2 summarizes the parameters used in the model.

Table 5-2. Parameters for the shower model

Parameter	Symbol	Value	Unit	Source
Liquid mass transfer coefficient for CO_2	k_l (CO_2)	20	cm/hr	calculated
Gas mass transfer coefficient for H_2O	k_g (H_2O)	3000	cm/hr	calculated
Reference temperature	T_{ref}	293	K	
Viscosity of water at reference temperature	μ_{ref}	1.05	cp	Perry's
Temperature of shower water	T_s	318	K	
viscosity of water at shower temperature	μ_s	0.65	cp	Perry's
droplet diameter	d	1	mm	Foster & Chrostowski
shower water droplet free-fall time	t_s	1.5	sec	assumed
flow rate in shower	FR	20	L/min	assumed
shower volume	SV	12	m^3	assumed
time at which concentration is being calculated	t	12	min	EPA
duration of shower	D_s	12	min	EPA
air exchange rate	R	0.03	1/min	assumed
gas constant x temperature	RT	2.4×10^{-2}	atm-m^3/mole	

ABB ES, 1992a

6. Toxicity Assessment

Dose-response data for the contaminants of concern can be found in Table 6-1, Table 6-2, and Table 6-3. Three of the CS-4 contaminants are considered carcinogenic: PCE, TCE, and TeCA. Both PCE and TCE belong to Group B2 (no epidemiological data is available but there is data from animal studies). DCE belongs to Group D (not classifiable as to human carcinogenicity). None of the contaminants produce non-carcinogenic effects when humans are exposed through the inhalation route, but effects are induced by PCE, TCE and DCE when ingested.

Table 6-1. Oral cancer dose-response data

Chemical	EPA Class	Oral Slope Factor $(mg/kg/d)^{-1}$	Source	Study Type	Test Species	Tumor Site	EPA Date
PCE	B2	5.1×10^{-2}	HEAST	Gavage	Mouse	Liver	1/92
TCE	B2	1.1×10^{-2}	HEAST	Gavage	Mouse	Liver	1/92
DCE	D	NA	-	-	-	-	-
TeCA	C	2×10^{-1}	IRIS	Gavage	Mouse	Liver	1/92

ABB ES, 1992a

Table 6-2. Inhalation cancer dose-response data

Chemical	EPA Class	Inhalation Slope Factor $(mg/kg/d)^{-1}$	Source	Study Type	Test Species	Tumor Site	EPA Date
PCE	B2	1.8×10^{-3}	HEAST	Inhalation	Mouse	Liver	1/92
TCE	B2	1.7×10^{-2}	HEAST	Inhalation	Mouse	Lung	1/92
DCE	D	NA	-	-	-	-	-
TeCA	C	2×10^{-1}	HEAST	Gavage	Mouse	Liver	1/92

ABB ES, 1992a

Table 6-3. Oral non-cancer dose-response data

Chemical	Chronic RfD	Study Type	Test Species	Critical Effect	Uncertainty Factor	EPA Date
PCE	1×10^{-2}	Gavage	Mouse	Hepatotoxicity and weight gain	1000	1/92
TCE	7×10^{-3}	Inhalation	Rat	Increased liver weight	1000	8/92
DCE	2×10^{-2}	Drinking water study	Mouse	Increased serum alkaline phosphatase	1000	1/92
TeCA	NA	-	-	-	-	-

data from ABB ES, 1992a

7. Risk Characterization

This section quantifies the risks associated with three different remedial alternatives for the CS-4 plume. These alternatives are first described briefly before the risks are characterized.

7.1 No Action Alternative

This alternative involves simply letting the plume flow uncontained and is used as a base case for comparison with the other scenarios. The groundwater concentrations analyzed are those measured since no attempt is made to reduce these. Contaminant concentrations can be found in Table 2-1.

7.2 Pump and Treat System

A pump and treat system is presently being used to contain CS-4. This system consists of a 13-well fence at the toe of the plume and a granular activated carbon (GAC) treatment setup. Contaminated water is pumped from the aquifer, passed through the GAC adsorbers to remove the contaminants, and is returned to the aquifer.

A new pumping scheme as well as a different treatment system has been proposed for the CS-4 plume (Lopez-Calva, 1996 and Tillman, 1996). The new pumping scheme utilizes seven wells rather than 13, and the alternative treatment system uses zero-valent iron in conjunction with the GAC.

The present pump and treat system as well as the new proposed pumping scheme and treatment system result in basically the same contaminant concentrations. The VOC's are reduced to their MCL's (maxiumum contaminant limits, Table 7-1). The treated water will on the average contain less than these prescribed amounts; these concentrations are taken as the maximum that contaminants will reach since the treatment media (either carbon or iron) is regenerated once these threshold concentrations are detected in the treated water.

Table 7-1. Contaminant levels after cleanup through pump and treat.

μg/L	PCE	TCE	DCE	TeCA
Maximum	5	5	26	2
Average	5	5	1.1	2

7.3 Bioremediation Scheme

Bioremediation is a relatively new treatment technology which has been proposed as the final remedial strategy for the CS-4 site (Skiadas, 1996). This approach utilizes naturally-occurring bacteria to degrade the chlorinated solvents present in the groundwater. The contaminants are ultimately degraded to ethylene, which is not hazardous. It is anticipated that 99% of PCE, 97% of TCE, and virtually all of the DCE can be degraded. However, 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 7-2 shows the resulting concentrations.

Table 7-2. 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

7.4 Risk

The resulting risks from the above remediation schemes are depicted graphically in Figures 7-1 and 7-2.

Figure 7-1. Carcinogenic risk
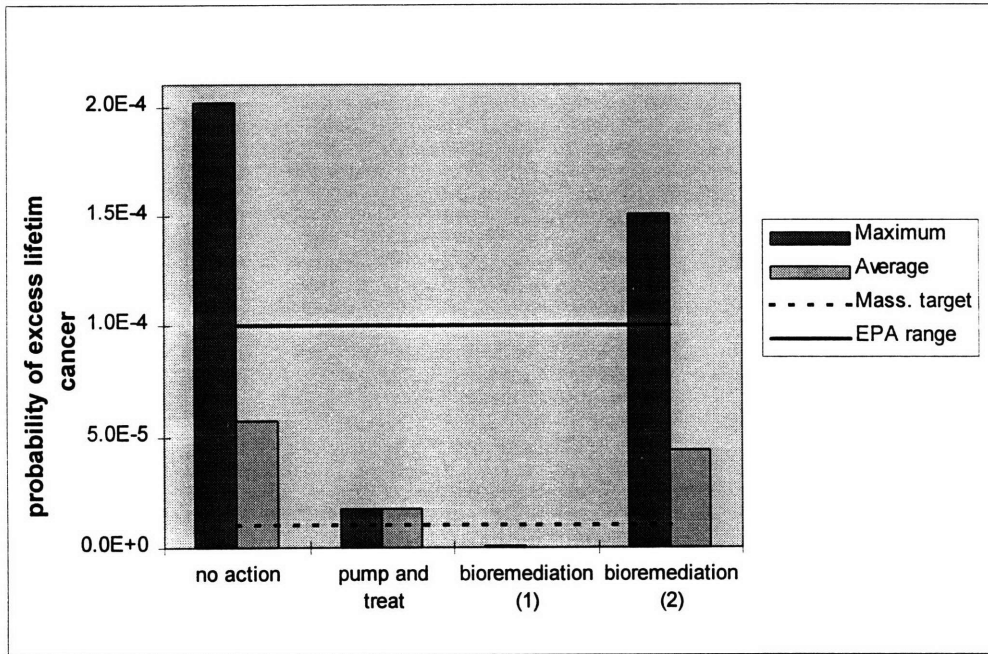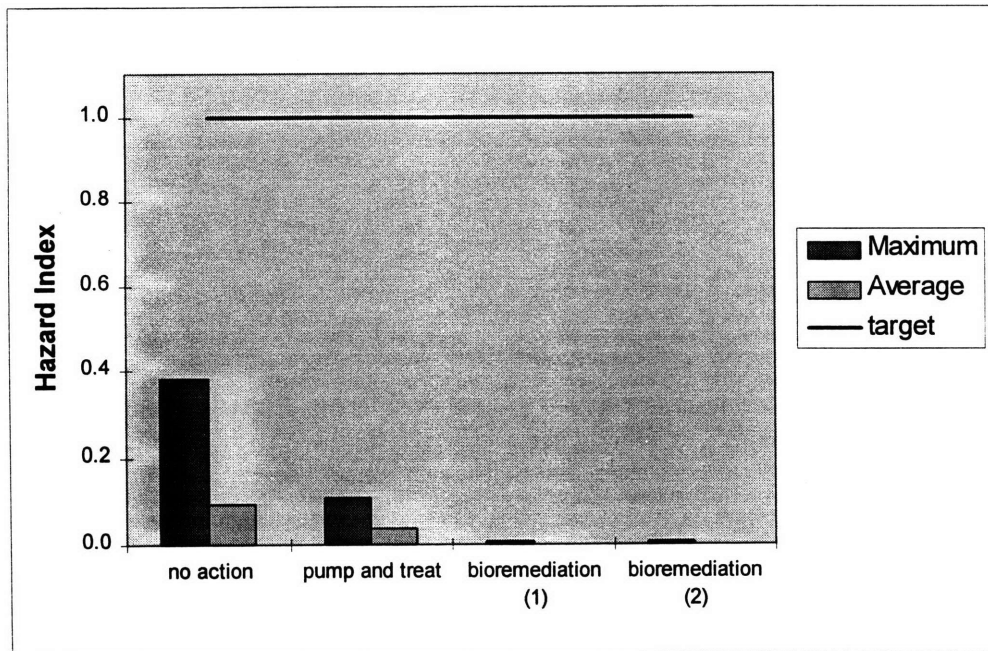

Figure 7-2. Non-carcinogenic risk

Figure 7-3 shows the average carcinogenic risk (from Figure 7-1), broken down into the contribution of each chemical component, while Figure 7-4 compares the contribution of ingestion with that of inhalation.

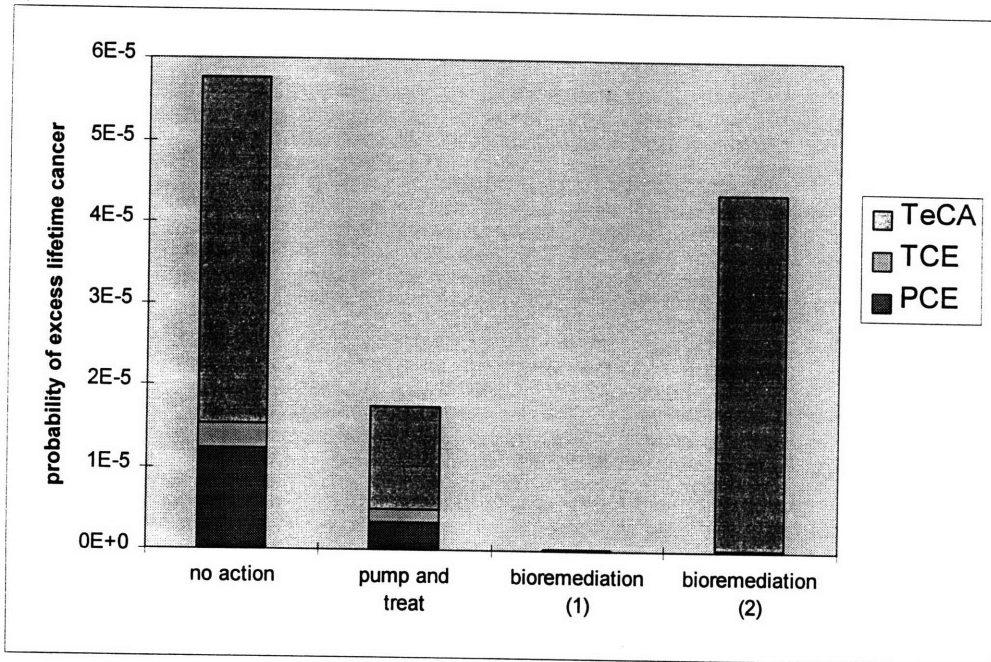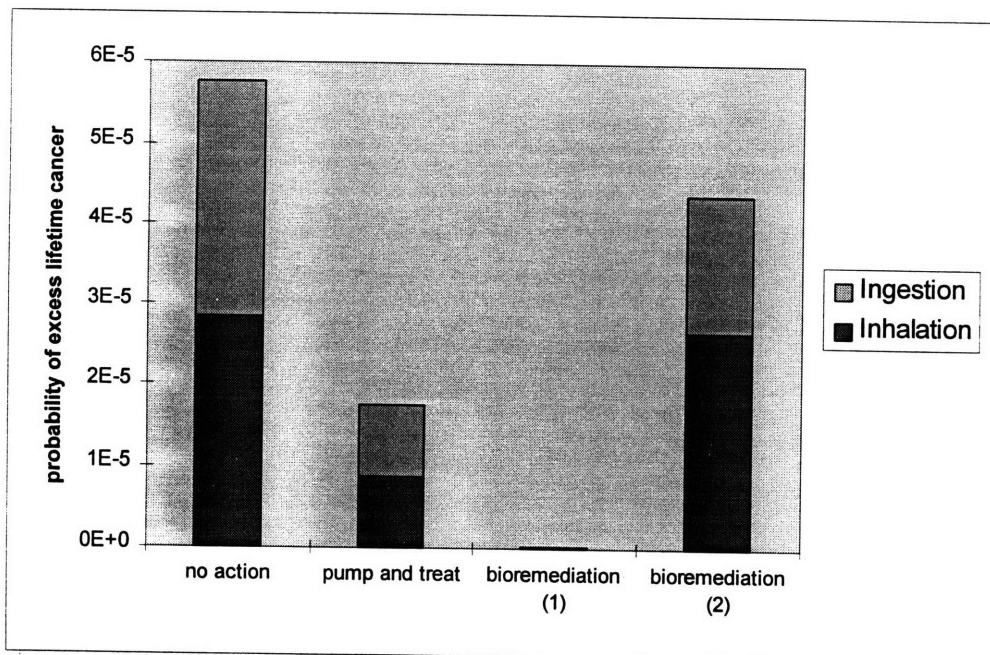*Figure 7-3. Contribution of each chemical to average carcinogenic risk*

Figure 7-4. Breakdown of average carcinogenic risk by pathway

7.5 Discussion

The process of calculating risk involves the use of approximations and conservative assumptions. Thus the risks calculated are estimates. Keeping in mind that the primary purpose of risk assessment in this paper 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 contaminant 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.

Figure 7-2 shows 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 7-1 shows that in contrast to non-carcinogenic risks, carcinogenic risks for the no action alternative are above the hazard index limit. The various treatment schemes yield risks within acceptable range, except for the bioremediation case where TeCA is assumed to resist degradation. In this particular case a pump and treat system is necessary to remove TeCA, making the use of bioremediation impractical. However, it is expected that bioremediation will reduce the TeCA concentration, although the extent of biodegradation is not known. A pilot test of the bioremediation scheme can be an effective way to determine the TeCA degradation.

It should be noted that the maximum risk associated with the pump and treat scheme is the maximum; this occurs when the effluent concentrations reach maximum target levels. At this point the carbon is then regenerated. At other times concentrations are below these levels.

Figure 7-3 shows that a majority of the risk is contributed by TeCA because it has the largest cancer slope factor. This indicates that TeCA is the critical component to remove from the groundwater. Figures 7-4, on the other hand, shows that the ingestion pathway dominates the risk except in the bioremediation (2) case, where TeCA accounts for almost all the risk involved

(the probability of developing cancer by exposure to TeCA is greater through inhalation than through ingestion).

From a risk point of view, any of the alternatives which reduce the risk to permissible levels is acceptable. Therefore both the pump and treat system, the bioremediation scheme (assuming satisfactory TeCA degradation), and a combination of the two schemes is also acceptable. However, the alternative which realistically yields the lowest risk, namely the combination, is the recommended one. The bioremediation scheme which assumes complete TeCA removal results in the lowest calculated risk, but if this is true then adding a 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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Appendix A: CS-4 Group Results

A. Results

This appendix is adapted from the CS-4 group project (Khachikian et al, 1996).

A.1 Site Characterization

A.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: the Sandwich Moraine (SM), the Buzzards Bay Moraine (BBM), and 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 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 feet near the Cape Cod Canal in the northwest to approximately 325 feet in its thickest portion in the BBM; it then decreases to 250 feet near Nantucket Sound in south. The thickness of the MPP outwash sediments ranges from approximately 225 feet near the moraines, to approximately 100 feet near shore of Nantucket Sound (E.C. Jordan, 1989a).

A.1.2 Hydrology

Cape Cod's temperate climate produces an average annual precipitation of about 48 inches, 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 one 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.

A.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).

A.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).

A.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 of the CS-4 group project (Khachikian et al, 1996). Typical anisotropy values range from 10:1 to 3:1.

A.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.

A.1.3.4 Hydraulic Gradient

The hydraulic gradient will be affected by the variations in water table elevations. These typically fluctuate about three feet 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).

A.1.4 Chemistry of the Water

The properties of the chemicals of particular interest to the bioremediation design are shown Table A-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 A-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)

A.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 coefficients. 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 asses the behavior of contaminants.

A.1.5.1 Equilibrium Sorption Results

The sand samples used in this study were obtained from the USGS Well S315 (Figure A-1)
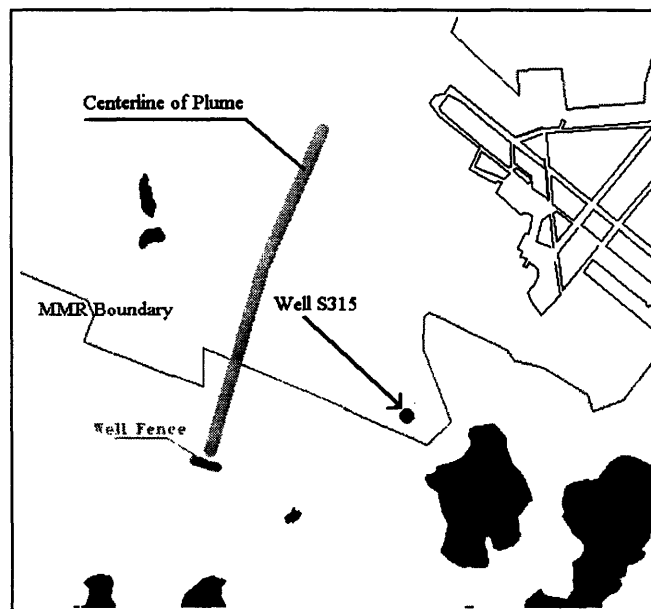

Figure A-1. Location of Well S315 relative to the centerline of the CS-4 plume, the base boundary and the current location of the extraction well fence.

The organic carbon content (f_{oc}) of the sands used in this study are listed in Table A-2. The f_{oc} is the part of the solid matrix primarily responsible for sorption.

Table A-2. Sand Identification including laboratory measured focs and hydraulic conductivities, K. Samples were obtained from Well S315

Sand ID	Sand Depth (feet)	f_{oc} ($\pm\sigma$), (%)	K, cm/s[a]
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

[a] The K values approximated from Figure 4.8.5 of Thompson (1994).

Using these f_{oc} values, equilibrium distribution coefficients are calculated (Table A-3). The f_{om} values listed in Table A-3 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 A-3. Kd' values calculated from the linear equilibrium sorption equation $K_d{}'=K_{om}f_{om}$.

Sample ID	f_{om}, %	$K_d{}'$ (L/kg) 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

A.1.5.2 Effects of Sorption on Contaminant Transport

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

Table A-4. 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 A-2).

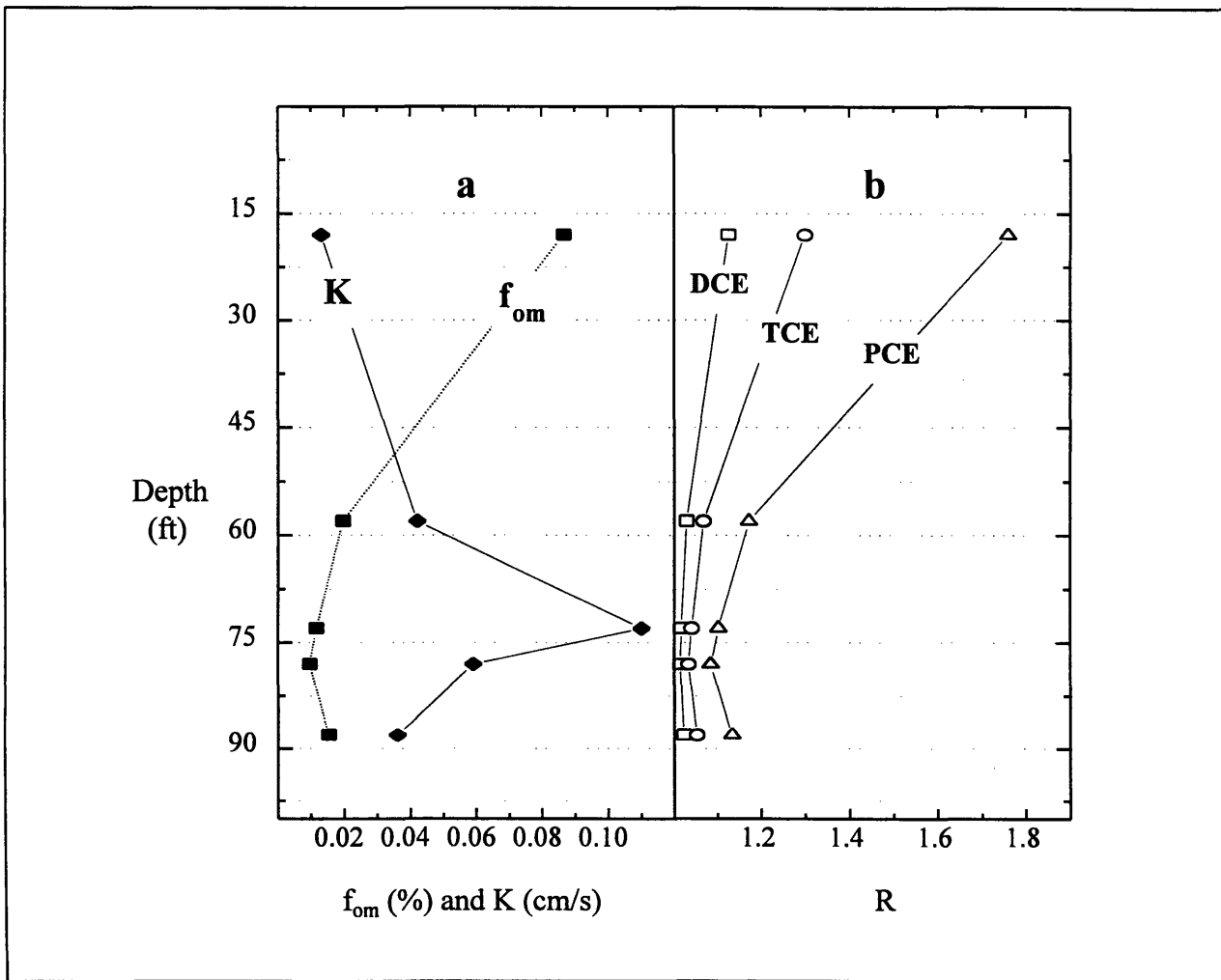Figure A-2. The relationship between f_{om} and K with depth is shown in figure a. The experimentally determined retardation factors are shown in figure b. As expected, the f_{om} and K and the R and K are inversely related.

The values of the retarded longitudinal macrodispersivity, A_{11}, are included in Table A-5. 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 A-5. 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.

A.2 Modeling Under Natural Conditions

A.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 and Ashumet Ponds were included in the model as fixed head boundary conditions, and the rest of the eastern boundary was compromised by the Childs river. Coonamessett Pond is the most

important surface water body within the modeled area because of its proximity to the toe of the CS-4 plume region.

A.2.2 Model Recalibration Using Particle Tracking

The flow model was first calibrated considering hydraulic head only. This 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 A-6 summarizes the hydraulic parameters in the final calibrated model.

Table A-6: 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 (CS-4 area)	0.8 ft/day
Anisotropy Ratio	5:1, 10:1 and 12.5:1
Recharge	19 in/yr
Head Mean Difference (calc. - obs.)	0.24 ft
Head Standard Deviation	1.61 ft

A.3 Contaminant Transport Modeling

A.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.

A.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 A-3).

Figure A-3: Source Loadings for the CS-4 Model
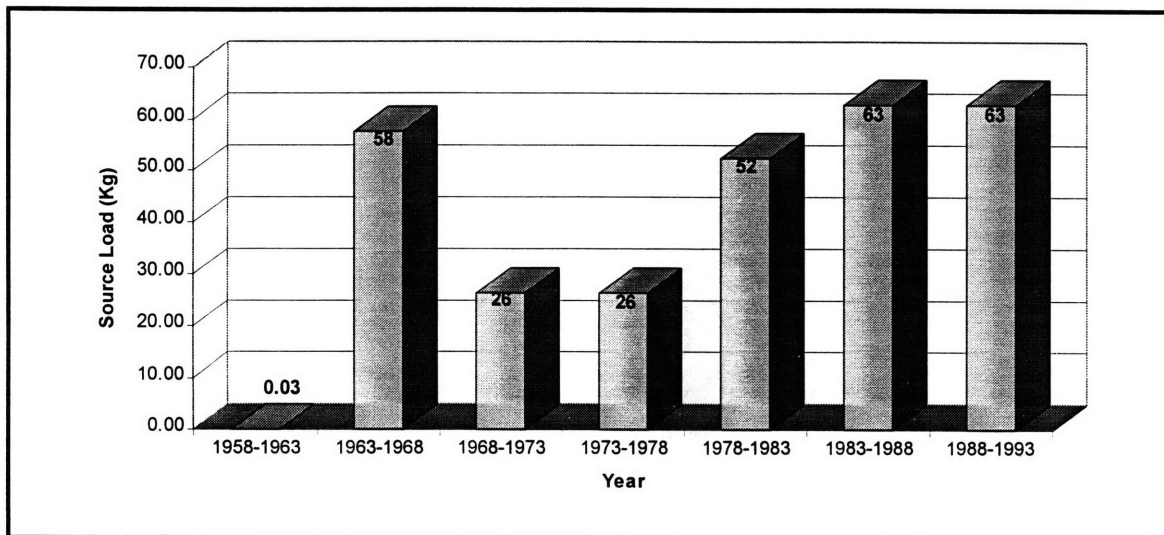
A.3.1.2 Dispersivity

Garabedian et al. (1988) calculated dispersivities using the data obtained during the Ashumet Valley tracer test. The method of spatial moments; which was regarded by Gelhar et al. (1992) as having a high degree of reliability, was used to interpret the data. Values of dispersivity obtained by Garabedian et al. (1988) are summarized in Table A-7 below.

Table A-7. 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 from 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) conclude 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 thus is beyond the scope of this work.

A.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 A-4 to A-6) show the graphical output of the model.

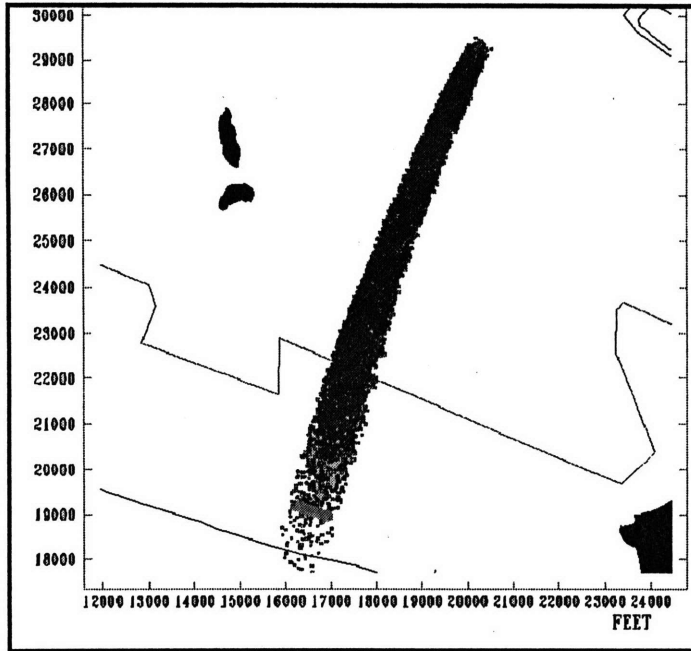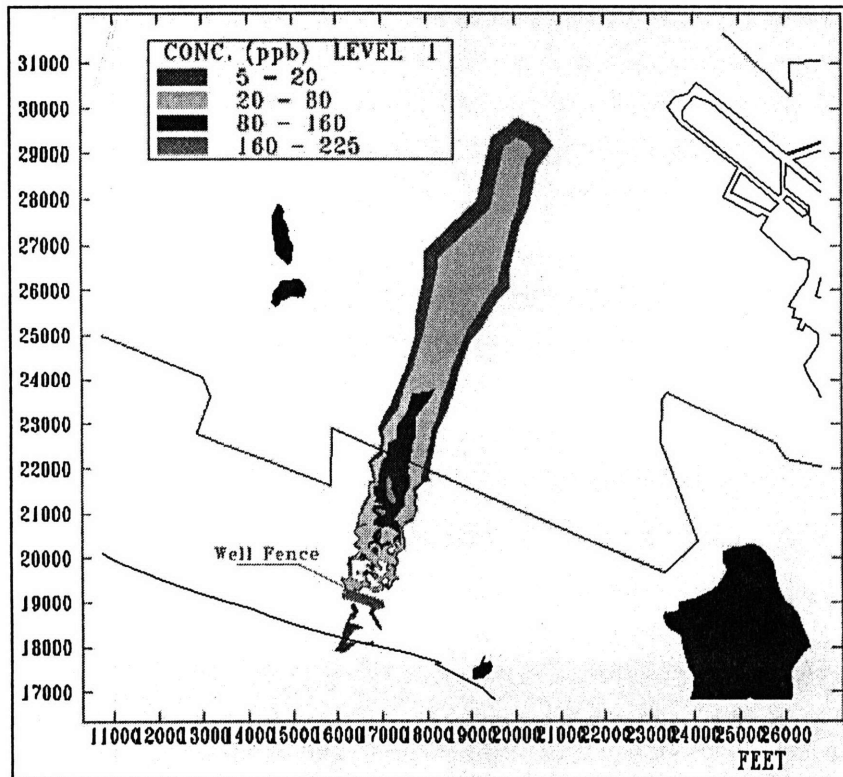*Figure A-4: Distribution of Particles in the CS-4 Plume Simulation*

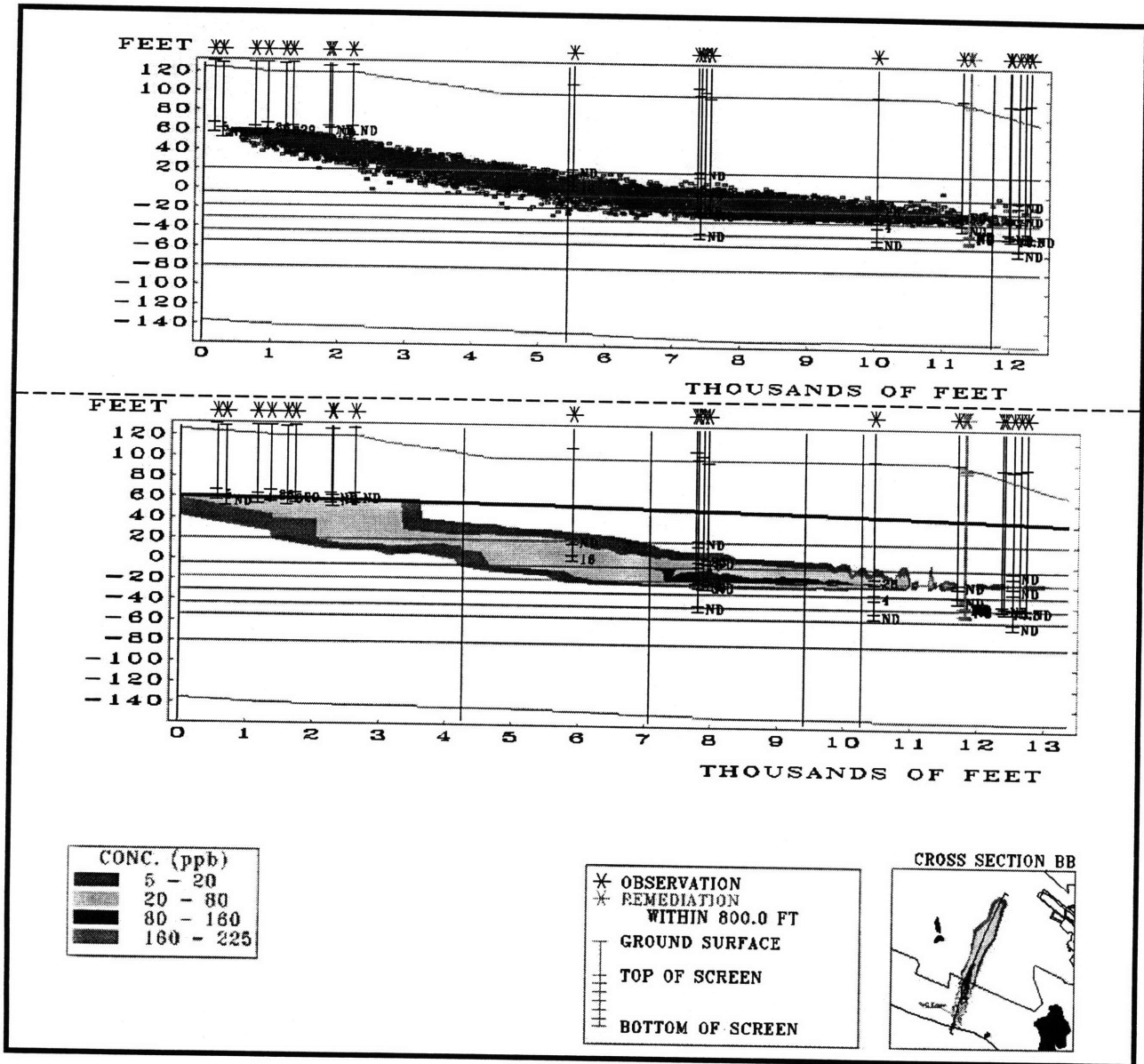*Figure A-5: Plan View of Maximum Concentration Contours*

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Figure A-6: North-South Cross Section of CS-4 Plume Showing Particle Distribution (top), Concentration Contours (bottom)

Table A-8: 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 are greater than the ones reported by ABB Environmental Services Inc.(1992b) (Table A-8). 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 applied field observations and site characterization data to a calibrated natural conditions model of the Cape Cod aquifer, and thus probably produced a more appropriate representation of the real plume. Nevertheless, there are many assumptions that are made and factors that are taken into account 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 actual plume. This suggests that site characterization should be improved in order to obtain a clearer understanding of the subsurface conditions.

A.3.3 Transport Simulations

The CS-4 plume model described above was used to simulate two different remediation alternatives. Both simulations were started with the plume as shown in Figure A-4 (in the simulation year 1993). These simulations attempted to forecast the clean-up times for the alternatives examined.

The first simulation was the no action 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; but of course, the model does not

realistically represent mixing, volatilization and degradation in the pond. 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. Acceptable levels were reached 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.

A.4 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. In order to calibrate the model under stress conditions, this aquifer test was simulated using the model.

A.4.1 Pumping Schemes for Remediation

The first step in the design of a pump and treat system is to determine the quantity of groundwater that must 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 simulated remedial system needs to consider this discharge as its minimum pumping rate.

a) Analysis of the capture zones under different pumping schemes

The particles which reach the well fence between 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 wells. This factor was important in the geometry of 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 rates.

b) Flexibility of the current well fence

The existing well fence was simulated. A particle tracking simulation using 13 wells, pumping a total flow rate of 140 gpm (530 L/min), located 60 feet apart, as in the existing well fence, was run.
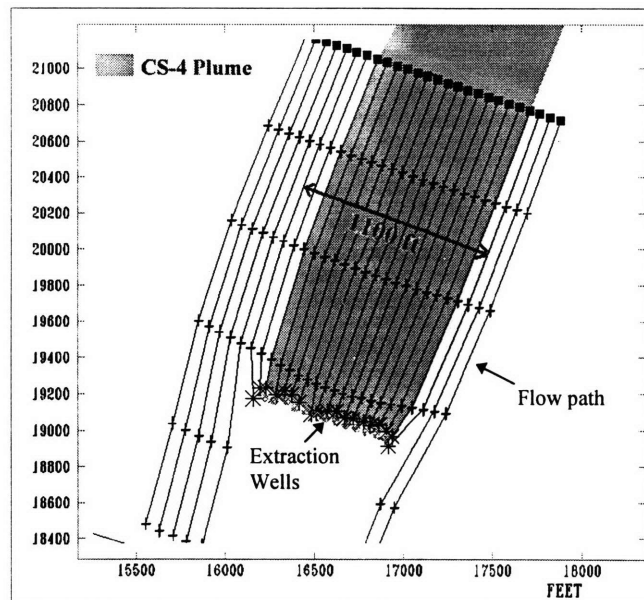
Figure A-7. Capture curve simulation of the IRP well fence.

The pumping rate and the number and spacing of wells in the existing well fence can be considered adequate (Figure A-7). In the horizontal view, a capture curve about 1,100 feet wide is observed. However, this horizontal view of the capture zone does not show 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 feet 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

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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 A-8 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 feet upgradient of the well fence.
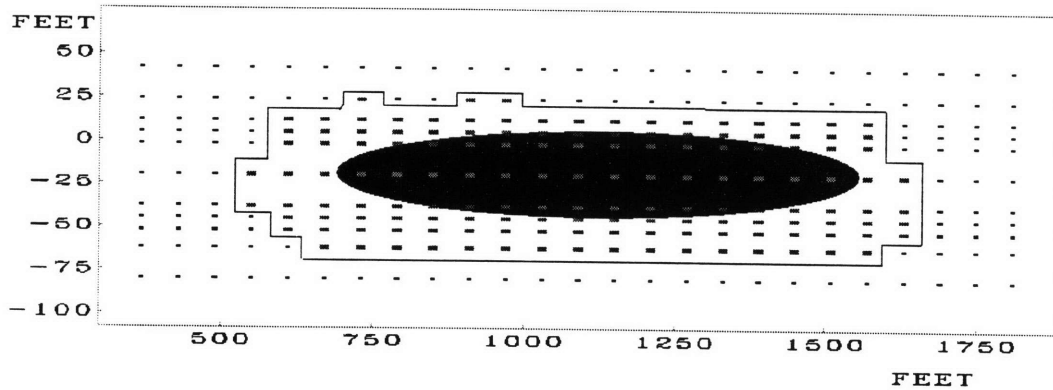
Figure A-8. Cross-sectional areas of the capture curve 1,500 feet upgradient of the 13-well system (IRP well fence).The capture curve is represented by the larger dots.

From the analysis of the cross-sectional area of the capture zone (Figure A-8), the pumping scheme is sufficient both vertically and horizontally to capture the plume. The capture zone was calculated to be approximately 250 feet wider and 25 feet 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 twice the cross-section area of the plume. This guarantees the removal of all contaminated water.

The simulated plume described in section A.3.2 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 with 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 by increasing the pumping rate. The 220 gpm pumping rate, however, would be enough to capture a plume with the dimensions of that simulated in this study (section A.3.2) pumping at a higher rate.

c) Prediction of an Alternative Pumping Scheme

After the analysis of the current 13-well fence, and the response of the aquifer to different pumping scenarios, the option of an alternative containment system was addressed. The different simulations run for this purpose are presented in Table A-9.

Table A-9. 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 the 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 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 A-9.
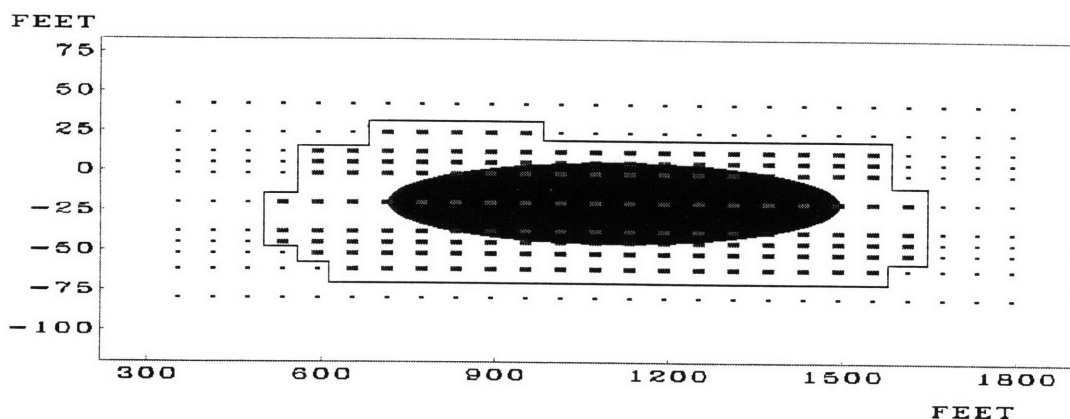
Figure A-9. Cross-sectional areas of the capture curve 1,500 feet upgradient of the 7-well system, pumping a total of 140 gpm. The capture curve is represented by the larger dots.

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, which is 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 feet 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.

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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.

A.5 Bioremediation

Bioremediation engineering is the application of biological process principles to the treatment of water or soil contaminated with hazardous substances (Cookson, 1995). 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 (3) use the subsurface as a bioreactor eliminating the need to pump the water to the surface for treatment; and (4) treat the contaminant "in place" causing minimal disturbance to the subsurface.

A.5.1 General Considerations

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. This generally requires the addition of a substrate, oxygen, and nutrients.

The engineering of the delivery systems and their control present the engineer more challenge than understanding the biochemical process. The main problem with traditional applications of in situ bioremediation is that the delivery of the added agents is in the liquid form resulting in displacement of the contaminated water and therefore inadequate mixing. This results to minimal biodegradation.

To overcome this problem, all agents of choice are added in the gaseous form. The injected gases move through the aquifer in discrete channels (Hayes, 1996) diffusing into the water on their way to the surface (carried by buoyancy). This creates a continuous source of the injected agent in the water.

A.5.2 Cometabolic Oxidation and Reductive Dechlorination

Xenobiotic compounds (i.e. foreign to natural biota) such as the chlorinated solvents found at the CS-4 site cannot be utilized by microorganisms for growth and energy (Nyer, 1992).

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The process of aerobic cometabolic oxidation has been proven to biodegrade TCE and other aliphatic compounds. Methane-oxidizing microorganisms have been found to be capable of cometabolically oxidizing TCE, DCE, and vinyl chloride (VC) in aerobic environments (Semprini et al., 1991).

PCE, however, can only be removed in anaerobic environments in a process termed reductive dechlorination. In this process, PCE loses a chlorine atom (turning into TCE) and achieves a lower oxidation state becoming susceptible to cometabolic oxidation.

A.5.3 Process Design

A successful bioremediation scheme for CS-4 should consist of an aerobic phase (for the treatment of TCE and DCE) and an anaerobic phase (for the treatment of PCE and TeCA). This design was incorporated in three phases (Figure A-10).

Horizontal wells were utilized to inject the gases. Horizontal wells are advantageous over vertical ones because they can extend along a wide plume replacing up to 10 wells (Parmentier
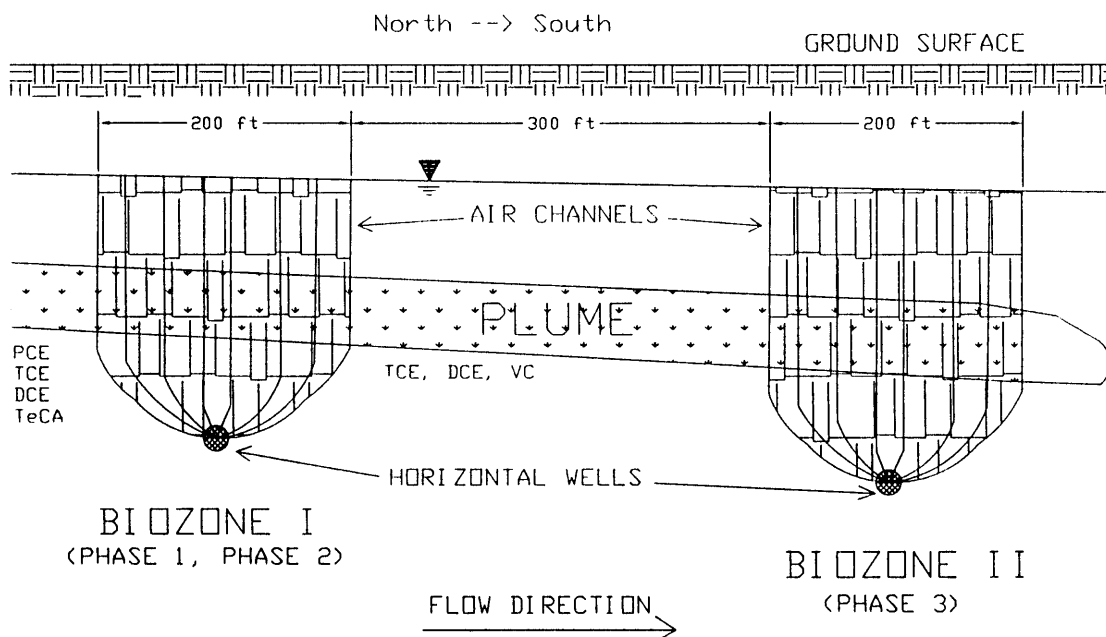
Figure A-10. North-south cross-section of the bioremediation scheme

and Klemovich, 1996). The area of influence of the injected gases creates a biozone where the treatment takes place. It was assumed that a methane concentration of 1 mg/L and DO concentration of 10 mg/L can be achieved in the biozone.

A pilot field test conducted at another site consisted the modeling basis of the aerobic cometabolic part of the system design at CS-4 (Semprini and McCarty 1991b, Semprini and McCarty 1992a). The reductive dechlorination estimations were based on lab studies as discussed by Collins (1996).

A.5.4 Phase 1

The objective of phase 1 was to stimulate microbial growth by injecting methane, air, and nutrients so a steady-state methanotrophic biomass (SSMB) concentration was reached.. Once SSMB was reached, phase 2 begins. It was calculated that it took about 5 days to create a SSMB of 5 mg/L.

A.5.5 Phase 2

Phase 2 was an anaerobic phase. Its objective was the removal of PCE and TeCA. To create an anaerobic environment, the injection of methane and nutrients was continued while the injection of air was stopped. This exerted a biochemical oxygen demand to the aquifer turning it anaerobic in about 2 days. The DO carried into the biozone by the water was consumed in just 2 ft. Collins (1996) calculated that under these conditions a 99% removal of PCE can be achieved if adequate residence time is allowed. Degradation of TeCA would also occur but it cannot be quantified due to lack of relevant studies in the literature. The residence time can be increased by the addition of horizontal wells which will extent the biozone by 200 ft per well. This corresponds to a residence time of 250 days per well since the seepage velocity is 0.8 ft/d (Lázaro, 1996).

A.5.6 Phase 3

Biozone II was placed downstream at a distance where no interference with biozone I would be possible (about 300 ft). In phase 3, methane and air were injected into the subsurface

to stimulate cometabolic oxidation of TCE, DCE, and VC (VC be a by-product of phase 2). The resulting normalized concentrations of the contaminants are shown in Table A-10).

Table A-10. Resulting normalized concentration of TCE, DCE, and VC.

	TCE	c-DCE	t-DCE	VC
k_{deg} (d^{-1})	0.014	0.068	1.36	1.36
t (d)	250	250	250	250
Cc/Cc_o	0.03	0	0	0

Figure A-11 shows the degradation of the contaminants within the biozone as a function of distance.
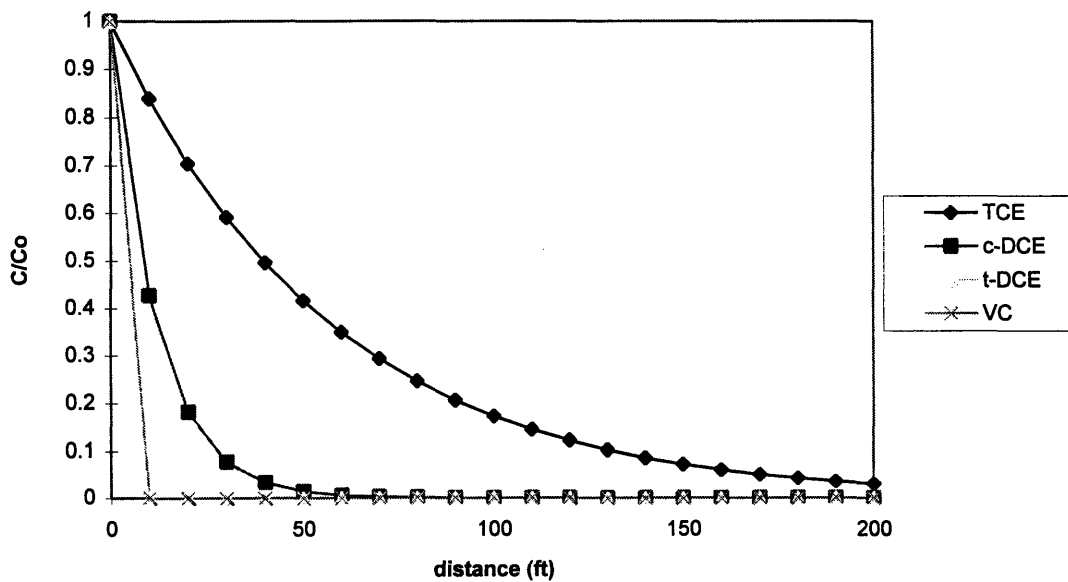
Figure A-11. Normalized contaminant concentrations as a function of distance.

A.5.7 Discussion

A 97% removal of TCE, 99 % removal of PCE, and complete removal of the rest of the contaminants (except TeCA for which no information exists) was achieved by this scheme. The

conditions required (1.0 mg/L methane aqueous concentration and 10.0 mg/L of DO) were assumed to be achievable in the field through proper engineering measures.

Field conditions are complex and hard to control. Factors affecting the in situ bioremediation of contaminants vary from site to site and caution must be given in the interpretation of the results obtained in this design. The contaminant removal calculated must serve for estimation purposes only. The mass transfer limitations and the spatial heterogeneity encountered at a site create conditions that cannot be adequately predicted by theoretical approaches. A pilot test is necessary to predict the efficacy of the system and to determine relative design parameters.

A.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 cost are relatively high. Principal cost contributions are due to the periodical exchange and reactivation of the exhausted carbon when the adsorption capacity of the carbon at equilibrium with the influent concentrations becomes depleted. A successful pump and treat remediation requires operation of the system over a long period of time (for CS-4 this is estimated as 70 to 75), thus 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 by reductive dehalogenation (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Gillham, 1996). It was examined whether this emerging, zero-valent iron technology could be combined with the existing GAC in order to reduce long-term operation costs (Figure A-12). This combination may be feasible implementation at the CS-4 site.
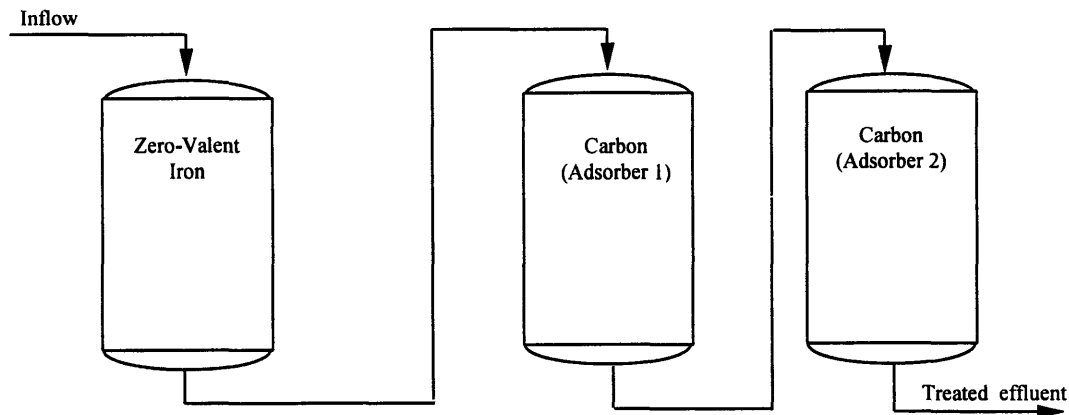
Figure A-12. Combination of Zero-Valent Iron with GAC (not to scale)

The basic concept is to pretreat the contaminated water by passing it through a 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, destroying part of the contaminants. The rest of the contaminants are adsorbed by the following GAC step. If enough contaminants are degraded before they enter the GAC columns, the carbon does not get exhausted as quickly and therefore carbon exchange and reactivation costs can be reduced. Assuming the innovative zero-valent iron technology is feasible, a comparison between investment (capital cost of zero-valent iron technology) and savings (reduction in carbon exchange costs) gives an indication of the worth of the concept.

A.6.1 Scenarios of inflow concentration

The size of the treatment facility depends on two major parameters. The first one is the flowrate of water that has to be treated and the second one is the characteristics of the contaminants and their concentrations. Since only about 20 samples determine the range of contaminant concentrations, there is large uncertainty regarding the concentrations. In order to understand the behavior of the treatment system with respect to different inflow concentrations, the following calculations were made for two different scenarios (Table A-11).

- Scenario 1: Assuming the maximum concentrations (e.g. PCE @ 62 ppb) throughout the whole plume. This scenario represents the worst case.

- Scenario 2: Assuming average concentrations (e.g. PCE @ 18 ppb) throughout the whole plume.

Table A-11. Four scenarios for influent concentrations

Contaminant of concern	Scenario 1: maximum concentrations (ppb)	Scenario 2: average concentration (ppb)
PCE	62	18
TCE	32	9.1
1,2-DCE	26	1.1
1,1,2,2-TeCA	24	6.8

A.6.2 Combination of Zero-Valent Iron and GAC

The build up of vinyl chloride (VC) as a result of the degradation of the chlorinated hydrocarbons by the iron was a major concern and was modeled using kinetic expressions. For scenario 1 it was shown that an increase of VC over regulatory limits must be expected if contact time of the contaminated water with the iron is more than 0.17 hr. Depending on the degradation rate of VC, a worst case increase up to 50 ppb was modeled. Therefore, the system was designed with a residence time of the water in the iron pores of 0.17 hr in order to impede excessive build up of VC. This residence time translates to a required bulk volume of iron of 500 ft^3. The build up of VC in scenario 2 is less due to lower initial PCE and TCE concentrations.

A comparison between expected cost with and without iron pretreatment (Table A-12) shows that no savings can be achieved due to the iron pretreatment at the CS-4 site. For scenario 1, a loss of $ 200,000 is expected. The main reason for this is the build up of vinyl chloride, which impedes longer residence times of the water in the iron pores. Therefore, the TCE concentration does not decrease enough to reduce carbon exchange cost. In scenario 2, the iron vessel is able to reduce all contaminants below their MCLs. While carbon exchange cost can be reduced to approximately zero, the capital cost of installing the iron vessel balance the savings in carbon cost.

Table A-12. Net savings yielding in combination of GAC with zero-valent iron.

	Scenario 1	Scenario 2
Savings: Present worth of carbon exchange cost ($)	500,000	200,000
Investment: ● Installation of zero-valent iron system ($) ● Carbon exchange for combination ($)	200,000 500,000	200,000 0
Total lifetime savings ($)	*-200,000*	*0*

Despite the uncertainty of some design parameters, the results indicates that for both conservative (scenario 1) and optimistic (scenario 2) concentration assumptions, no net savings can be expected.

A.6.3 Conclusions

The results indicate that the combination of granular activated carbon with zero-valent iron could be feasible, but would not result in a more economic aboveground treatment than the existing one. However, since the iron process is expected to progress in the near future, and since the combined system could be tested easily without major construction, it would be interesting to conduct a bench scale or a pilot test in order to verify the results.

The build up of VC due to reductive dehalogenation of PCE, TCE and DCE seems to be a major concern and must be taken into account in designing a zero-valent iron treatment system. This contrasts with the conclusions made in the literature (Gillham, 1996) for other sites, where zero-valent iron was implemented.

A.7 Risk

A.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 et al., 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 et al., 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 (ABB ES, 1992a) is used for this purpose. For a more detailed study see Picazo (1996).

A.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 A-13 shows the resulting concentrations.

Table A-13. 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 A-14).

Table A-14. 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

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The risks associated with the various schemes can be viewed graphically in Figures A-13 and A-14. The graphs 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.
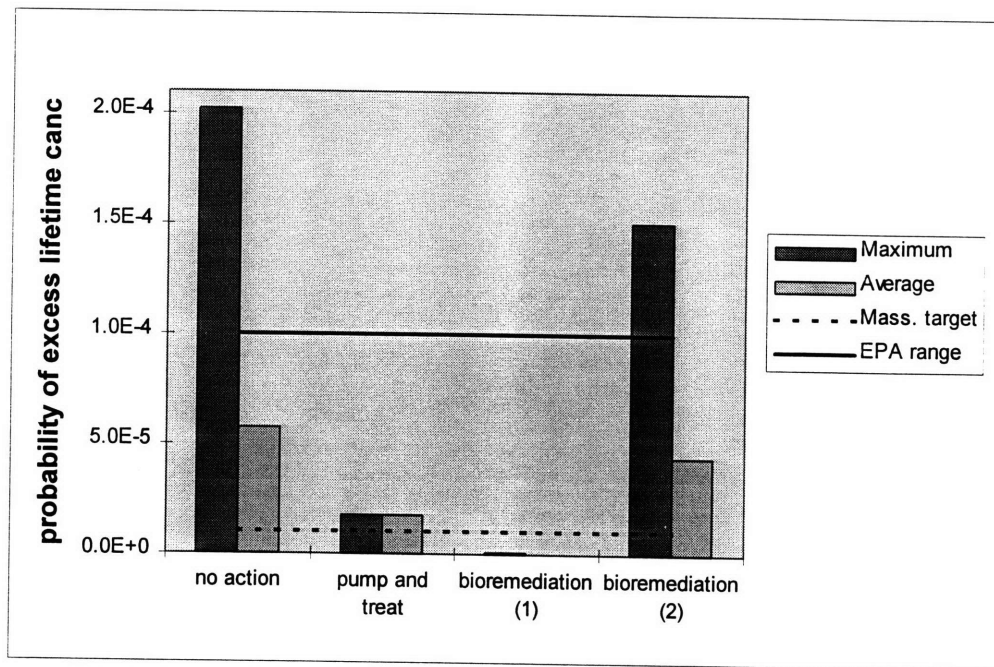
Figure A-13. Carcinogenic risk
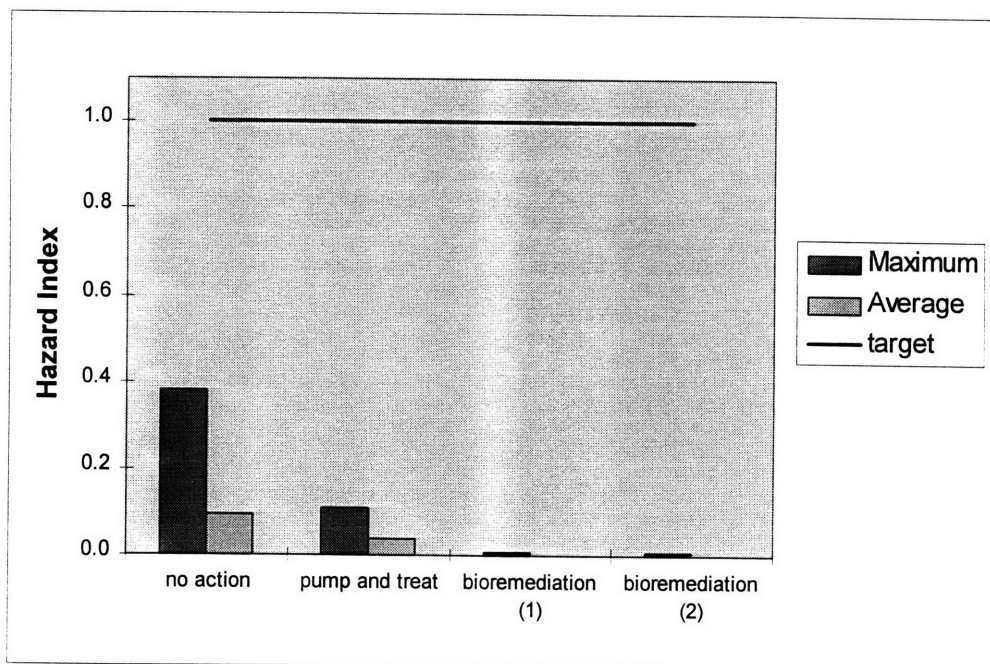
Figure A-14. Non-carcinogenic risk

A.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 A-13 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 A-14 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, and the bioremediation scheme (assuming satisfactory TeCA degradation). A pilot test will be useful in determining the actual TeCA degradation, as well as the actual degradation of the other contaminants. The bioremediation scheme which assumed complete TeCA removal results in the lowest calculated risk, but if this is true then use of pump and treat system to polish the cleanup 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. This 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.

Appendix B: Calculations

The risk calculations performed are tabulated below. These tables show the calculations for the inhaled concentration, the intake dosage, and the risk.

B.1 No Action Alternative

Table B-1. Inhaled concentrations, no action alternative

	PCE	TCE	DCE	TCA	
k_g	9.88E+2	1.11E+3	1.29E+3	9.82E+2	cm/hr
k_l	1.03E+1	1.16E+1	1.35E+1	1.02E+1	cm/hr
K_L	1.02E+1	1.13E+1	1.34E+1	6.18E+0	cm/hr
K_{al}	1.35E+1	1.50E+1	1.77E+1	8.18E+0	cm/hr
C_{wd} (max)	1.77E+1	1.00E+1	7.51E+0	4.44E+0	μg/L
C_{wd} (ave)	5.14E+0	2.84E+0	3.93E-1	1.26E+0	μg/L
S (max)	2.95E+1	1.67E+1	1.25E+1	7.40E+0	μg/m^3-min
S (ave)	8.57E+0	4.74E+0	6.55E-1	2.10E+0	μg/m^3-min
C_b (max)	2.97E+2	1.68E+2	1.26E+2	7.46E+1	μg/m^3
C_b (ave)	8.63E+1	4.78E+1	6.61E+0	2.11E+1	μg/m^3

Table B-2. Intake doses, no action alternative

		PCE	TCE	DCE	TCA
	μg/kg-day	**Carcinogenic**			
Inhalation	max	1.81E+0	1.02E+0	7.68E-1	4.54E-1
	ave	5.26E-1	2.91E-1	4.02E-2	1.29E-1
Ingestion	max	7.59E-1	3.92E-1	2.57E-1	2.94E-1
	ave	2.20E-1	1.11E-1	1.35E-2	8.33E-2
		Non-carcinogenic			
Inhalation	max	4.22E+0	2.39E+0	1.79E+0	1.06E+0
	ave	1.23E+0	6.78E-1	9.38E-2	3.00E-1
Ingestion	max	1.77E+0	9.14E-1	6.00E-1	6.86E-1
	ave	5.14E-1	2.60E-1	3.14E-2	1.94E-1

Table B-3. Risk calculations, no action alternative

		PCE	TCE	DCE	TCA	sum	total risk
		Carcinogenic					
Maximum	Inhalation	3.26E-6	6.13E-6		9.08E-5	1.00E-4	
	Ingestion	3.87E-5	4.31E-6		5.88E-5	1.02E-4	
							2.02E-4
Average	Inhalation	9.46E-7	1.74E-6		2.57E-5	2.84E-5	
	Ingestion	1.12E-5	1.23E-6		1.67E-5	2.91E-5	
	total	1.22E-5	2.97E-6		4.24E-5		5.75E-5
		Non-carcinogenic					
Maximum	Inhalation						
	Ingestion	1.77E-1	1.31E-1	7.43E-2		3.82E-1	
							3.82E-1
Average	Inhalation						
	Ingestion	5.14E-2	3.71E-2	3.14E-3		9.17E-2	
							9.17E-2

B.2 Pump and Treat Scheme

Table B-4. Inhaled concentrations, pump and treat scheme

	PCE	TCE	DCE	TCA	
k_g	9.88E+2	1.11E+3	1.29E+3	9.82E+2	cm/hr
k_l	1.03E+1	1.16E+1	1.35E+1	1.02E+1	cm/hr
K_L	1.02E+1	1.13E+1	1.34E+1	6.18E+0	cm/hr
K_{al}	1.35E+1	1.50E+1	1.77E+1	8.18E+0	cm/hr
C_{wd} (max)	1.43E+0	1.56E+0	7.51E+0	3.70E-1	μg/L
C_{wd} (ave)	1.43E+0	1.56E+0	3.93E-1	3.70E-1	μg/L
S (max)	2.38E+0	2.60E+0	1.25E+1	6.17E-1	μg/m^3-min
S (ave)	2.38E+0	2.60E+0	6.55E-1	6.17E-1	μg/m^3-min
C_b (max)	2.40E+1	2.62E+1	1.26E+2	6.21E+0	μg/m^3
C_b (ave)	2.40E+1	2.62E+1	6.61E+0	6.21E+0	μg/m^3

Table B-5. Intake dose, pump and treat scheme

		PCE	TCE	DCE	TCA
	μg/kg-day	Carcinogenic			
Inhalation	max	1.46E-1	1.60E-1	7.68E-1	3.78E-2
	ave	1.46E-1	1.60E-1	4.02E-2	3.78E-2
Ingestion	max	6.12E-2	6.12E-2	2.57E-1	2.45E-2
	ave	6.12E-2	6.12E-2	1.35E-2	2.45E-2
		Non-carcinogenic			
Inhalation	max	3.41E-1	3.73E-1	1.79E+0	8.83E-2
	ave	3.41E-1	3.73E-1	9.38E-2	8.83E-2
Ingestion	max	1.43E-1	1.43E-1	6.00E-1	5.71E-2
	ave	1.43E-1	1.43E-1	3.14E-2	5.71E-2

Table B-6. Risk calculations, pump and treat scheme

		PCE	TCE	DCE	TCA	sum	total risk
		Carcinogenic					
Maximum	Inhalation	2.63E-7	9.58E-7		7.56E-6	8.79E-6	
	Ingestion	3.12E-6	6.73E-7		4.90E-6	8.69E-6	
							1.75E-5
Average	Inhalation	2.63E-7	9.58E-7		7.56E-6	8.79E-6	
	Ingestion	3.12E-6	6.73E-7		4.90E-6	8.69E-6	
	total	3.39E-6	1.63E-6		1.25E-5		1.75E-5
		Non-carcinogenic					
Maximum	Inhalation						
	Ingestion	1.43E-2	2.04E-2	7.43E-2		1.09E-1	
							1.09E-1
Average	Inhalation						
	Ingestion	1.43E-2	2.04E-2	3.14E-3		3.78E-2	
							3.78E-2

B.3 Bioremediation

Table B-7. Inhaled concentrations, bioremediation (1)

	PCE	TCE	DCE	TCA	
k_g	9.88E+2	1.11E+3	1.29E+3	9.82E+2	cm/hr
k_l	1.03E+1	1.16E+1	1.35E+1	1.02E+1	cm/hr
K_L	1.02E+1	1.13E+1	1.34E+1	6.18E+0	cm/hr
K_{al}	1.35E+1	1.50E+1	1.77E+1	8.18E+0	cm/hr
C_{wd} (max)	1.77E-1	3.00E-1	0.00E+0	0.00E+0	μg/L
C_{wd} (ave)	5.14E-2	8.53E-2	0.00E+0	0.00E+0	μg/L
S (max)	2.95E-1	5.00E-1	0.00E+0	0.00E+0	μg/m^3-min
S (ave)	8.57E-2	1.42E-1	0.00E+0	0.00E+0	μg/m^3-min
C_b (max)	2.97E+0	5.04E+0	0.00E+0	0.00E+0	μg/m^3
C_b (ave)	8.63E-1	1.43E+0	0.00E+0	0.00E+0	μg/m^3

Table B-8. Intake dose, bioremediation (1)

		PCE	TCE	DCE	TCA
	μg/kg-day	Carcinogenic			
Inhalation	max	1.81E-2	3.07E-2	0.00E+0	0.00E+0
	ave	5.26E-3	8.72E-3	0.00E+0	0.00E+0
Ingestion	max	7.59E-3	1.18E-2	0.00E+0	0.00E+0
	ave	2.20E-3	3.34E-3	0.00E+0	0.00E+0
		Non-carcinogenic			
Inhalation	max	4.22E-2	7.16E-2	0.00E+0	0.00E+0
	ave	1.23E-2	2.03E-2	0.00E+0	0.00E+0
Ingestion	max	1.77E-2	2.74E-2	0.00E+0	0.00E+0
	ave	5.14E-3	7.80E-3	0.00E+0	0.00E+0

Table B-9. Risk calculations, bioremediation (1)

		PCE	TCE	DCE	TCA	sum	total risk
		Carcinogenic					
Maximum	Inhalation	3.26E-8	1.84E-7			2.17E-7	
	Ingestion	3.87E-7	1.29E-7			5.16E-7	
							7.33E-7
Average	Inhalation	9.46E-9	5.23E-8			6.18E-8	
	Ingestion	1.12E-7	3.68E-8			1.49E-7	
	total	1.22E-7	8.91E-8				2.11E-7
		Non-carcinogenic					
Maximum	Inhalation						
	Ingestion	1.77E-3	3.92E-3			5.69E-3	
							5.69E-3
Average	Inhalation						
	Ingestion	5.14E-4	1.11E-3			1.63E-3	
							1.63E-3

Table B-10. *Inhaled concentrations, bioremediation (2)*

	PCE	TCE	DCE	TCA	
k_g	9.88E+2	1.11E+3	1.29E+3	9.82E+2	cm/hr
k_l	1.03E+1	1.16E+1	1.35E+1	1.02E+1	cm/hr
K_L	1.02E+1	1.13E+1	1.34E+1	6.18E+0	cm/hr
K_{al}	1.35E+1	1.50E+1	1.77E+1	8.18E+0	cm/hr
C_{wd} (max)	1.77E-1	3.00E-1	0.00E+0	4.44E+0	μg/L
C_{wd} (ave)	5.14E-2	8.53E-2	3.58E-1	1.26E+0	μg/L
S (max)	2.95E-1	5.00E-1	0.00E+0	7.40E+0	μg/m^3-min
S (ave)	8.57E-2	1.42E-1	5.96E-1	2.10E+0	μg/m^3-min
C_b (max)	2.97E+0	5.04E+0	0.00E+0	7.46E+1	μg/m^3
C_b (ave)	8.63E-1	1.43E+0	6.00E+0	2.11E+1	μg/m^3

Table B-11. *Intake dose, bioremediation (2)*

		PCE	TCE	DCE	TCA
	μg/kg-day	Carcinogenic			
Inhalation	max	1.81E-2	3.07E-2	0.00E+0	4.54E-1
	ave	5.26E-3	8.72E-3	3.66E-2	1.29E-1
Ingestion	max	7.59E-3	1.18E-2	0.00E+0	2.94E-1
	ave	2.20E-3	3.34E-3	1.22E-2	8.33E-2
		Non-carcinogenic			
Inhalation	max	4.22E-2	7.16E-2	0.00E+0	1.06E+0
	ave	1.23E-2	2.03E-2	8.53E-2	3.00E-1
Ingestion	max	1.77E-2	2.74E-2	0.00E+0	6.86E-1
	ave	5.14E-3	7.80E-3	2.86E-2	1.94E-1

Table B-12. *Risk calculations, bioremediation (2)*

		PCE	TCE	DCE	TCA	sum	total risk
		Carcinogenic					
Maximum	Inhalation	3.26E-8	1.84E-7		9.08E-5	9.10E-5	
	Ingestion	3.87E-7	1.29E-7		5.88E-5	5.93E-5	
							1.50E-4
Average	Inhalation	9.46E-9	5.23E-8		2.65E-5	2.65E-5	
	Ingestion	1.12E-7	3.68E-8		1.71E-5	1.73E-5	
	total	1.22E-7	8.91E-8		4.36E-5		4.38E-5
		Non-carcinogenic					
Maximum	Inhalation						
	Ingestion	1.77E-3	3.92E-3			5.69E-3	
							5.69E-3
Average	Inhalation						
	Ingestion	5.14E-4	1.11E-3			1.63E-3	
							1.63E-3

B.4 Data in Graphs

Tables B-13, B-14 and B-15 contain the data points that are plotted in Figures 7-1, 7-2, 7-3 and 7-4.

Table B-13. Summary of risk (plotted in Figures 7-1 and 7-2)

	Carcinogenic risk		Non-carcinogenic risk	
	Maximum	Average	Maximum	Average
no action	2.02E-4	5.75E-5	3.82E-1	9.17E-2
pump and treat	1.75E-5	1.75E-5	1.09E-1	3.78E-2
bioremediation (1)	7.33E-7	2.11E-7	5.69E-3	1.63E-3
bioremediation (2)	1.50E-4	4.38E-5	5.69E-3	1.63E-3

Table B-14. Breakdown of contribution to risk by chemical (plotted in Figure 7-3)

	PCE	TCE	TeCA
no action	1.22E-5	2.97E-6	4.24E-5
pump and treat	3.39E-6	1.63E-6	1.25E-5
bioremediation (1)	1.22E-7	8.91E-8	
bioremediation (2)	1.22E-7	8.91E-8	4.36E-5

Table B-15. Breakdown of contribution to risk by pathway (plotted in Figure 7-4)

	no action	pump and treat	bioremediation (1)	bioremediation (2)
Inhalation	2.84E-5	8.79E-6	6.18E-8	2.65E-5
Ingestion	2.91E-5	8.69E-6	1.49E-7	1.73E-5