Design of a Sequential *In-Situ* Anaerobic/Aerobic Enhanced Bioremediation System for a Chlorinated Solvent Contaminated Plume

by

Michael M. Collins

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Signature of Author ....

Michael M. Collins
May 10, 1996

Certified by .

Lynn W. Gelhar
or, Civil and Environmental Engineering
Thesis Supervisor

Accepted by ....

Joseph M. Sussman
Chairman, Departmental Committee on Graduate Studies

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Abstract

Bioremediation is a term which refers to the degradation of chemicals in the environment by microorganisms. This process has been harnessed by man in the form of enhanced bioremediation technologies which stimulate the growth of microbes in the subsurface in order to destroy pollution *in-situ*. These systems typically utilize a number of vertical wells to pump water amended with nutrients to enhance microbial activity into the aquifer. This type of scheme is often costly and ineffective at removing all of the pollution in the ground.

Horizontal well drilling has emerged as a new technology in environmental remediation and promises to be an important tool in the future. These wells can be drilled to follow the course of a plume or to cut underneath and across it. Gaseous nutrients can be injected beneath a plume and allowed to diffuse into it and stimulate microbial degradation of contaminants within it.

A gaseous enhanced biodegradation system is designed to treat a plume of chlorinated solvents emanating from the main base landfill at the Massachusetts Military Reservation on Cape Cod, Massachusetts by injecting gases to create a treatment zone into which the plume will migrate as a result of the ambient groundwater flow. The system is designed in two sequential stages; an anaerobic stage to treat tetrachloroethylene (PCE), which is resistant to aerobic degradation, and an aerobic stage to degrade the trichloroethylene (TCE), cis-dichloroethylene (c-DCE), trans-dichloroethylene (t-DCE), and vinyl chloride (VC) within the plume.

The major conclusion of this design study is that a system of this type can potentially treat the groundwater so that the concentrations of chlorinated solvents within it are reduced below drinking water maximum contaminant levels (MCLs). The system also promises to be less costly than other remediation options, though a pilot study will be necessary to determine the operating characteristics of the system and its efficacy in the field.

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

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1.0 Introduction

This thesis is part of a group research project undertaken to characterize environmental impacts of groundwater contamination emanating from the Main Base Landfill at the Massachusetts Military Reservation [MMR], located at Cape Cod, Massachusetts. The United States Environmental Protection Agency placed the MMR on the Superfund National Priorities List (NPL) in 1989. The goal of the work presented hereafter was to design an innovative bioremediation system to clean up a plume of chlorinated solvents at the MMR. This work was conducted in conjunction with and based in part on the results of the members of the group who focused on other areas of interest relevant to the site.

The objective of this thesis is to design an innovative enhanced bioremediation system to treat a plume of PCE and TCE contaminated groundwater that emanates from the landfill. The system integrates several different innovative concepts and technologies into its overall design. It is comprised of two distinct treatment phases, an anaerobic phase and an aerobic phase, which have never been combined into a single *in-situ* treatment scheme. In addition, biodegradation will be enhanced within the treatment zones through the injection of gaseous nutrients from a series of horizontal injection wells which will be placed below and perpendicular to the plume's path. This type of system has been used before in remediation actions but it is still a relatively new technology. The work presented hereafter demonstrates that a sequential bioremediation system utilizing gaseous nutrient injection via horizontal wells is a potential *in-situ* treatment solution for the chlorinated solvent plume, and that this system has several operational and cost advantages over other treatment and containment options.

2.0 Background and Site Description

2.1 Upper Cape Geography and Land Use

The Massachusetts Military Reservation (MMR) is located in the northwestern portion of Cape Cod, Massachusetts, covering an area of approximately 30 square miles (ABB, 1992(a)). See Figure 1 for regional and base maps. Military use of the MMR began in the early 1900's, and may generally be categorized as mechanized forces training and military aircraft operations. Since commencement of military operations, the base has seen use by several branches of the armed services, including the United States Air Force, Army, Navy, Coast Guard, and the Massachusetts Air National Guard. Operations by the Air National Guard and Coast Guard are ongoing.

The area of present study is the Main Base Landfill site, termed LF-1 by the MMR Installation Restoration Program. The landfill is about 10,000 feet from the western and southern MMR boundaries and occupies approximately 100 acres. The landfill has operated since the early 1940's as the primary waste disposal facility at MMR (CDM Federal, 1995). Unregulated disposal of waste at LF-1 continued until 1984, at which time disposal began to be regulated by the Air National Guard.

Waste disposal operations at LF-1 took place in five distinct disposal cells and a natural kettle hole, as shown in Figure 2. These are termed the 1947, 1951, 1957, 1970, post-1970, and kettle hole cells. The date designations indicate the year in which disposal operations ceased at that particular cell. Accurate documentation of the wastes deposited at LF-1 does not exist. The wastes may include any or all of the following: general refuse, fuel tank sludge, herbicides, solvents, transformer oils, fire extinguisher fluids, blank small arms ammunition, paints, paint thinners, batteries, DDT powder, hospital wastes, municipal sewage sludge, coal ash, and possibly live ordnance (ABB, 1992(a)). Wastes were deposited
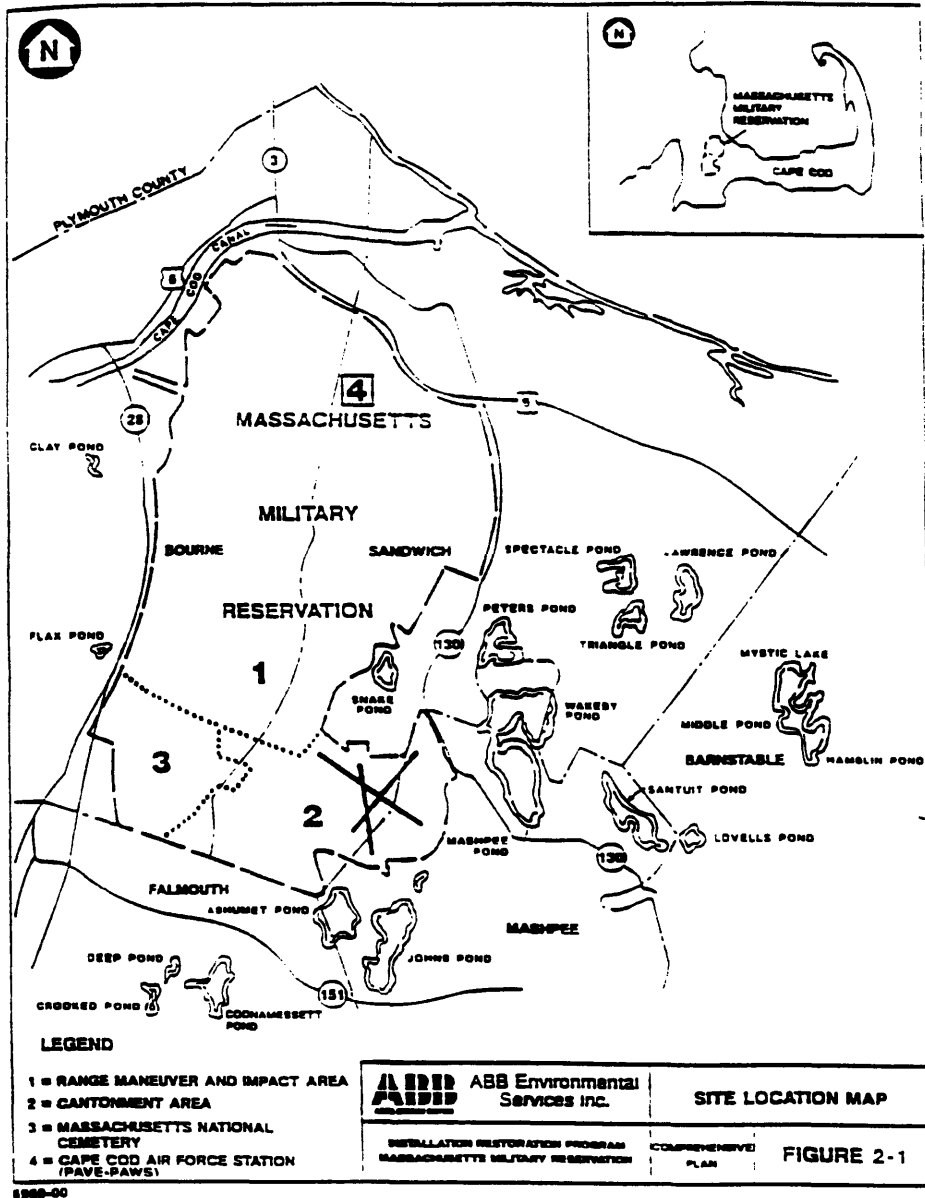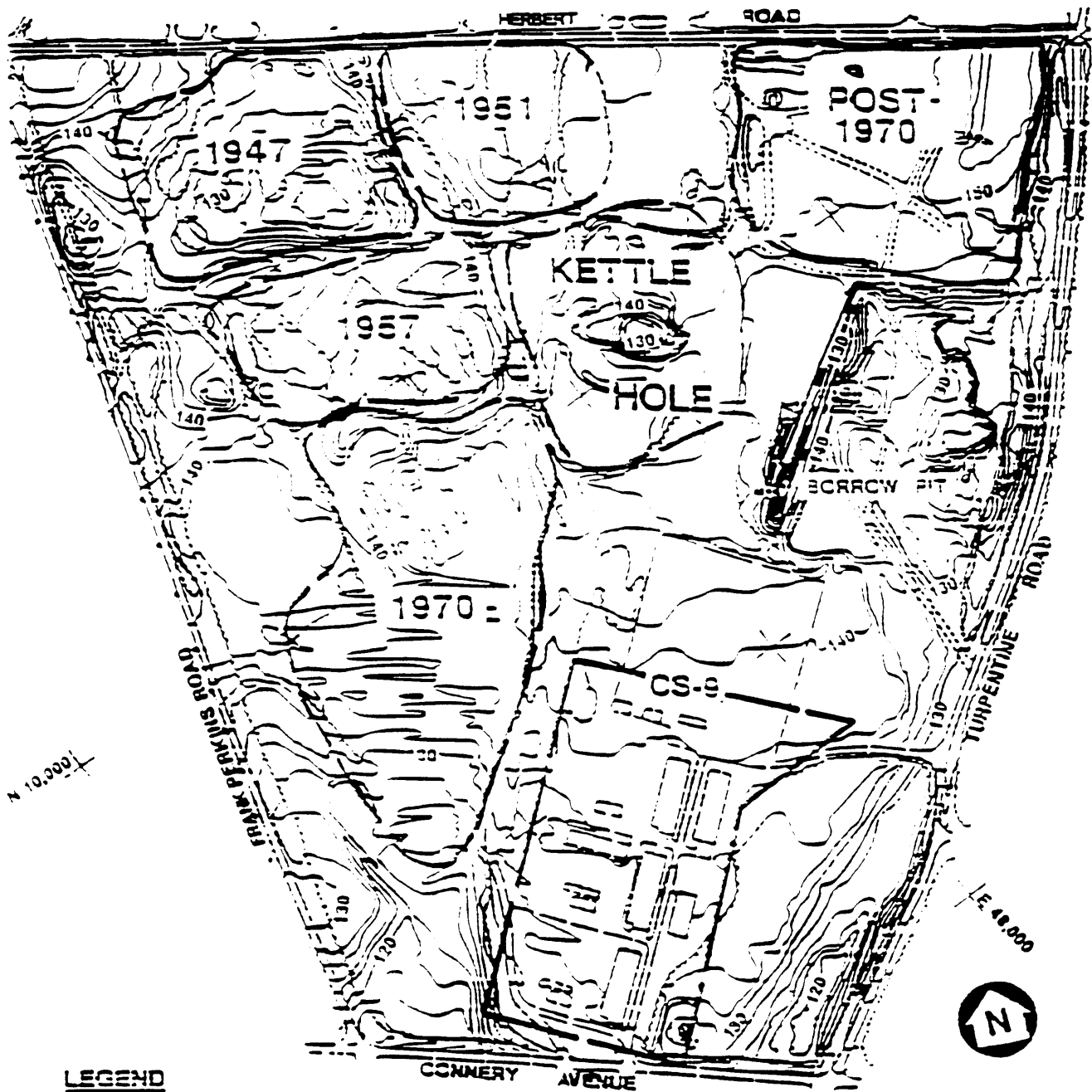
Figure 1: Site Location Map (ABB, 1992(a))
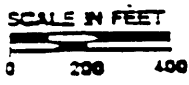
Figure 2: Photogrammetric Map of Landfill Layout (ABB, 1992(a))

in linear trenches, and covered with approximately 2 feet of native soil. Waste depth is uncertain, but estimated to be approximately 20 feet below the ground surface on average. Waste disposal at the landfill ceased in 1990. A plume of dissolved chlorinated volatile organic compounds, primarily tetrachloroethylene (PCE) and trichloroethylene (TCE), has developed in the aquifer downgradient of the landfill.

The four towns of interest on the western Cape are Bourne, Sandwich, Mashpee, and Falmouth. The total population of this area, according to 1994 census, is 67,400. The area is mostly residential, with some small industry. A significant amount of economic activity is associated with restaurants, shops, and other tourist-type industry. The total population of Cape Cod is estimated to triple in summer, when summer residents and tourists make up most of the population. The total base population has doubled in the last twenty years. Cape Cod has been one of the fastest growing areas in New England. In 1986, 27% of economic activity was attributed to retirees; tourism accounted for 26%; seasonal residents, 22%; manufacturing, 10%; and business services (fishing, agriculture, and other), 15%. The economy is currently experiencing a shift from seasonal to year-round jobs. (Cape Cod Commission, 1996).

2.2 Climate

The Cape Cod climate is categorized as a humid, continental climate. Average wind speeds range from 9 mph from July through September to 12 mph from October through March. Precipitation is fairly evenly distributed, with an average of approximately 4 inches per month. Average annual precipitation is approximately 47 inches. There is very little surface runoff. Approximately 40% of the precipitation infiltrates the ground and enters the groundwater system (CDM Federal, 1995).

2.3 Geology

The Cape Cod Basin consists of material deposited as a result of glacial action during the Wisconsinian stage between 7000 and 80,000 years ago. Advancing glaciers from the north transported rock debris gouged from the underlying bedrock until reaching the southernmost point of advance at Martha's Vineyard and Nantucket Island. The glacial action also resulted in a thin layer of basal till being deposited over the bedrock. The entire sedimentation process occurred as a sequence of glacial deposition, erosion and re-deposition. In later periods, the glaciers melted, receded, and reached a stagnation point near the western and northern shores of Cape Cod. The remaining glacial till was deposited there and formed the Buzzards Bay and Sandwich moraines. The present day Sandwich Moraine is thought to be of glacio-tectonic origin, due to pro-glacial sediments being thrusted over older morainal deposits during a readvance of the Cape Cod Bay glacier (Oldale 1984).

The regional geology in the LF-1 study area can be classified into three main sedimentary types. These are the Buzzards Bay and Sandwich moraines (BBM and SM), the Mashpee Pitted Plain (MPP) and the Buzzards Bay Outwash (BBO). The geographic distribution of these materials is depicted in Figure 3. The MPP consists of stratified coarse to fine grained sands that were transported from the melting Buzzards Bay and Cape Cod Bay ice sheets, and deposited over a bed of fine-grained glacio-lacustrine sediments and basal till. The general trends in the glacial outwash deposits in terms of grain size are coarsening upwards and fining north to south. The thickness of the coarse material decreases north to south, as the distance from the outwash source increases.

The morainal sediments were deposited directly as the ice-sheets melted. Thus, these deposits are not stratified like the MPP glacial outwash and are thought to occur in layers of poorly sorted sediment-flow deposits and finer till material. These sandy sediments overlie a fining sequence of sand, silt, clay and basal till. The unsorted glacial till that comprise the BBM ranges in size from boulders to fine

clays. This complex heterogeneity leads to wide variations in observed hydrogeological parameters in the moraine. A general trend of fining in material size results in lower hydraulic conductivities (LeBlanc, 1986).

The Buzzards Bay Outwash (BBO) was deposited as a result of sedimentation between the retreating ice sheets and the newly deposited Buzzards Bay Moraine. BBO sediments are generally sand and gravel, and are considered to be stratified in the same manner as the MMP outwash, with a general trend of fining downwards.

The geologic structure described above lies atop a Paleozoic crystalline bedrock. The bedrock contours range in depth from 70 to 500 feet below sea level (Oldale, 1984). The bedrock is of a much lower hydraulic conductivity than the surrounding sediments, and therefore acts as an impermeable barrier to groundwater flow and thus forms the bottom boundary of the Cape Cod aquifer.

2.4 Groundwater System

Cape Cod is underlain by a large, unconfined groundwater flow system. This phreatic aquifer has been designated a sole source aquifer by the Federal Environmental Protection Agency. The aquifer is divided into six flow cells according to the hydraulic boundaries of the flow system. The Massachusetts Military Reservation and LF-1 plume are located in the west Cape flow cell, the largest of the six flow cells. The aquifer system and water table contours in the west Cape region are depicted in Figure 4.

The water table in this region occurs at a depth of 40-80 feet below the ground surface. Surface water is also present in the study area as intermittent streams in drainage swales and, more importantly, as ponds in kettle holes on the Mashpee Pitted Plain. However, there are a few large kettle ponds that can significantly influence the flow regime near the LF-1 site and plume. Cranberry bogs can also occur at

surface discharges of groundwater, but it is thought that the cranberry bogs west of the LF-1 site are underlain by localized perched water tables, and thus hydrologically disconnected from the larger aquifer system (CDM Federal, 1995). This fact, and the depth of the contaminant plume near these cranberry bogs makes it unlikely that contaminants from LF-1 will discharge into these important agricultural areas.

2.4.1 Vertical Hydraulic Gradients

Vertical gradients that have been calculated for the LF-1 site are very small. Most gradients calculated in the IRP hydrologic investigations were below the survey accuracy threshhold. Significant upward vertical gradients do exist where groundwater discharges into large ponds and near coastal areas where the aquifer discharges into the ocean. Small downward gradients of about 10^{-3} to 10^{-4} ft/ft are observed throughout the rest of the study area (CDM Federal, 1995). Such vertical gradients generally indicate upward flow near the shoreline and surface water bodies and downward flow elsewhere.

2.4.2 Horizontal Hydraulic Gradients

Groundwater flow in the region is driven mostly by horizontal gradients. These can be measured by dividing a groundwater elevation contour interval by the horizontal distance between the contours. The latter value can be estimated from a contour map similar to Figure 4. Horizontal gradients calculated for the LF-1 study area using February 1994 water levels range from 1.3×10^{-3} to 6.8×10^{-3} ft/ft (CDM Federal, 1995). These gradients are observed to steepen from the LF-1 source area westwards.

2.4.3 Seepage Velocity

Calculated seepage velocities in the LF-1 study area indicate that advective contaminant transport takes place at velocities ranging from 0.10 ft/day to over 3 ft/day. Since seepage velocity is a function of hydraulic conductivity, the differential permeabilities of the various sediment types strongly influence

calculation of seepage velocities at this site. An estimate of seepage velocity of contaminants made using observed LF-1 plume migration distance and time yielded an average seepage velocity of 0.9 ft/day (CDM Federal, 1995).

2.5 MMR's Listing on the National Priorities List

The MMR is one of 1,236 sites that have been placed on the National Priority List (NPL) by the U.S. Environmental Protection Agency (EPA). NPL sites are those to which the EPA has given particularly high human health and environmental risk ranking. Rankings are determined from an evaluation of the relative risk to public health and the environment from hazardous substances identified in the air, water and geologic surroundings local to a site. Once placed on the NPL, sites are targeted for remedial clean-up financed by the Superfund, which is the federal government's fiduciary and political device for remediating hazardous waste sites. Additional funding for cleanup is provided by potentially responsible parties (PRPs), those individuals and organizations whose activities have resulted in contamination.

2.6 Present Activity

Due to the health and environmental risks which have been attributed to activities at the MMR, federal activity is underway to further quantify and reduce, to the extent required, the risk imposed upon human health and the environment. As part of remediation operations at MMR, several of the landfill cells have recently been secured with a final cover system. These cells include the 1970 cell, the post-1970 cell, and the kettle hole. The remaining cells (1947, 1951, and 1957) have collectively been termed the Northwest Operable Unit (NOU). Remedial investigations as to the necessity of a final closure system for these cells is ongoing. Other IRP activities associated with the LF-1 site include design of a plume containment system and further plume delineation and groundwater modeling.

BHW
239

200 —

Fine to coarse sand;
gravel

Dense sandy till; silt

100 —

Dense sandy till; gravel;
boulders

SEA
LEVEL

Clayey till; silt; lenses
of clay

100 —

Fine to medium sand;
gravel
Sand with boulders
Silty clay

A1W
314

SEA
LEVEL

Sandy, gravelly poorly sorted
till; silt and clay lenses.
pebbles and cobbles

100 —

Interbedded sandy and clayey
silt; clay layers; scattered
thin sand and gravel lenses
Fine to coarse sand; some
gravel, silt, and pebbles
Very dense bouldery till or
weathered bedrock

200 —

SM

MPP

BHW
212

100 —

SEA
LEVEL

Sandy, gravelly till; lenses of
silty sand and clay; numerous
cobbles and boulders
Dense silty, clayey till; lenses
of dense silty clay; lenses
of sand and gravel

100 —

Fine to very coarse sand and
gravel; some silty sand

Bouldery till
Bedrock

BBM →

BOURNE

BBO →

41°40' +

BUZZARDS
BAY

FSW
322

SEA
LEVEL

Fine to coarse sand; some silt
gravel, cobbles, boulders
Silty fine to medium sand
Interbedded fine to coarse sand.
silty fine sand, and clayey silt
Fine to coarse sand; some silty
and gravelly sand; zones of
cobbles and boulders

100 —

Bedrock

70°49'

MIW
26

SEA
LEVEL

Fine to very coarse sand;
gravel

100 —

200 —

Fine to coarse sand; some
very fine sand

300 —

Very fine to medium sand

400 —

Sandy till, some silt and
clay; gravel; pebbles

BBM- Buzzards Bay Moraine
BBO- Buzzards Bay Outwash
MPP-Mashpee Pitted Plain
SM- Sandwich Moraine

Figure 3: West Cape Cod Glacial Deposits
(Automated Sciences, 1994)
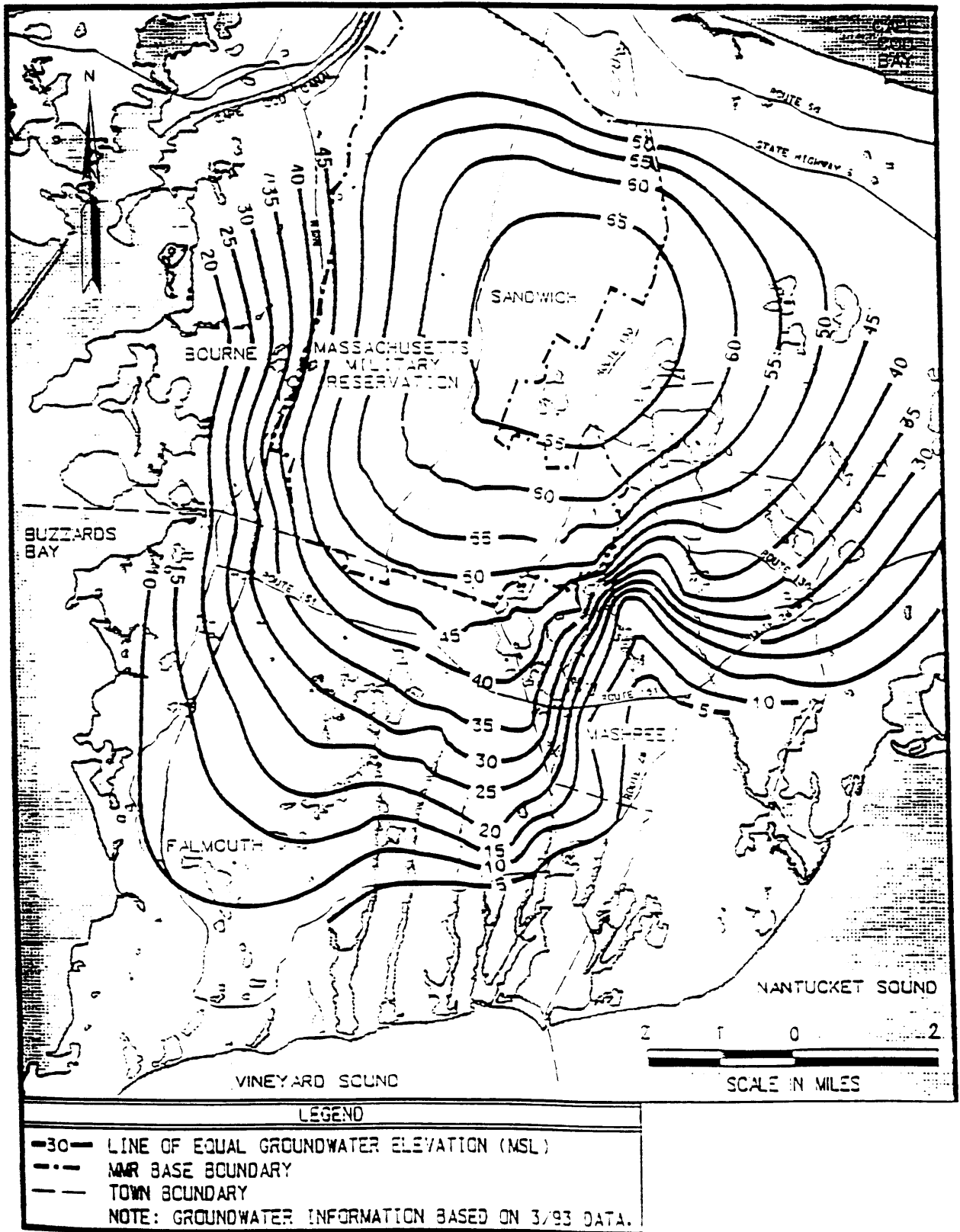
Figure 4: MMR Groundwater Contour Map
(Automated Sciences, 1994)

3.0 The Sequential *In-Situ* Bioremediation System

Conventional *in-situ* bioremediation schemes involve driving numerous vertical wells into a contaminated plume of groundwater. Water is then withdrawn from the aquifer, amended with oxygen and nutrients to promote microbial growth, and reinjected into the ground (O'Brien & Gere Engineers Inc., 1995). In this way, engineers hope to mix the nutrients evenly into the subsurface so that microbes throughout the plume are stimulated and feed upon the contaminants in the water and soil. There are many problems with this approach. When water is reinjected into the aquifer, it tends to displace water that is in its path rather than mixing with it. Furthermore, in many environmental situations, some portion of the chemicals contaminating the groundwater are sorbed into the aquifer materials (Domenico and Schwartz, 1990). They remain locked deep within the matrix of the soils and are therefore not metabolized by microorganisms. These sorbed chemicals are eventually released over time and can continue to pollute the aquifer long after a remediation action has been completed.

This thesis proposes a design for an innovative enhanced bioremediation technique that involves the use of a series of horizontal wells to inject gaseous nutrients and oxygen into the chlorinated solvent plume emanating from the landfill at the MMR. The wells will be driven below the plume so that the gas will flow up in channels and diffuse out into the aquifer water, stimulating the growth of microorganisms that will feed on the contaminants in the plume. The system is a passive system so that biodegradation will take place as the plume flows over the wells and through the biozones that they create. This offers a distinct advantage over standard *in-situ* bioremediation systems because it avoids the high pumping costs associated with the continued withdrawal and recirculation of contaminated groundwater.

The flow-through bioremediation system will use multiple horizontal injection wells to create two biozones, one located downgradient of the other. This design is necessary because the LF-1 plume

contains concentrations of PCE that exceed Federally mandated drinking water standards (ABB Environmental, 1992). Unlike TCE, DCE and other contaminants in the plume, PCE is a fully chlorinated ethene, which makes it too oxidized to be susceptible to aerobic degradation (Semprini, 1995). PCE can be biologically reduced through the process of reductive dechlorination, but this can only take place under anaerobic conditions Therefore, the first set of wells will be used to turn the aquifer anaerobic, so that the PCE in the plume can be transformed to TCE or other lower chlorinated ethenes. After this, the plume will flow through the biozone created by the second set of horizontal wells and the contaminants will be aerobically co-metabolized by the bacteria within them. A conceptual diagram of this two-stage system is represented in Figure 5.

Since this treatment system is a flow-through system that degrades the contaminants as they are carried over the biozones by natural hydraulic gradients, it must be designed to operate until the last of the groundwater plume flows past the horizontal wells. Particle tracking models show that if the landfill is completely capped by the year 2000 so that the plume source is shut off, it will take 110 years for the last of the contaminants to flow from the landfill to the Buzzards Bay Outwash (Amarasekera, 1996). Therefore, the bioremediation system must be designed to operate for a little over a century. This means that the system design must take into account that the wells and other major equipment will need to be replaced after thirty to fifty years, since this is the maximum operating time for most major environmental projects. The replacement of major equipment is not only necessary, it may also be beneficial because technological advances may permit the installation of less expensive or more efficient equipment.
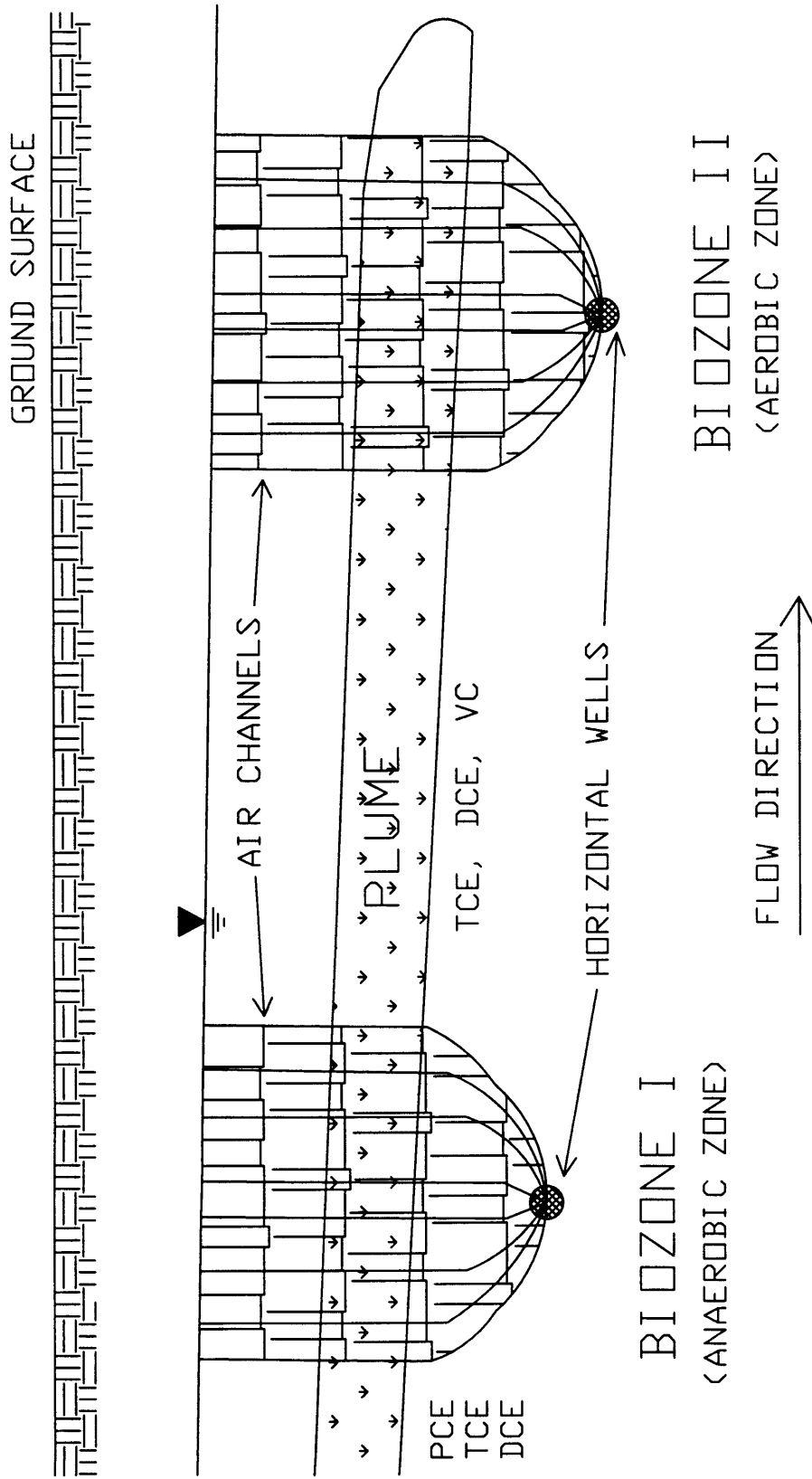
GROUND SURFACE

AIR CHANNELS

PLUME

TCE, DCE, VC

HORIZONTAL WELLS

PCE
TCE
DCE

BIOZONE I
(ANAEROBIC ZONE)

BIOZONE II
(AEROBIC ZONE)

FLOW DIRECTION

FIGURE 5: CONCEPTUAL DIAGRAM OF THE SEQUENTIAL BIOREMEDIATION SYSTEM

(SKIADAS, 1996)

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4.0 Horizontal Well Technology

Horizontal wellbore technology has been in use for many years within the petroleum industry, but since 1989 it has gained growing recognition as a potential tool in a variety of environmental restoration projects (Cooper, 1994). One such project was the Savannah River Integrated Demonstration (SRID), in which a horizontal well was used to inject gaseous methane, air, and other nutrients in order to stimulate the aerobic biodegradation of a plume of TCE (Brockman et al, 1995). Horizontal wells can also be used to reach sites where it is difficult or impossible to install a vertical well, such as when the contamination is under a building or other surface obstruction. Furthermore, groundwater plumes tend to develop so that they are much longer than they are wide. A horizontal well could be placed along the long axis of the plume and collect contaminated water much more efficiently than a large number of vertical wells. The well is drilled at an angle, so it could even be installed to follow a plume's vertical profile as it dives deeper within the aquifer.

A horizontal well is emplaced using a steerable drillbit which is directed from the surface. The well is drilled according to a preset plan derived from sampling wells on the site, but the wellbore can also be used to sample the aquifer material around the drillbit. Site engineers can recover five foot sections of intact borings and test this material on site to determine if the well is still within the plume (Karlsson, 1993). Using this data, horizontal wells can be placed where they will most effectively remediate the contaminated area. The well itself is drawn into the boring behind the drillbit. Horizontal wells are usually constructed of high-density polyethylene (HDPE) and screened with steel composite mesh inserts. PVC, which vertical wells are traditionally constructed of, is not used because it is highly susceptible to long-term strain effects. The well can be screened over some or all of its length, depending upon the desired pumping characteristics.

Experience has shown that horizontal wells are most effective when the contamination is relatively shallow, two-hundred feet or less below the surface. In addition, wells can be driven horizontally for distances up to a mile in length (Cooper, 1994). The nature of the contamination at the LF-1 site falls well within the limits set by these parameters. The groundwater plume is found at a maximum depth of one hundred fifty feet below the surface, and is six thousand feet across at its widest point. This means that several sections of horizontal well can be used to construct each of the two biozones that are required in this system. The exact number and length of the sections would need to be determined based on the pumping parameters of the gas injection system.

The potential use of a horizontal well gas injection system as a bioremediation tool at the LF-1 site has been previously proposed and studied. In his thesis, Hayes (1996) modeled the injection of a mixture of methane and oxygen into the Cape Cod aquifer and its effect on the degradation of TCE within the LF-1 plume. The gas would be pumped through a series of ports into the plume, and would flow upwards in a series of channels. Methane and oxygen then diffuse out of these channels of gas and into the plume, stimulating microbial growth. Hayes assumed a channel density of one channel per square meter, and a well radius of influence of thirty meters. The nature and formation of these subsurface channels is not well understood, so these same values were used for the design of the sequential bioremediation system.

5.0 System Design

5.1 The Anaerobic Biozone

The process of reductive dechlorination can only occur under a certain set of conditions. It is carried out by methanogenic bacteria, and therefore reductive dechlorination can only take place in anoxic waters and sediments (Holliger et al., 1993). The bacteria also need a reduced form of carbon in addition to the chlorinated solvent. Since chlorinated organics are highly oxidized, bacteria utilize the organic carbon for growth and energy and transfer electrons to the solvent in a biologically mediated redox reaction. In the case of chlorinated ethenes, the reduction series goes in the following order:

$$PCE \longrightarrow TCE \longrightarrow DCE \longrightarrow VC \longrightarrow ETHENE$$

The biozone created by the first set of horizontal injection wells will serve a dual purpose, it will turn the aquifer anaerobic in addition to stimulating an increase in microbial biomass which will eventually be used to fuel the process of reductive dechlorination. The well will be used to inject a mixture of methane, air, nitrous oxide, and triethyl phosphate through a series of injection ports. The methane will be degraded by methanotrophs in the aquifer which will grow in biofilms that are attached to the surfaces of aquifer materials. Then, when the biozone has created the desired amount of biomass, the injection wells will pump only methane and the oxygen in the plume will be depleted. As the plume flows through the biozone, it will remain anaerobic until it reaches the second biozone. Research has shown that infiltrating water does not mix with existing groundwater, so there will be little or no reaeration of the plume (Domenico and Schwartz, 1990).

There are several assumptions that must hold true in order for this concept to work. First, methanogenic bacteria which carry out the dechlorination process must be present within the aquifer

and be stimulated to grow within the biozone. This type of bacteria exists in a variety of environmental situations, and can probably be found in anaerobic microsites within the Cape Cod aquifer (Pavlostathis and Zhuang, 1993). Furthermore, the biozone must be capable of creating a sufficient amount of biomass for the methanogenic bacteria to utilize in PCE dechlorination.

There are no kinetic studies detailing the rates at which reductive dechlorination occurs in the environment, but those experiments which have been done indicate that the amount of dechlorination that occurs is directly related to the ratio of the electron donor (dead organic matter) to the electron acceptor (chlorinated solvent.) An experiment conducted by Gibson and Sewell (1992) provides a convenient starting point for the calculation of the amount of dead organic matter that the first biozone must be designed to create. In a microcosm study of a chlorinated solvent contaminated aquifer, sediment from the aquifer was placed in teflon-stoppered serum bottles. This sediment was amended with 5 ppm PCE and 240 ppm organic material and incubated at room temperature (20-25 degrees Celsius) for ninety days. The level of PCE and its dehalogenated products, TCE and DCE, were measured over the course of the experiment. After ninety days had passes, all of the PCE molecules had lost at least one chlorine, and the rising levels of DCE in the serum bottles indicated that even more extensive reduction was taking place.

In this experiment, 240 mg/L of organic matter was added to bottles containing 5 mg/L of PCE. If this system were used to treat the LF-1 plume, the highest concentration of solvent that the system would ever see would be one-hundred micrograms per liter. The plume consists of a mixture of chlorinated ethenes, but as a conservative measure it can be assumed that all of the contaminant is present as PCE. If this assumption is made, it is apparent that the first biozone must contain approximately five milligrams of organic matter per liter of passing groundwater in order to ensure that an extensive amount of dechlorination will occur within the anaerobic treatment zone.

The process of reductive dechlorination is dependent upon pH and temperature as well as the ratio of electron donors and acceptors, and these considerations must be accounted for when calculating the time it takes for extensive dechlorination to occur within the first biozone. The pH in the aquifer where the LF-1 plume is located varies from place to place, but it is roughly neutral (ABB Environmental, 1992(a)). Studies have shown that a pH in the range of 7 to 7.5 is optimal for reductive dechlorination, so pH effects can be neglected. However, the temperature of the groundwater in the Cape Cod aquifer is about ten degrees Celsius, lower than the temperature range in which the microcosm study was conducted. The temperature difference between twenty-five and ten degrees Celsius can result in as much as a six-fold decrease in the dechlorination rate, so the plume must have a residence time of five hundred and forty days within the anaerobic biozone in order to ensure that all of the PCE has been dechlorinated (Zhuang and Pavlostathis, 1995).

The seepage velocity of the groundwater at the toe of the LF-1 plume is about 1.13 ft per day (Amarasekera, 1996), while the retardation factor of the PCE in the aquifer is 1.25 (Khachikian, 1996). This means that PCE flows in the subsurface at an average rate of .904 ft per day. Since the PCE must have a residence time of 540 days within the anaerobic biozone, the biozone must be at least 488 ft long. The radius of influence of one horizontal well is about thirty meters, so each well creates a biozone that is 200 ft long. Therefore, three horizontal wells would be needed to create the anaerobic biozone which will be roughly 600 ft in length. PCE will have a residence time of 664 days within the anaerobic zone, enough to ensure that all of it is subjected to some degree of dechlorination. Furthermore, some of the other solvents in the plume will be dechlorinated as a result of this process, which will make the entire plume more susceptible to aerobic degradation.

After the wells are turned on, it will take a few days for the concentration of biomass within the first biozone to reach a concentration of five milligrams per liter (Skiadas, 1996). After five days have

passed, the horizontal wells will be used to pump only methane into the biozone. Methanotrophs within the biozone will utilize this methane to continually deplete the oxygen in the groundwater which flows through the biozone. Furthermore, they will grow on this carbon source and continually replace the biomass that is utilized by methanogens which are carrying out the process of reductive dechlorination.

Even though the ratio of organic matter to chlorinated solvent is quite large, over time methanogenic bacteria will use up most of the organic matter in the biozone. As the ratio is decreased, the bacteria will be less effective at reductively dechlorinating the solvents in the plume. This problem will be counteracted in part by the steady influx of oxygenated water which, together with the methane in the biozone, will promote the growth of methanotrophs and the steady addition of biomass to the system. However, the long operating life of this system (110 years) will mean that the effluent from the anaerobic biozone must be continually monitored to ensure that reductive dechlorination is still taking place within it. If a significant amount of PCE is found flowing out of the biozone it may be necessary to reinject a mix of air and methane into the anaerobic zone in order to restore the concentration of organic matter within it. The time between these periodic injections can be reduced by building up an excess of biomass during each injection, for instance injecting nutrients for a period of time until 10-15 mg/L biomass is created within the anaerobic biozone.

5.2 The Aerobic Biozone

After the PCE in the groundwater plume has been dechlorinated, the plume will pass through a second biozone which will degrade the chlorinated solvents to a level that is below the established MCLs for each contaminant. The second biozone will be aerobic: a mixture of methane, air, nitrous oxide, and triethyl phosphate will be injected from a horizontal well below the plume in order to stimulate methanotrophs within the biozone. Methanotrophs degrade methane via an enzyme called methane

monooxygenase (MMO). MMO is a nonspecific oxygenase that is capable of oxidizing a wide range

of chemicals in the environment including the chlorinated solvents found within the LF-1 plume

(Sawyer et al, 1994). As the methanotrophs grow on methane they will also degrade TCE and other

plume contaminants in a process termed co-metabolic oxidation. This process will also occur during

the early operation of the injection wells in the anaerobic zone before all of the oxygen is depleted.

However, due to the short time period of air injection only a small amount of solvent will be

aerobically degraded within the first biozone.

The injection well for the aerobic zone must be placed at least 200 feet downgradient from the last

injection well in the anaerobic biozone in order to ensure that the zones of influence from each well do

not interfere with each other. The degradation rates for each contaminant were calculated by Skiadas

(1996) and were based on the assumption that a steady state concentration of 1 mg/L methane and 10

mg/L oxygen were achievable within the aerobic biozone. The extent of the degradation achieved

within the aerobic biozone was calculated using:

$$\frac{C_c}{C_{co}} = e^{-k_{deg}t} \tag{1}$$

In the above equation C_c is the concentration of the contaminant in the plume after passing through the

aerobic biozone, C_{co} is the initial concentration of the contaminant within the plume, k_{deg} is the first-

order degradation constant for the contaminant, and t is the contaminant residence time within the

biozone (Skiadas, 1996).

If one horizontal well is used to create the aerobic biozone, the contaminants will have a residence time

in that biozone of 221 days. The extent of the dechlorination within that biozone is shown in Table 1.

	TCE	c-DCE	t-DCE	VC
k_{deg} (d^{-1})	.014	.068	1.36	1.36
t (d)	221	221	221	221
$\dfrac{C_c}{C_{co}}$	.045	0	0	0

Table 1: Aerobic Biozone Treatment Efficiency

The highest concentration of chlorinated solvents that is likely to pass through the biozone at any time is about 100 ppb. It is apparent that even if all of this solvent were TCE, the aerobic biozone would treat the plume so that the groundwater flowing out of it had a TCE concentration of 4.5 ppb, which is below the MCL of 5 ppb. Therefore, if this bioremediation scheme works according to the calculations made above, only one horizontal well will be needed to create the aerobic biozone.

5.3 Aquifer Clogging

During the operation of this system, the injection ports of the wells or the aquifer itself may become clogged by biomass or metal deposits. Biofouling is a problem associated with the operation of enhanced bioremediation systems and occurs when the microbes that are stimulated within the aquifer grow to such a density that they clog the injection ports of wells or the pores of the aquifer surrounding the injection wells (Vandevivere et al, 1995). This type of fouling is more likely to be a problem within the second biozone because more microbial mass will be produced through the continuous injection of methane and oxygen. Clogging of the injection ports can be avoided by injecting the different gaseous nutrients out of sequence, so that growth is not stimulated in the area directly adjacent to the well. However, clogging of the aquifer pore spaces may still a problem.

Deposition of metals may also prove to be a problem within the second biozone. When the aquifer is turned anaerobic in the first biozone, the pe is decreased and iron and other metals within the aquifer will be reduced and become more soluble (Morel, 1983). These metals will travel with the groundwater until they reach the second biozone, where they will be reoxidized and deposited and may build up in sufficient quantities to block up injection ports or pore spaces. The potential problem posed by metal mobilization and transport may be estimated by conducting some simple lab tests. A core of aquifer material could be taken from the Cape Cod aquifer and brought into a laboratory, where it would be contained under anaerobic conditions. Anoxic water would be flushed through the core and the metal concentration in the effluent measured. This would give an indication of the amount of metals that would be mobilized in the subsurface by turning part of the aquifer anaerobic.

5.4 Cost Analysis

A rough estimate of the potential cost benefits of this system can be obtained by comparing it to other remediation options that may be used on the LF-1 plume. Currently, efforts at the MMR seem focused on containing the plume before it flows off-site. The design of this containment plan has not been completed yet, but it will most likely consist of a series of wells which extract contaminated groundwater and pump it through granular activated carbon (GAC) to remove the solvents. This type of system is already in operation at the Chemical Spill-4 site (ABB Environmental, 1992(b)).

The CS-4 plume is a long, 800 foot wide plume that is also deep within the aquifer. The containment fence is comprised of thirteen extraction wells and a GAC device, and was constructed at capital cost of 2.7 million dollars. The system was designed to operate for thirty years at an additional 2.7 million dollar operating and maintenance (O&M) cost. The LF-1 plume is six-thousand feet wide and would require a much larger containment system. If it is assumed that the size and cost of the well fence are

roughly proportional to the width of the plume, then a containment system for the LF-1 plume would have a capital cost of 20.3 million dollars and an additional 20.3 million dollar O&M cost.

Horizontal wells cost about 200 dollars per foot to install in the ground (Parmentier and Klemovich, 1996), and four wells are used in this system design, each of which is six-thousand feet in length. This translates to a combined cost of 4.8 million dollars to install the wells. It is difficult to estimate the capital and O&M cost for the pumps and controls for the system, but they would probably cost significantly less than those required for a containment system because the bioremediation plan does not involve pumping and recirculating massive quantities of water or GAC treatment. Most of what is injected into the ground is air which can be pulled from the atmosphere by a compressor. Therefore, it is apparent that there is a potential cost advantage to this system if it proves to be effective in remediating plumes of chlorinated solvents *in-situ*.

It is important to remember that like the CS-4 containment system, the bioremediation system can only be designed to last about thirty years, while the system needs to operate for 110 years. At some point during its lifetime, the gas injection system will need to be completely overhauled and most of its equipment will need to be replaced. This will result in an additional set of costs that must be accounted for when different treatment options are considered for the LF-1 site.

5.5 Pilot Study

Despite the potential cost and technological advances that are possible using the type of enhanced bioremediation system described above, this type of system has never been designed or implemented, so a pilot study should be conducted at another site before a system is constructed at the MMR. The site for the pilot study should be carefully chosen based on technical and cost criteria.

The pilot study should be conducted at a site where the aquifer materials are similar to those in the Cape Cod aquifer and the contamination is also located deep within the subsurface. The formation of gas channels within the aquifer is a poorly understood process, so it is important that conditions at both sites are comparable so that pumping data from the pilot test can be extrapolated with some degree of accuracy to the LF-1 plume. A shallow site would be easier to pump and to monitor, but the data would not be useful because channel formation is highly dependent upon the depth of water and the amount of heterogeneity that exists in the treatment zone above the injection well. Both of these factors are in turn a function of the depth of the injection well below the water table.

In addition, the pilot test should target a relatively narrow plume with a low concentration of chlorinated solvents (a few hundred ppb or less) in order to minimize the drilling and equipment costs of the test. The plume needs to be well defined before a remediation system can be emplaced to treat it, and a narrow plume will require fewer wells to monitor and remediate the system. Costs can also be reduced if the site has a very low seepage velocity, because this will impart longer residence times to the contaminants as they will spend more time in the biozones. This will permit the use of shorter biozones which will in turn require fewer horizontal wells.

6.0 Conclusions and Recommendations

It is apparent that the sequential anaerobic/aerobic bioremediation system designed in this thesis has both technological and cost advantages over traditional *in-situ* systems. It is a passive, flow-through system so it avoids the expense and difficulty of pumping and recirculating large quantities of water within the aquifer. Furthermore, it is a treatment strategy that will remove the contamination from the ground rather than simply containing it.

A pilot study should be conducted at a test site prior to constructing this type of system at the MMR. The expense of the system and the large extent of the LF-1 plume make it a poor candidate for testing an innovative technology. Therefore, a site should be chosen for a pilot-scale test which has characteristics that are similar to those found at the MMR. A test at a site which has these properties will yield valuable information about installing and operating a sequential bioremediation system that can be used to design a scaled-up system for the LF-1 plume. Data on pumping rates and the mass transfer of gas into the groundwater is especially important because this process is poorly understood in the subsurface environment. Coupled anaerobic/aerobic bioremediation treatment systems are a potential solution to the widespread contamination of groundwater by chlorinated solvents, so they must be studied to see if they can become a useful remediation technology.

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