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**Natural Attenuation of Chlorinated Ethenes  
by Anaerobic Reductive Dechlorination  
Coupled with Aerobic Cometabolism**

THESIS

Derek D. Veerkamp, 1<sup>st</sup> Lt., USAF  
AFIT/GEE/ENV/99M

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**THESIS**

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Derek D. Veerkamp, B. S.

1<sup>st</sup> Lieutenant, USAF

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Derek D. Veerkamp, B.S.  
First Lieutenant, USAF

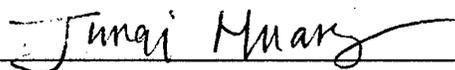
Approved:

  
\_\_\_\_\_  
Dr. Mark Goltz  
Chair, Advisory Committee

10 Mar 99  
Date

  
\_\_\_\_\_  
Dr. Charles Bleckman  
Member, Advisory Committee

10 Mar 99  
Date

  
\_\_\_\_\_  
Dr. Junqi Huang  
Member, Advisory Committee

3/10/99  
Date

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### **Abstract**

Chlorinated solvents are the most common contaminants of groundwater at industrial and military facilities in the United States. Limitations of conventional technologies have intensified efforts to find alternative methods to remediate contaminated sites to regulatory goals. Natural attenuation of chlorinated solvents is a promising alternative to traditional remediation methods, but the mechanisms by which natural attenuation of chlorinated solvents occurs and the conditions necessary to promote attenuation are not well understood. This lack of understanding has hindered the acceptance of natural attenuation as an approach for addressing chlorinated contaminants.

This modeling study investigated the ability of naturally occurring processes to promote the complete degradation of chlorinated solvents such as trichloroethylene (TCE) under various conditions. It was hypothesized that reductive dechlorination, coupled with aerobic cometabolism, could be important mechanisms promoting complete mineralization of chlorinated contaminants. It was found that high rates of contaminant mass transfer due to advection and dispersion in groundwater led to a condition where the contaminant could reach environmental and human receptors prior to degradation. High concentrations of sulfate or nitrate in groundwater were shown to inhibit creation of methanogenic conditions necessary to promote complete degradation of the chlorinated contaminant. It was also shown that a co-contaminant that could serve as an electron

donor to create methanogenic conditions was critical in establishing an environment that was conducive to total dechlorination of the contaminant.

The model was applied to data obtained from a former landfill site at Moody AFB. Model simulations demonstrated that the observed contaminant distribution down gradient from the landfill were consistent with the model that hypothesized natural attenuation of chlorinated contaminants due to the coupling of reductive dechlorination and aerobic cometabolism

## 1.0 INTRODUCTION

### 1.1 MOTIVATION

Chlorinated solvents and their daughter products are the most common contaminants of groundwater at industrial and military facilities in the United States. The major chlorinated solvent contaminants in groundwater are tetrachloroethene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane and carbon tetrachloride (CTC) (McCarty, 1993). TCE, a suspected human carcinogen (Fan, 1988), has been found in approximately 745 of the 1,300 hazardous waste sites on the National Priorities List (NPL). Various surveys estimate between 9 and 34% of the water supply sources in the United States may be contaminated with TCE. (EPA, 1994).

The Federal government is responsible for 151 of the 1,300 NPL sites (USGAO, 1997). The Department of Defense (DoD) is responsible for 126 of the 151 Federal sites on the NPL list (USGAO, 1995). In addition, DoD has identified 8,336 sites requiring some type of remediation at an estimated cost of \$30 billion (Astin and Sanders, 1996). Of the 8,336 DoD sites, 2,231 are owned by the Air Force. The estimated cost for remediating these Air Force sites is \$7.4 billion (USEPA, 1997).

The technology of choice to remediate contaminated groundwater has been pump-and-treat. However, the limitations to pump-and-treat technologies have become apparent and it is understood that pump-and-treat methods are typically unable to remediate a site

(Travis and Doty, 1991). The NRC (1994) studied 77 sites where conventional pump-and-treat systems are operating and found 29 of the 77 sites cleanup goals had not yet been reached.

The limitations of conventional technologies have intensified efforts to find alternative methods to remediate contaminated sites to regulatory goals set by CERCLA. During the last decade bioremediation has been recognized as a promising alternative to pump-and-treat technologies. Bioremediation utilizes the ability of naturally occurring microbes to degrade the contaminant. In-situ bioremediation takes place underground, without the need to bring contaminated groundwater to the surface for treatment. Often, in-situ bioremediation requires some type of intervention to spur the bioremediation process such as injecting substrates. Most recently bioremediation without intervention, called natural attenuation or intrinsic bioremediation, has been studied. Natural Attenuation depends upon microbial processes that can successfully occur with no human intervention to naturally degrade the contaminant to safe levels.

Unlike natural attenuation of petroleum hydrocarbons which is thought to occur in most cases, natural attenuation of chlorinated solvents is more rare. Chlorinated solvents are more resistant to degradation than petroleum hydrocarbons. The mechanisms for the degradation of chlorinated solvents are more complex than aromatic solvents such as benzene, alkylbenzenes, toluene, and xylene (BTEX) and therefore have taken longer to understand. The EPA, Air Force, DOE, and other public interest groups published the Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in

Groundwater (Wiedemeier et. others, 1996). This document has used to help determine if natural attenuation is reducing the risk of chlorinated solvents in groundwater at a particular site.

The NRC (1994) found a lack of adequate technical expertise is one of the barriers to implementing new and innovative technologies. Before an innovative technology can be implemented in the field, remedial project managers, regulators and other stakeholders require adequate tools to help them assess the applicability of the technology, design the implementation, and optimize its use based on cost considerations. One method of providing these tools and for improving technical expertise is through the use of models and modeling studies. A properly applied model in conjunction with field evaluations and case studies can (1) assist in the problem evaluation, (2) aid in the design of the remedial strategy, (3) improve the conceptual model developed to describe the processes, (4) provide additional quantitative information for decision making, and (5) identify limitations in the data and guide collection of new data (NRC, 1990).

Nationwide, if natural attenuation mechanisms can be shown to reduce concentrations of chlorinated solvents to low (below health-risk) levels, savings in active remediation costs would potentially be in the billions of dollars. The product of this research will be the ability to identify important parameters needed to determine whether or not natural attenuation is occurring by the processes discussed in this report. This will allow DoD to better evaluate the efficacy of natural attenuation of chlorinated solvents, thereby freeing up resources for application to active remediation efforts.

## 1.2 RESEARCH OBJECTIVES

1. Utilize a computer model that incorporates transport and rate reactions to simulate behavior of contaminants in an aquifer under various conditions
2. Illustrate the ability of sequencing reductive dechlorination and cometabolism by utilizing the methane produced from methanogenesis as the primary substrate in cometabolism to mineralize TCE

## 1.3 DEFINITION OF TERMS

Abiotic - referring to processes which occur in the absence of living organisms.

Advection - Transport of molecules dissolved in water along the groundwater flow path at an average expected velocity.

Aerobic - Environmental conditions where oxygen is present.

Aerobic Respiration - The process whereby microorganisms use oxygen as the electron acceptor (NRC, 1993).

Aliphatic Hydrocarbon - A compound built from carbon and hydrogen atoms joined in a linear chain. Petroleum products are composed primarily of aliphatic hydrocarbons.

Anthropogenic - Man-made (Wiedemeier et others, 1996)

Bacteria - Members of a group of diverse and ubiquitous prokaryotic (i.e. cells lacking a nucleus), single-celled organisms (Atlas and Bartha, 1993).

Bioremediation - a managed or spontaneous process whereby microbiological interactions act on contaminant compounds, thereby remedying or eliminating environmental contamination (Madsen, 1991).

Biodegradation - The simplification of an organic compound's structure by breaking of intermolecular bonds (Madsen, 1991).

Biotic - Processes of or relating to living organisms, caused by living things.

Biotransformation - Microbiologically catalyzed transformation of a chemical to some other product.

Chlorinated Solvent - A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compounds structure. Chlorinated solvents commonly are used for grease removal in manufacturing, dry cleaning, and other operations.

Cometabolism - The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound. (fortuitous metabolism may be more descriptive) (Wiedemeier et others, 1996).

Competitive Inhibition - Deleterious process which occurs when the binding of cometabolite (target contaminant) and growth supporting a substrates are mutually exclusive (e.g. they bind to the same site on the enzyme). Thus, when primary substrate and target contaminant are simultaneously present, the target contaminant degradation is inhibited.

Daughter Product - A compound that results directly from the biodegradation of another compound. For example cis-1,2-dichloroethene (cis-1,2-DCE) is commonly a daughter product of trichloroethene (TCE) (Wiedemeier et others, 1996).

Dechlorination - The removal of chlorine atoms from a compound.

Desorption - The release of chemicals attached to solid surfaces.

Diffusion - Dispersive process that results from the movement of molecules along a concentration gradient. Molecules move from areas of high concentration to low concentration.

Dispersion - The spreading of molecules along and away from the expected groundwater flow path during advection as a result of mixing of groundwater in individual pores and channels.

Electron Acceptor - The compound that is reduced (receives electrons) in the energy-producing oxidation-reduction reactions essential for the growth of microorganisms (NRC, 1993).

Electron Donor - The compound that is oxidized in the oxidation-reduction enzyme reactions essential for growth of microorganisms (NRC, 1993).

Enzyme - An organic catalyst which influences a reaction without becoming a reactant.

Heterotroph - Organism that uses organic carbon as an external energy source and as a carbon source (Wiedemeier et others, 1996).

Hydrogenolysis - A reductive reaction in which a carbon-halogen bond is broken, and hydrogen replaces the halogen substitute (Wiedemeier et others, 1996).

In situ Bioremediation - In situ is Latin for "in its original place." In situ bioremediation is the activation of microbial population found in the subsurface for the destruction of contaminant in place (Madsen, 1991).

Lithotroph - Organism that uses inorganic carbon such as carbon dioxide or bicarbonate as a carbon source and an external source of energy (Wiedemeier et others, 1996).

Metabolism - The chemical reactions in living cells that convert food sources to energy and new cell mass.

Microorganism - An organism of microscopic scale capable of reproduction and growth on primary substrates (NRC, 1993).

Methanogen - A microorganism that exists in anaerobic environments and produces methane as the end product of its metabolism. Methanogens use carbon dioxide or simple carbon compounds such as methanol as an electron acceptor.

Methanogenesis - The process of creating methane from  $H_2$  and  $CO_2$  during the respiration of methanogens (Atlas and Bartha, 1993).

Methanotroph - Microorganism which utilizes methane as an energy source.

Mineralization - The conversion of an organic compound to its inorganic constituents

Monooxygenase - A microbial enzyme that catalyzes reactions in which one atom of the oxygen molecule is incorporated into a product and the other atom appears in water (Wiedemeier et others, 1996).

Natural Attenuation - naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media.

Obligate Aerobe - Microorganisms that can use only oxygen as an electron acceptor.

Thus, the presence of molecular oxygen is a requirement for these microbes (Wiedemeier et others, 1996).

Obligate Anaerobes - Microorganisms that can grow only in the absence of oxygen; the presence of molecular oxygen either inhibits growth or kills the organism. For example, methanogens are very sensitive to oxygen and can live only under strictly anaerobic

conditions. Sulfate reducers, on the other hand, can tolerate exposure to oxygen, but cannot grow in its presence (Chapelle, 1993).

Oxidation - Loss of electrons from a compound, such as an organic contaminant. The oxidation can supply energy that microorganisms use for growth. Often (but not always) oxidation results in the addition of an oxygen atom and/or the loss of a hydrogen atom.

Primary Substrates - The electron donor and electron acceptor that are essential to growth and reproduction of microorganisms (NRC, 1993).

Reduction - Transfer of electrons to a compound such as oxygen. It occurs when another compound is oxidized.

Reductive Dechlorination - the removal of chlorine atoms from an organic compound and their replacement with hydrogen atoms.

Sorption - Attachment of a substance on the surface of a solid by physical or chemical attraction.

Substrate - A compound that microorganisms can use in the chemical reactions catalyzed by their enzymes.

Transmissivity - The rate at which water of a prevailing density and viscosity is transmitted through a unit width of an aquifer or confining bed under a unit hydraulic gradient. It is a function of properties of the liquid, the porous media, and the thickness of the porous media.

## **2.0 LITERATURE REVIEW**

### **2.1 OVERVIEW**

In the literature review we will explain how contaminants are transported in an aquifer. We will then focus in on the biochemical processes that affect the fate of chlorinated ethenes in the subsurface. Knowing the relevant fate and transport processes, we will review existing numerical models that account for these processes. Finally, we will present field analyses that have appeared in the literature that suggest natural attenuation of chlorinated ethenes under the conditions hypothesized in this study.

### **2.2 PHYSICAL/CHEMICAL TRANSPORT**

#### **2.2.1 Advection**

Advection is the primary mechanism for dissolved or suspended chemical transport in an aquifer. Advection is the transport due to the average bulk fluid movement, as measured by the average linear velocity of the fluid (i.e. the ground water). The flux of chemical is a function of its concentration and the average linear velocity of the ground water. Note that the average linear velocity is not necessarily the rate at which the water molecules actually are moving along individual flow paths. The actual velocity of individual molecules is greater than the average linear velocity due to tortuosity of the porous media (Fetter, 1994).

#### **2.2.2 Dispersion**

Dispersion is a process that causes mixing and spreading of contaminants in groundwater. Dispersion is attributed to two processes--molecular diffusion and mechanical dispersion. Molecular diffusion is the migration of contaminants along concentration gradients from zones of higher to lower concentrations. Because molecular diffusion is the dominant dispersion mechanism only at extremely low groundwater velocities, it is often ignored in ground-water studies (Davis et al, 1993).

Mechanical dispersion results from local variations in flow velocity that are caused by microscopic and macroscopic heterogeneities of the porous aquifer medium (Domenico and Schwartz, 1990). If all the ground water containing a contaminant were to travel at exactly the same rate, it would displace water that does not contain the contaminant and create an abrupt interface between the "clean" and "dirty" waters. Dispersion dilutes the contaminant by mixing it with less contaminated groundwater. Mixing that occurs in the direction of average flow path is called longitudinal dispersion. The traveling solute will also tend to spread in the direction orthogonal to the direction of flow. The spreading of the solute normal to the direction of flow is called transverse dispersion.

### **2.2.3 Sorption**

Sorption is a general term that includes adsorption, chemisorption, absorption, and ion exchange. Regardless of the specific process, sorption is the transfer of solute from the aqueous to the solid phase.

Sorption is a reversible process that retards the movement of the contaminant plume relative to the advective ground-water-flow velocity. Because of their nonpolar structure, chlorinated VOC's are hypothesized to sorb by hydrophobic partitioning into the natural organic matter that exists as part of the solid phase of sediments and soils (Chiou et al., 1979; Schwarzenbach and Westall, 1981). In most groundwater systems, therefore, the organic fraction of the aquifer matrix controls sorption of organic contaminants, although clay minerals can also be an important sorbent. Distribution coefficients ( $K_d$ 's) that describe the partitioning of hydrophobic contaminants between sorbed and dissolved phases have been found to correlate well with the fraction of organic carbon in the soil or sediment, if the fraction of organic carbon is greater than about 0.1 percent (Schwarzenbach and Westall, 1981). Sorption to mineral surfaces, especially clay minerals, can be dominant in sediments with low organic carbon content.

Sorption can be modeled using a linear isotherm, Freundlich isotherm, or Langmuir isotherm. The linear sorption isotherm assumes the sorbed concentration for solute  $w$  ( $S_w$ ) is directly proportional to the dissolved concentration of solute  $w$  ( $C_w$ ):

$$S_w = K_{oc,w} f_{oc} C_w$$

**Equation 2.1**

$S_w$	sorbed-phase concentration of solute $w$ ( $MM^{-1}$ )
$K_{oc,w}$	organic-carbon partitioning coefficient for solute $w$ ( $L^3M^{-1}$ )
$f_{oc}$	fraction of organic carbon in the porous medium ( $MM^{-1}$ )
$C_w$	dissolved-phase concentration of solute $w$ ( $ML^{-3}$ )

The retardation factor for the linear sorption isotherm is defined as:

$$R_w = 1 + \frac{\rho_b}{\theta} K_{oc,w} f_{oc}$$

**Equation 2.2**

$R_w$  retardation coefficient for solute  $w$  (dimensionless)

$\rho_b$  dry bulk density of the porous medium ( $\text{ML}^{-3}$ )

$\theta$  saturated porosity of the porous medium ( $\text{L}^3\text{L}^{-3}$ )

The Freundlich isotherm is a non-linear isotherm and expressed as:

$$S_w = K_{f,w} (C_w)^{a_w}$$

**Equation 2.3**

$K_{f,w}$  Freundlich constant for solute  $w$  (units depends on exponent  $a_w$ )

$a_w$  Freundlich exponent for solute  $w$  (dimensionless)

Both  $K_{f,w}$  and  $a_w$  are empirical constants. When  $a_w$  is equal to 1, the Freundlich isotherm simplifies to the linear isotherm. The retardation factor for the Freundlich isotherm is expressed as:

$$R_w = 1 + \frac{\rho_b}{\theta} a_w K_{f,w} C_w^{a_w-1}$$

**Equation 2.4**

The Langmuir isotherm is expressed as:

$$S_w = \frac{K_{l,w} N_s C_w}{1 + K_{l,w} C_w}$$

**Equation 2.5**

$K_{l,w}$  Langmuir constant for solute  $w$  ( $L^3M^{-1}$ )

$N_s$  total concentration of sorption sites available ( $MM^{-1}$ )

The retardation factor for the Langmuir isotherm is defined as

$$R_w = 1 + \frac{\rho_b}{\theta} \left( \frac{K_{l,w} N_s}{(1 + K_{l,w} C_w)^2} \right)$$

**Equation 2.6**

#### 2.2.4 General Transport

The general equation expressed as a partial differential equation describes the movement of a solute by combining the transport mechanisms of advection, dispersion, sink-source mixing (injection or extraction of solute by wells), retardation, and transformation. A simplified, one dimensional general transport equation can be expressed as:

$$R_w \frac{\partial C_w}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij,m} \frac{\partial C_w}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C_w) + \frac{q_s}{\theta} C_{s,w} + G_{R,w}$$

**Equation 2.7**

$C_w$  dissolved-phase concentration of solute  $w$  ( $ML^{-3}$ )

$T$  time (T)

$R_w$  retardation coefficient for solute  $w$  (dimensionless)

$x_i$  distance along the respective Cartesian coordinate axis (L)

$D_{ij,w}$  hydrodynamic dispersion coefficient for solute  $w$  ( $L^2T^{-1}$ )

- $v_i$  average linear groundwater velocity (L/T)
- $q_s$  volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative) ( $T^{-1}$ )
- $C_{s,w}$  dissolved-phase concentration of sources/sinks for solute  $w$  ( $ML^{-3}$ )
- $G_{R,w}$  general reaction term for solute  $w$ , including biotransformations and rate limited NAPL dissolution ( $ML^{-3}T^{-1}$ )

## **2.3 BIOLOGICAL NATURAL ATTENUATION PROCESS**

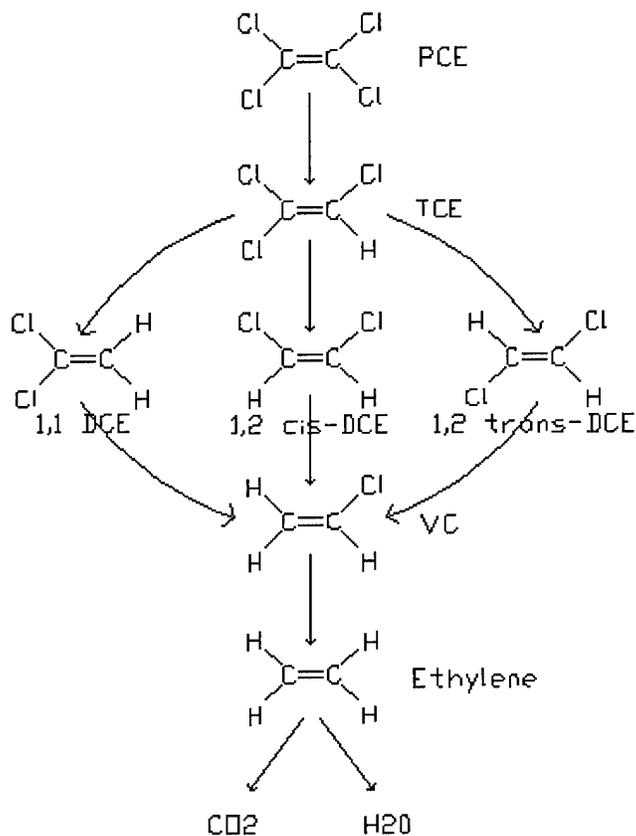
### **2.3.1 Anaerobic Processes**

#### **2.3.1.1 Reductive Dechlorination**

Reductive dechlorination may occur by two different processes. In the first process, halorespiration, the chlorinated hydrocarbon is used as an electron acceptor. The electron donor is another organic compound that is also present (either naturally, or due to contamination). In effect, microorganisms “breathe” the chlorinated compound in the same way aerobic organisms use oxygen (McCarty, 1997). The second route for dechlorination is using a cometabolic pathway. During anaerobic cometabolic degradation, microorganisms use and gain energy by oxidizing a source of organic carbon, using electron acceptors other than oxygen (e.g. nitrate, sulfate). The target chlorinated compounds is fortuitously reduced (dehalogenated) by the microorganism (Gossett and Zinder, 1996).

Because TCE and PCE are highly chlorinated VOC's, the carbon atoms have relatively high oxidation states and therefore are microbially reduced relatively easily under anaerobic conditions via hydrogenolysis. Hydrogenolysis entails the sequential replacement of chlorine atoms by hydrogen to produce more reduced, less-chlorinated products (Vogel et al., 1987; Bouwer, 1992). In general, the rate of hydrogenolysis decreases as the degree of chlorination of the aliphatic hydrocarbon decreases. As noted, hydrogenolysis of chlorinated compounds is a cometabolic process, requiring that other electron donors be present to serve as primary substrate. Possible primary substrates to serve as electron donors are hydrogen, low-molecular weight organic compounds (lactate, acetate, methanol, or glucose), and fuel hydrocarbons that are easily oxidized (benzene, toluene, and ethylbenzene) (Bouwer, 1994).

PCE is reductively dehalogenated by hydrogenolysis to TCE. Hydrogenolysis of TCE, produces DCE. Of the three possible DCE isomers, several studies have indicated that the cis isomer of 1,2-dichloroethylene (cis-1,2DCE) predominates over trans-1,2-DCE and that 1,1-DCE is the least significant intermediate (Bouwer, 1994). The DCE isomers can be reduced to vinyl chloride (VC), which can be further reduced to ethylene (Figure 2.1) (Freedman and Gossett, 1989; Beeman et. al., 1994) and ethane (de Bruin and others, 1992). Ethylene and ethane are desirable nontoxic end products, whereas the daughter products DCE and VC are problematic. VC in particular is a known carcinogen. The desirable end products could be difficult to achieve in most subsurface environments because of a lack of sufficient natural organic matter to provide electron donors (Chapelle, 1993, p.370).



**Figure 2.1**

Laboratory experiments have shown that hydrogenolysis can occur under iron-, nitrate-, and sulfate-reducing and methanogenic conditions (Freedman and Gossett, 1989; Bagley and Gossett, 1990; Bouwer, 1994). The rates of hydrogenolysis of highly chlorinated VOC's, however, tend to be greater under the highly reducing conditions associated with methanogenesis than under less reducing conditions (McCarty and Semprini, 1994). Although a sulfate-reducing enrichment culture was capable of dechlorinating tetrachloroethylene to 1,2-DCE, the rates were slower than those observed under similar

laboratory conditions with methanogenic systems (Bagley and Gossett, 1990). The reduction process also is more complete under methanogenic conditions. Pavlostathis and Zhuang (1991) and Bagley and Gossett (1990) found that sulfate-reducing enrichment cultures could transform TCE to 1,2-DCE, but further dechlorination to VC and ethylene did not occur. In contrast, many laboratory and field studies have reported TCE degradation to VC and, in some cases, to ethylene and ethane, under methanogenic conditions (Vogel and McCarty, 1985; Belay and Daniels, 1987; McCarty and Semprini, 1994). Freedman and Gossett (1989) reported that acclimated methanogenic cultures could completely dehalogenate tetrachloroethylene and TCE to ethylene and carbon dioxide if sufficient electron donor, such as methanol or hydrogen gas, was supplied. In several ground-water studies at waste disposal sites where tetrachloroethylene or TCE were the parent compounds, detection of VC (Kastner, 1991; Lorah and Clark, 1996) coincided with the presence of methane.

Reductive dechlorination requires a primary substrate and reducing conditions. Hydrogen concentration also needs to be above 1nM (Wiedemeier, 1997). If too little electron donor is present then not enough H<sub>2</sub> is produced to sustain reductive dechlorination.

<u>Redox Zone</u>	<u>H<sub>2</sub> Concentration (nmol)*</u>
Denitrification	< 0.1
Iron Reduction	0.1 - 0.8
Sulfate Reduction	1.0 - 4.0

\* (Chapelle et al., 1995)

**TABLE 2.1 Hydrogen Concentrations Needed to Sustain Redox Zone**

Reductive dechlorination can be modeled as a first-order reaction or as a first-order substrate-limited reaction. Given that reductive dechlorination reactions compete with the reduction of inorganic electron acceptors, the rate of reductive dechlorination is dependent on the rate of hydrogen production (which is dependent on the type and concentration of the primary substrate), as well as the concentration of the inorganic electron acceptors. These species control the intracellular availability of hydrogen (Gossett and Zinder, 1996; Zmaltka et al., 1996). Wrenn and Rittmann (1995) proposed a kinetic model for reductive dechlorination rates. Based on this model, the rates of reductive dechlorination are directly proportional to the concentrations of primary substrates, and are indirectly proportional to the concentrations of available electron acceptors because of competitive inhibition. A general model describing the effects of primary electron donor concentrations on the first-order rate of reductive dechlorination is:

$$k_{ap} = \frac{k_{\min} + k_{\max} \frac{C_{ED}}{C_{av}}}{1 + \frac{C_{ED}}{C_{av}}}$$

**Equation 2.8**

$k_{ap}$       apparent first-order rate coefficient ( $T^{-1}$ )

$k_{min}$	minimum first-order rate coefficient when electron donor concentration is zero ( $T^{-1}$ )
$k_{max}$	maximum first-order rate coefficient when electron donor concentration is very large ( $T^{-1}$ )
$C_{ED}$	electron donor concentration ( $ML^{-3}$ )
$C_{av}$	electron donor concentration when $k_{ap}$ is equal to the arithmetic average of $k_{min}$ and $k_{max}$ ( $ML^{-3}$ )

This equation assumes constant concentrations of biomass and inorganic electron acceptor concentrations. Assuming  $k_{min}$  is zero, the equation can be simplified to give:

$$k_{ap} = k_{max} \frac{C_{ED}}{C_{av} + C_{ED}}$$

**Equation 2.9**

An apparent first order rate coefficient ( $k_{ap}$ ) is created for each solute (TCE, DCE, VC, etc.).

### **2.3.1.2 Methanogenesis**

Methanogens are strictly anaerobic, unicellular organisms originally thought to be bacteria but are now recognized as belonging to a separate phylogenetic domain, the archaeobacteria. Methanogens are obligate anaerobes and are extremely sensitive to even low levels of oxygen. Methanogens are a consortium of bacteria species that work together to produce methane by consuming  $CO_2$  and  $H_2$ . Methanogens cannot effectively

compete until nitrate, iron, and sulfate ions are reduced. The methanogens use  $\text{CO}_2$  as a carbon source,  $\text{H}_2$  as an electron donor and the organic compound as the electron acceptor (Atlas and Bartha, 1993). From these substrates, two independent pathways are generally associated with methanogenesis: the reduction of  $\text{CO}_2$  with electrons from the oxidation of  $\text{H}_2$  or fermentation of acetate to methane and  $\text{CO}_2$  (Ferry, 1993). Methane gas is generated during methanogenesis; however, carbon dioxide is also produced from the acetate pathway while also being consumed as a substrate for the other methanogenesis pathways. As the acetogens and methanogens work to transform and consume the organic acids, the pH within the aquifer will rise to more neutral values (Gottschalk, 1986; Oremland, 1988).

For methane fermentation to occur in an aquifer, the presence of sufficient organic co-contaminant is required to reduce all of the oxygen, nitrate, nitrite, and sulfate present. Some organics will be required to reduce the CAHs, and perhaps iron (II) as well, if present in significant amounts. Carbon sources for the microbes may include natural organic matter, fuel hydrocarbons, or anthropogenic organic compounds such as those found in landfill leachate.

## **2.3.2 Aerobic Degradation**

### **2.3.2.1 Co-Metabolism**

In early studies, TCE and other higher chlorinated hydrocarbons were found to be biologically transformed under anaerobic conditions but resistant to degradation under aerobic conditions (Alvarez-Cohen and McCarty, 1991). Wilson and Wilson (1985) first

showed that TCE may be susceptible to aerobic degradation through use of soil microorganisms that were fed natural gas as a primary substrate in laboratory experiments. Other laboratory studies (Little and others, 1988; Tsien and others, 1989) have since confirmed that methanotrophic bacteria, aerobic microorganisms that oxidize methane for energy and growth, are able to transform TCE and many other chlorinated hydrocarbons through cometabolism. Methane monooxygenase, the enzyme methanotrophs use to catalyze the initial step of methane oxidation, has a broad substrate specificity and can fortuitously oxidize chlorinated aliphatic hydrocarbons. Other oxygenases have been found to be capable of TCE transformation under aerobic conditions, including those used by microorganisms oxidizing toluene and other aromatic hydrocarbons, propane, ethylene, and ammonia. Most research to date has focused on the methanotrophs and the group of bacteria producing toluene oxygenase (McCarty and Semprini, 1994).

The aerobic degradation process is similar for these groups of microorganisms. With unsaturated chlorinated aliphatic hydrocarbons such as TCE, oxygenases add oxygen across the double bond to form epoxides. The epoxides are chemically unstable and can be transformed rapidly by abiotic hydrolysis to nonvolatile products, including chlorinated aldehydes and acids. Heterotrophic microorganisms can further metabolize these products to carbon dioxide, chlorine, and water (Little and others, 1988). Because of the unstable nature of the intermediate degradation products and the difficulty of obtaining mass balances, oxidation of chlorinated VOC's is extremely difficult to detect

through field studies at contaminated sites and has not been demonstrated conclusively (Vogel, 1994).

The activity of methanotrophic bacteria in natural aerobic aquifers is believed to be too low to allow significant degradation of TCE and other organics, because concentrations of methane are commonly very low (Chapelle, 1993, p. 369). Aerobic degradation of TCE has been demonstrated, however, in a small-scale field study where methane and oxygen were injected into a shallow aquifer to manipulate the activity of methanotrophic bacteria (Semprini et al., 1990).

In contrast to anaerobic biodegradation processes where the degradation rate generally decreases as the degree of chlorination of the aliphatic hydrocarbon decreases, the less chlorinated VOC's are more easily degraded through oxidation reactions under aerobic conditions than are the higher chlorinated compounds. 1,2-DCE and VC oxidation rates, therefore, are relatively fast compared to TCE oxidation rates (Pfaender, 1990). Some highly chlorinated VOC's, including CT and PCE, are not known to be degraded under aerobic conditions (McCarty and Semprini, 1994).

#### **2.3.2.2 Aerobic Metabolism**

Murray and Richardson (1993) write that microorganisms are generally believed to be incapable of growth using PCE and TCE as a primary substrate (i.e. electron donor).

However, under aerobic conditions the less oxidized chlorinated aliphatic hydrocarbons such as VC can be used as the primary substrate in biologically mediated oxidation-

reduction reactions (McCarty and Semprini, 1994). In this process, the facilitating microorganism obtains energy and organic carbon from the degraded CAH. Vinyl chloride acts as an electron donor (Hartmans and deBont, 1992). McCarty and Semprini (1994) describe investigations in which VC was shown to serve as a primary substrate under aerobic conditions. In addition, Bradley and Chapelle (1996) show evidence of mineralization of VC under iron-reducing conditions (anaerobic) so long as there is sufficient bioavailable iron (Fe III).

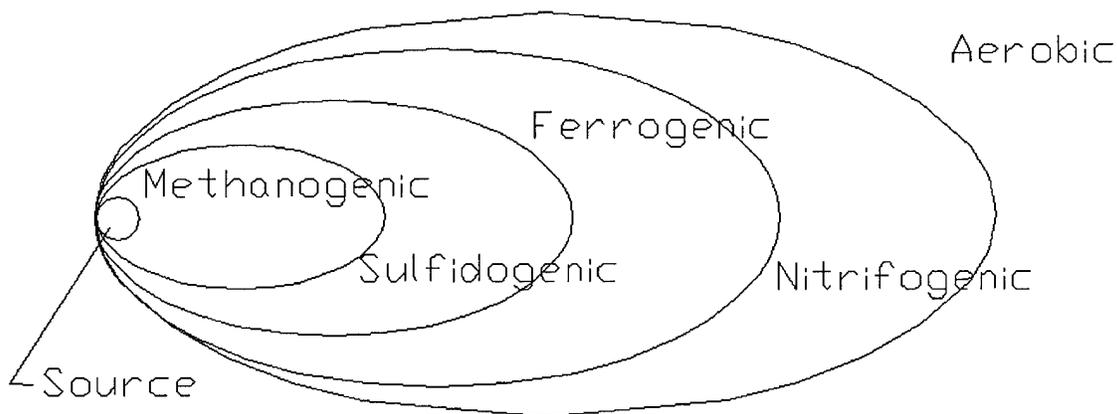
The oxidation of chlorinated aliphatic hydrocarbons can be modeled as an instantaneous reaction. The utilization of oxygen is rapid, and is typically limited by the availability of the electron acceptor rather than the degradation kinetics. In cases when the degradation rate is limiting, a first-order reaction model can be used. Another possibility is using the Monod kinetics to model the reaction (Carey et al., 1998).

### **2.3.3 Aquifer Redox Conditions**

The oxidation of an organic compound results in the breakdown of the organic molecule, which provides carbon for microbial cell growth. The oxidation of the compound also results in an electron transfer from the organic substrate (the electron donor or primary substrate) to available electron acceptors, which become reduced during the process. It is the electron transfer that provides the energy required for microbial metabolism.

There is typically an abundance of electron acceptors that may be available to support the biodegradation of organic compounds. In general, however, microbes will only use those

electron acceptors that will result in the greatest release of energy for microbial metabolism. Typical electron acceptors available in groundwater, in the order of those that release the greatest energy to those that release the least energy, are as follows: dissolved oxygen (aerobic), nitrate, manganese (IV) oxide and iron (III) hydroxide coatings on soil sediments, dissolved sulfate (sulfidogenic), and carbon dioxide (methanogenic) (Baedecker and Back, 1979; Lyngkilde and Christensen, 1992a). Table 1 illustrates the relative energy available from reducing the typical electron acceptors found in ground water. Over time, oxidation of a continuous source of primary substrate depletes the supply of available electron acceptors in a sequential manner starting with those releasing the most energy such that the redox potential in groundwater becomes more reducing as biodegradation proceeds. Thus, in an area of high contamination (large quantities of electron donor), the groundwater will become very reduced (carbon dioxide or sulfate as the electron acceptor). Moving away from the area of high contamination, the groundwater becomes less and less reduced.



**Figure 2.2**

<b>Terminal Electron Acceptors, Microorganisms, and Energy</b>				
Reduction Potential of Half Reaction (Eh) (mV/electron equivalent)	Terminal Electron Acceptor	Common Organism	Oxidation state, marginal conditions, organisms, or activities	Process or Reduced End Product
+810	Oxygen	Aerobes	Aerobic	H <sub>2</sub> O
+750	Nitrate (NO <sub>3</sub> <sup>-</sup> )	Nitrate Reducers	Aerotolerant Anaerobes Anoxic Conditions Facultative Anaerobes	N <sub>2</sub> , Nitrite (NO <sub>2</sub> )
+580	Manganese (MnIV)		Anaerobic	Mn(II)
+420 to +560	Halogenated Organics (RX)		Reductive Dehalogenation	Dehalogenated Carbons (RH, X <sup>-</sup> )
+60	Iron (FeIII)	Iron Reducers		FE(II)
-180	Organics Molecules (CH <sub>2</sub> O)	Fermentative Organisms	Strict Anaerobes	Alcohols, Fatty Acids, Ketones, H <sub>2</sub>
-210	Sulfate (SO <sub>4</sub> <sup>2-</sup> )	Sulfate Reducers	Simultaneous reactions of Fermentation, Sulfate reduction, and Methanogenesis	H <sub>2</sub> S, HS <sup>-</sup> , S, S <sub>2</sub> <sup>-</sup>
-240	Carbon Dioxide (CO <sub>2</sub> )	Methanogens		CH <sub>4</sub>

Stumm Morgan (1996), Dean (1992), Sawyer et al. (1994), Lovely et al. (1994)

**Table 2.2 Terminal Electron Acceptors, Microorganisms, and Energy**

The biodegradation (i.e. oxidation) of an electron donor in groundwater is always coupled with the reduction of an electron acceptor. Therefore, it is possible to have two different species of an electron acceptor present in groundwater: the oxidized species, which is the state that exists prior to the reduction of the electron acceptor; and the reduced species, which is the state that exists after the reduction of the electron acceptor.

### 2.3.4 Transformation Reactions

#### 2.3.4.1 Instantaneous Reactions

The reaction kinetics for the transformation of electron donors can be modeled assuming either instantaneous equilibrium reaction or first-order reaction. Equilibrium is typically assumed when the reaction is homogeneous (occurs in the aqueous phase) and rapid relative to groundwater flow.

In other words, the time required to mineralize the electron donor is nearly instantaneous when compared to other time scale reactions in the system. For example, the instantaneous model can be used to represent the oxygen-limited aerobic biodegradation of petroleum hydrocarbons.

$$G_{R,w} = \frac{C_a}{\mu_{ad} \Delta t}$$

**Equation 2.9**

$G_{r,w}$       general reaction rate for solute  $w$  ( $\text{ML}^{-3}\text{T}^{-1}$ )

$C_a$       concentration of electron acceptor  $a$  ( $\text{ML}^{-3}$ )

- $\mu_{ad}$  stoichiometric ratio expressed in mass of electron acceptor consumed per mass of electron donor utilized ( $\text{MM}^{-1}$ )
- $\Delta t$  time-step duration (T)

### 2.3.4.2 First-Order Kinetics

The complete reaction equation for a compound,  $w$ , incorporating the effects of both first order degradation to a daughter product and first order production of  $w$  from degradation of its parent compound,  $w-1$ , where degradation and production reactions occur in both the sorbed and aqueous phases is:

$$G_{R,w} = -\lambda_{a,w} C_w - \lambda_{s,w} \frac{\rho_b}{\theta} S_w + \mu_w \lambda_{a,w-1} C_{w-1} + \mu_w \lambda_{s,w-1} \frac{\rho_b}{\theta} S_{w-1}$$

**Equation 2.10**

- $G_{r,w}$  general reaction rate for solute  $w$  ( $\text{ML}^{-3}\text{T}^{-1}$ )
- $\lambda_{a,w}$  first-order, dissolved-phase degradation rate of solute  $w$  ( $\text{T}^{-1}$ )
- $\lambda_{s,w}$  first-order, sorbed-phase degradation rate of solute  $w$  ( $\text{T}^{-1}$ )
- $\mu_w$  stoichiometric coefficient for the transformation of parent solute  $w-1$  ( $\text{T}^{-1}$ )
- $\lambda_{a,w-1}$  first order, dissolved-phase degradation rate of the parent solute  $w-1$  ( $\text{T}^{-1}$ )
- $C_{w-1}$  dissolved-phase concentration of the parent solute  $w-1$  ( $\text{ML}^{-3}$ )
- $\lambda_{s,w-1}$  first-order, sorbed-phase degradation rate of the parent solute  $w-1$
- $C_w$  dissolved-phase concentration of solute  $w$  ( $\text{ML}^{-3}$ )
- $S_w$  sorbed-phase concentration of solute  $w$  ( $\text{MM}^{-1}$ )

## 2.4 MODELING

### **2.4.1 Motivation for Utilizing Models**

Models are an important tool that can be used to gain understanding of the fate and transport of chemicals in an aquifer. Models are a cost effective method of predicting the consequences of a proposed action. They are also useful as an interpretive tool to gain insight into the controlling parameters at a specific site. Models provide a framework for assembling and organizing field data and formulating ideas about system dynamics (Anderson and Woessner, 1992). A review of current fate and transport models follows. Although this review is not meant to be comprehensive, the most widely used and recognized groundwater contaminant fate and transport models that include biodegradation mechanisms are presented.

### **2.4.2 MT3D**

MT3D is a comprehensive three-dimensional solute transport model for simulation of advection, dispersion, chemical, and biological reactions of contaminants in groundwater systems. MT3D was first developed by Chunmiao Zheng in 1990 with partial support from the U.S. Environmental Protection Agency (USEPA). Since 1990, MT3D has been available as a public domain code from the USEPA (Zheng, 1990).

MT3D has a modular structure that permits simulation of transport of several components independently or jointly. MT3D interfaces directly with the U.S. Geological Survey finite-difference groundwater flow model, MODFLOW, and supports all the hydrologic and discretization features of MODFLOW. The MT3D code has a comprehensive set of solution options, including the method of characteristics (MOC), the modified method of

characteristics (MMOC), a hybrid of these two methods (HMOC), and the standard finite-difference method (FDM) (Zheng, 1990).

MT3D can be used to simulate changes in concentration of single-species miscible contaminants in groundwater considering advection, dispersion and some simple chemical reactions, with various boundary conditions and external sources or sinks. The chemical reactions included in the model are linear, Freundlich, or Langmuir equilibrium sorption and first-order irreversible decay or biodegradation (Zheng, 1990).

#### **2.4.3 RT3D**

RT3D is a Fortran 90-based software package for simulating three-dimensional, multi-species, reactive transport in groundwater. The code is based on the 1997 version of MT3D (DoD version 1.5), but has several extended reaction capabilities. RT3D can accommodate multiple sorbed and aqueous phase species with any reaction framework that the user wishes to define (Clement, 1997).

With a variety of pre-programmed reaction packages and the flexibility to insert user-specific kinetics, RT3D can simulate a multitude of scenarios. For example, natural attenuation processes can be evaluated or an active remediation can be simulated.

Simulations could potentially be applied to scenarios involving contaminants such as heavy metals, explosives, petroleum hydrocarbons, and/or chlorinated solvents. The users can enter their own reaction kinetic expressions or choose from a suite of 8 pre-programmed reaction packages. Pre-programmed packages include:

1. two species instantaneous reaction (Hydrocarbon & Oxygen)
2. instantaneous hydrocarbon biodegradation using multiple electron acceptors ( $O_2$ ,  $NO_3^-$ ,  $Fe^{3+}$ ,  $SO_4^{2-}$ ,  $CO_2$ )
3. kinetically limited hydrocarbon biodegradation using multiple electron acceptors ( $O_2$ ,  $NO_3^-$ ,  $Fe^{3+}$ ,  $SO_4^{2-}$ ,  $CO_2$ )
4. kinetically limited reaction with bacterial transport (hydrocarbon, oxygen, and Bacteria)
5. non-equilibrium sorption/desorption (can also be used for non-aqueous phase liquid dissolution)
6. reductive, anaerobic biodegradation of PCE/TCE/DCE/VC
7. combination of #3 and #6 (Clement, 1997).

#### 2.4.4 Bioplume III

BIOPLUME III is a new version of the BIOPLUME model that was developed at Rice University, by the developers of BIOPLUME II. BIOPLUME III is a two-dimensional, finite difference model for simulating the natural attenuation of organic hydrocarbon contaminants in groundwater due to the processes of advection, dispersion, sorption, and biodegradation. BIOPLUME III is based on the USGS solute transport code MOC. BIOPLUME III solves the solute transport equation six times to determine the fate and transport of the hydrocarbons, the electron acceptors ( $O_2$ ,  $NO_3^-$ ,  $Fe^{3+}$ ,  $SO_4^{2-}$ , and  $CO_2$ ), and the reaction by-products ( $Fe^{2+}$  and  $CH_4$ ). A number of aerobic and anaerobic electron acceptors such as oxygen, nitrate, sulfate, iron (III) and carbon dioxide have been considered in this model. Three different kinetic expressions can be used to simulate the aerobic and anaerobic biodegradation reactions. These include: first-order decay, instantaneous reaction and Monod kinetics. Time and space increments, hydrogeologic characteristics of the aquifer, initial and boundary conditions, sources and sinks, sorption, source decay, radioactive decay, ion-exchange and biodegradation variables can all be input into the model. The model solves the solute transport equation for both

hydrocarbon and oxygen, assumes an instantaneous reaction between oxygen and hydrocarbon, and combines the two plumes using the principle of superposition. Computations account for advection, dispersion, mixing, and biodegradation effects. Also, the program can simulate slow hydrocarbon plumes undergoing biodegradation and can simulate in situ bioremediation schemes such as the injection of oxygenated water. Moreover, the model can simulate reaeration and anaerobic biodegradation as a first-order decay in hydrocarbon concentrations (Bioplume, 1998).

#### **2.4.5 BioRedox**

BioRedox is a three-dimensional, multicomponent solute transport model that was developed to model the coupling between the biodegradation of organic compounds and the reduction of inorganic electron acceptors in groundwater. BioRedox is also capable of representing the sequential, redox-dependent biotransformation of chlorinated aliphatic hydrocarbons (CAHs) with the option of utilizing substrate-limited reaction kinetics. BioRedox is based on the public domain version of MT3D (Version DoD\_1.5) (Carey et al., 1998).

BioRedox is capable of simulating the fate and transport of aqueous-phase solutes, as well as interactions involving mineral-phase solutes such as manganese oxides or iron hydroxides. Transport processes that may be represented using BioRedox include:

- advection
- mechanical dispersion
- equilibrium sorption (linear or non-linear isotherms)

- biological or chemical sequential transformation assuming equilibrium or first-order kinetics with the option to specify co-metabolic or direct oxidation mechanisms
- halogen production during the degradation of halogenated solutes
- coupled oxidation-reduction reactions between multiple electron donors and electron acceptors, including representation of both the oxidized and reduced states of available electron acceptors

BioRedox provides three different equilibrium sorption isotherms to simulate the transfer between the dissolved and sorbed phases: linear, Freundlich, and Langmuir isotherms (Carey et al., 1998).

Transformation reactions contained within BioRedox are specific to each solute class. BioRedox is able to consider phase transitions between aqueous and mineral solutes during these transformation reactions. BioRedox also is able to couple transformation reactions involving aqueous and mineral solutes (Carey et al., 1998).

BioRedox contains two kinetic models for representing the transformation of electron donors: instantaneous reactions (electron acceptor-limited) and first order reactions. The instantaneous reactions may only be specified for the dissolved-phase of aqueous electron donors because it involves a coupling with the reduction of an electron acceptor solute. It assumes that instantaneous kinetic reactions are not applicable to mineral electron donors (such as native organic matter) or to the sorbed-phase of aqueous electron donors.

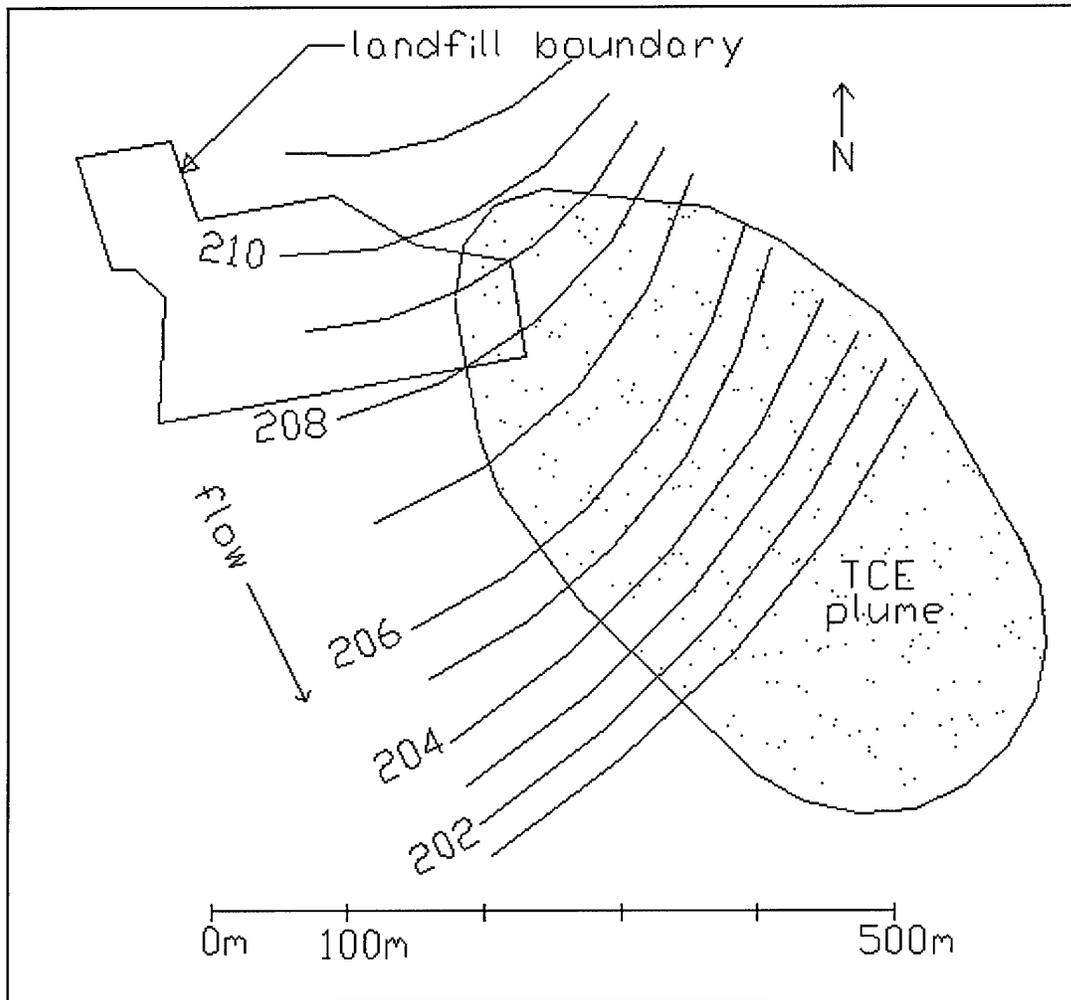
Oxidation of the electron donor will occur very rapidly compared to the rate of groundwater flow, and is only limited by the supply of the electron acceptor. The first-order reaction incorporates the effects of both solute degradation and solute production

assuming the sequential degradation of a parent solute as indicated in Section 2.3.11 (Carey et al., 1998).

## **2.5 FIELD SITE**

The case study is taken from a site at Moody AFB in Georgia. The site was a former landfill that was used between 1972 and 1978. Wastes deposited there include 50 cubic yards of fuel and solvent saturated soil. CDM Federal Programs Corp. studied the site in 1997. The aquifer is primarily sand/silty sand. The contaminants from the landfill have mobilized to the aquifer. Under the center of the former landfill site the highest concentration of TCE is 9.3 mg/L, 1,2-DCE is 1.6 mg/L, and VC is 3.2 mg/L. The site has many other organic contaminants including benzene, toluene, acetone, and xylene. Groundwater is highly reduced (methanogenic) under the landfill. The VC concentration decreases as flow moves from the source with no VC being detected downgradient when the plume becomes aerobic. Concentrations of ethene and ethane in the plume suggests TCE and its daughter products are completely mineralizing. With no down gradient measurable concentrations of the TCE, DCE, and VC at 800 ft and steady-state attenuation predicted by BioPlume III, the site appears to be naturally attenuating.

The groundwater movement beneath the landfill is toward the East and Southeast (Figure 2.3). The shallow aquifer is recharged from infiltration of precipitation. The water table is approximately 15 feet below the surface. The Grand Bay Swamp which is down gradient from the site, is possibly a discharge zone.



**Figure 2.3**

The following figure shows the location of sampling points (#):

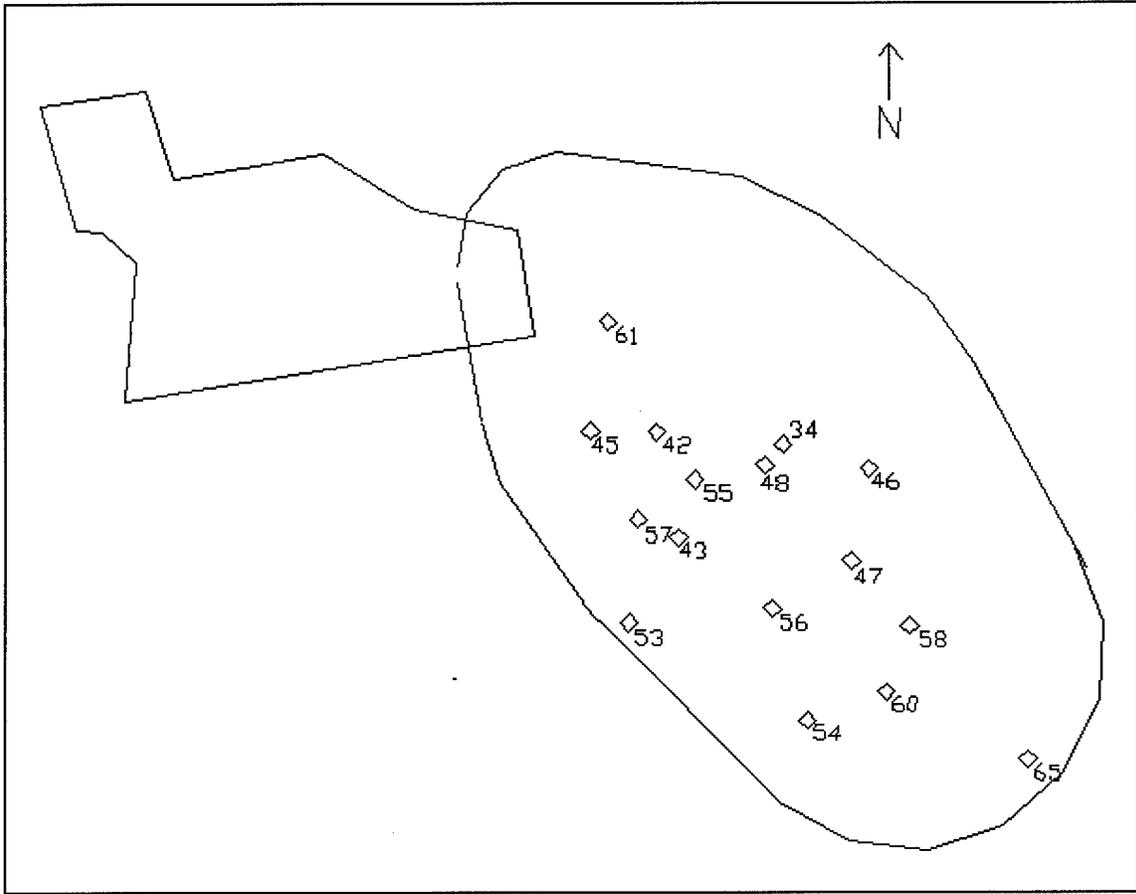


Figure 2.4

## **3.0 METHODOLOGY**

### **3.1 OVERVIEW**

In this chapter, we will develop a methodology to determine if the hypothesized mechanism of methanogenesis supported by cometabolism can potentially explain the natural attenuation of chlorinated aliphatic hydrocarbons. The methodology is based upon the BioRedox model. In the first section, layout of a hypothetical site and processes utilized in the model will be described. In the second section, a sensitivity analysis using BioRedox will be planned to identify the parameters most influential in determining the rate and extent of natural attenuation. In the third section, we will discuss a site that exhibits characteristics of these processes occurring and use BioRedox to characterize the site.

### **3.2 RESEARCH OBJECTIVES**

1. Determine if the methane generated anaerobically will be sufficient to support aerobic cometabolism of the dechlorinated daughter products (DCE and VC).
2. Model "typical" hydrogeologic conditions that support reductive dechlorination of TCE to DCE and VC before the compounds are transported to an aerobic zone.
3. Conduct an optimization and sensitivity analysis of advection/dispersion, bioavailability, and rate limited sorption on the effects to the fate and transport of the chemicals under study.

- Determine if competitive inhibition by methane will have the potential to significantly inhibit aerobic cometabolism of DCE and VC?

### 3.3 SITE LAYOUT AND RELEVANT PROCESSES

#### 3.3.1 Site Layout

The hypothetical site is a rectangular aquifer, 200 m wide by 500 m long (Figure 3.1). The site is discretized into 10 m x 10 m grid cells as shown on the figure. The East and West borders are constant head boundaries, while the North and South borders are no flow boundaries so that groundwater flows from the West to the East.

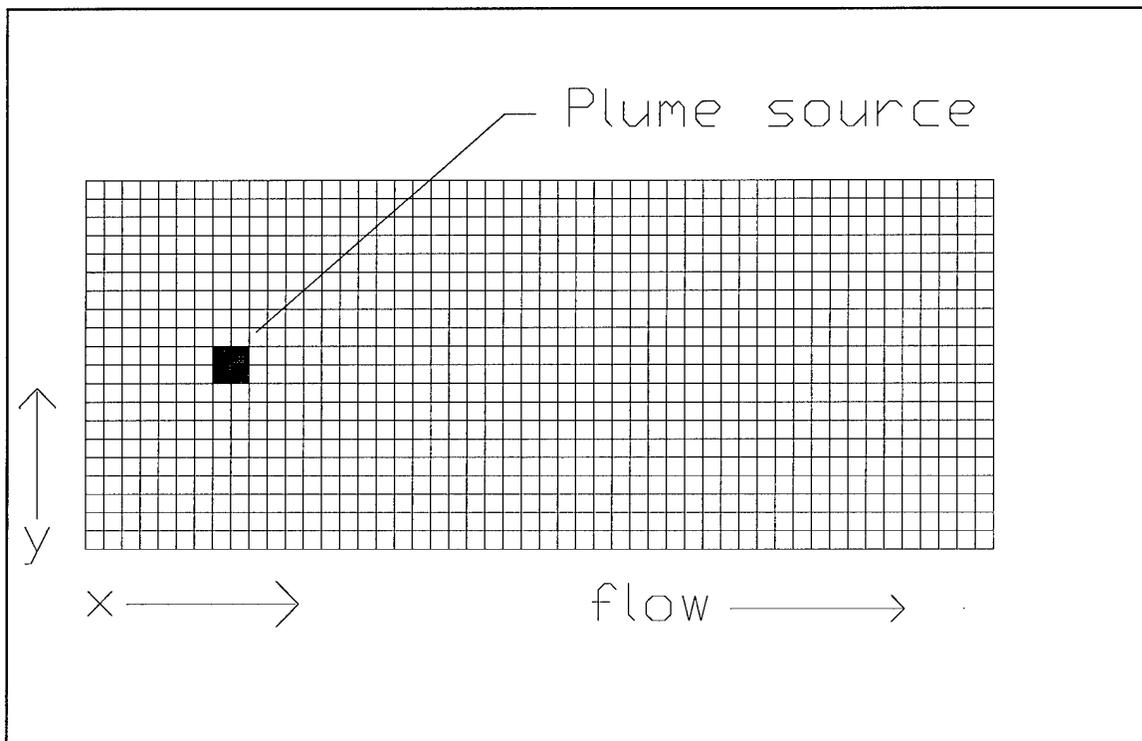


Figure 3.1

### **3.3.2 Bio-Chemical Reactions**

BioRedox was chosen because of its ability to model for sequential degradation of contaminants, electron acceptor and electron donor reactions, and its ability to simulate co-metabolic reactions. BioRedox allows the user to specify each transformation reaction. Each transformation reaction is specific to each solute class. Table 3.1 identifies each reaction for each solute in each redox zone. BioRedox is capable of representing phase transitions between aqueous and mineral phases during these transformation reactions. BioRedox can simulate instantaneous reactions (electron acceptor-limited), first-order reactions, and first-order substrate limited reactions.

REACTION				
Solute Name	Redox Zone	Reaction	Daughter Product	Halogen Product
TCE	Aerobic (cometabolic)	1st Order	none	Chloride
TCE	Ferrogenic	1st Order	cis-1,2-DCE	Chloride
TCE	Sulfidogenic	1st Order	cis-1,2-DCE	Chloride
TCE	Methanogenic	1st Order	cis-1,2-DCE	Chloride
cis-1,2-DCE	Aerobic (cometabolic)	1st Order	none	Chloride
cis-1,2-DCE	Methanogenic	1st Order	vinyl chloride	Chloride
vinyl chloride	Aerobic (direct oxidation)	1st Order	N/A	Chloride
vinyl chloride	Aerobic (cometabolic)	1st Order	none	Chloride
vinyl chloride	Ferrogenic	1st Order	N/A	Chloride
vinyl chloride	Methanogenic	1st Order	N/A	Chloride
BTEX	Denitrification	1st Order	N/A	N/A
BTEX	Ferrogenic	1st Order	N/A	N/A
BTEX	Sulfidogenic	1st Order	N/A	N/A
BTEX	Methanogenic	1st Order	N/A	N/A
Fe, 2+	Aerobic	instantaneous	N/A	N/A
methane	Aerobic	1st Order/instan	N/A	N/A
methane	Denitrificaiton	1st Order	N/A	N/A
methane	Ferrogenic	1st Order	N/A	N/A
methane	Sulfidogenic	1st Order	N/A	N/A
methane	Methanogenic	1st Order	N/A	N/A

**TABLE 3.1 Reaction Kinetics for each Solute in each Redox Zone**

### 3.3.3 Assumptions

The model assumes flow is steady-state. To further simplify the model we assume the aquifer is isotropic and homogenous and can be modeled as a 2-D system. We also assume the aquifer is confined. The contaminant is assumed to be in equilibrium between the sorbed and aqueous phases. This was modeled using a linear isotherm. The model assumed that there is no degradation in the sorbed phase.

### 3.4 BIOREDOX EXECUTION

The general algorithm of BioRedox is:

1. Define the simulation:
  - 1.1 Define solute properties database and redox reactions database.
  - 1.2 Define solutes for each class, and define all reaction rates/pathways.
  - 1.3 Define model dimensions and simulation options.
2. Allocate storage space for data arrays
3. Read and prepare all other input data relevant to the entire simulation.
4. For each stress period:
  - 4.1 Read and prepare input data relevant to each stress period.
  - 4.2 For each time step in a transient flow simulation:
    - 4.2.1 Read and prepare input data relevant to each time step.
    - 4.2.2 If first stress period, calculate initial mass in storage.
    - 4.2.3 Calculate dispersion coefficients constant within each time step.
    - 4.2.4 For each transport step:
      - 4.2.4.1 For each aqueous solute:
        - 4.2.4.1.1 Solve for the advection term.
        - 4.2.4.1.2 Solve for the dispersion term.
        - 4.2.4.1.3 Solve for the sink/source term.
        - 4.2.4.1.4 Proceed to next aqueous solute.
      - 4.2.4.2 Solve for the reactions of all aqueous and mineral solutes.
      - 4.2.4.3 Calculate mass budgets.
      - 4.2.4.4 Output relevant data.
      - 4.2.4.5 Proceed to next transport step.
    - 4.2.5 Proceed to next time step.
  - 4.3 Proceed to next stress period.
5. End simulation.

### 3.5 SENSITIVITY ANALYSIS

The purpose of a sensitivity analysis is to ascertain the relative effect of each parameter on the outcome. The attempt to quantify the uncertainty in the calibrated model is caused by uncertainty in the estimates of model parameters. Because we first develop a very simple hypothetical model under idealized conditions, the parameter that has the most effect will be identified by its deviation from the ideal condition.

Table 3.2 lists the parameter used to create the hypothetical aquifer studied in the sensitivity analysis. Values that were not changed can be found in Appendix B - Data Input files.

<b>AQUIFER CHARACTERISTIC RANGES</b>				
Transport Parameter	Units	Minimum	Baseline	Maximum
Hydraulic Conductivity	m/day	1.00E-03	4.00E-01	1.00E+01
Longitudinal Dispersivity	m	0.01	1	100

(Domenico & Schwartz 1998)

**Table 3.2 Aquifer Characteristics Ranges**

The first order constants in Table 3.3 for the base line case were taken from a study of Plattsburgh AFB site (Wiedemeier et al., 1996, Carey et al., 1998). Any chemical with a specified redox zone reaction omitted from Table 3.3 was not modeled.

<b>REACTION RATE RANGES</b>					
Solute Name	Redox Zone	Reaction	RC1* Min (1/day)	RC1* Baseline (1/day)	RC1* Max (1/day)
TCE	Aerobic (cometabolic)	1st Order substrate limited	4.50E-04	1.14E-02	3.00E-01
TCE	Ferrogenic	1st Order	4.50E-04	3.80E-03	3.00E-01
TCE	Sulfidogenic	1st Order	4.50E-04	3.80E-03	3.00E-01
TCE	Methanogenic	1st Order	4.50E-04	3.80E-03	3.00E-01
cis-1,2-DCE	Aerobic (cometabolic)	1st Order substrate limited	7.10E-04	1.14E-02	2.60E-02
cis-1,2-DCE	Denitrification	1st Order	7.10E-04	3.80E-03	2.60E-02
cis-1,2-DCE	Ferrogenic	1st Order	7.10E-04	3.80E-03	2.60E-02
cis-1,2-DCE	Sulfidogenic	1st Order	7.10E-04	3.80E-03	2.60E-02
cis-1,2-DCE	Methanogenic	1st Order	7.10E-04	3.80E-03	2.60E-02

vinyl chloride	Aerobic (direct oxidation)	1st Order	3.00E-05	7.60E-03	1.20E-02
vinyl chloride	Aerobic (cometabolic)	1st Order substrate limited	3.00E-05	1.14E-02	1.20E-02
vinyl chloride	Denitrification	1st Order	3.00E-05	7.60E-03	1.20E-02
vinyl chloride	Ferrogenic	1st Order	3.00E-05	3.80E-03	1.20E-02
BTEX	Aerobic	instantaneous	N/A	N/A	N/A
BTEX	Aerobic	1st Order	6.00E-05	2.30E-02	6.00E-01
BTEX	Denitrification	1st Order	6.00E-05	2.30E-02	6.00E-01
BTEX	Ferrogenic	1st Order	6.00E-05	1.90E-03	6.00E-01
BTEX	Sulfidogenic	1st Order	6.00E-05	1.90E-03	6.00E-01
BTEX	Methanogenic	1st Order	6.00E-05	1.90E-03	6.00E-01
Fe, 2+	Aerobic	instantaneous	N/A	N/A	N/A
methane	Aerobic (oxidation)	1st Order	1.00E-06	1.14E-02	6.00E-01
methane	Denitrification	1st Order	1.00E-06	8.50E-04	6.00E-01
methane	Ferrogenic	1st Order	1.00E-06	8.50E-04	6.00E-01
methane	Sulfidogenic	1st Order	1.00E-06	8.50E-04	6.00E-01

Wilson et al., 1996; Ellis, 1996, Chapelle, 1996, Wiedemeier et al., 1996, Carey et al., 1998

\*  $RC1 = \lambda_{a,w}$  (Equation 2.10)

**Table 3.3 Reaction Rate Ranges**

Each electron acceptor solute was analyzed based on a background concentration with groundwater flowing into the aquifer containing the constant background concentration (Table 3.4). The contaminants, TCE and BTEX, were given a constant concentration source. The compounds,  $Fe^{2+}$ , 1,2-cis DCE, VC,  $CH_4$  and Cl were not given initial values because they are product species of the transformation reactions.

INITIAL CONCENTRATION RANGES					
Name	Type	Phase	Minimum mg/L	Baseline mg/L	Maximum mg/L
BTEX	e-donor	aqueous	0	7	100
Fe, 2+	e-donor	aqueous	N/A	N/A	N/A
CH4	e-donor	aqueous	N/A	N/A	N/A
O2	e-acceptor	aqueous	0	5	10
NO3, -	e-acceptor	aqueous	0	5	100

Fe, 3+	e-acceptor	mineral	0	5	100
SO4, 2-	e-acceptor	aqueous	0	5	100
TCE	general	aqueous	0	5	100
DCE	general	aqueous	N/A	N/A	N/A
VC	general	aqueous	N/A	N/A	N/A
Cl	hologen	aqueous	N/A	N/A	N/A

**Table 3.4 Chemical Concentration Ranges**

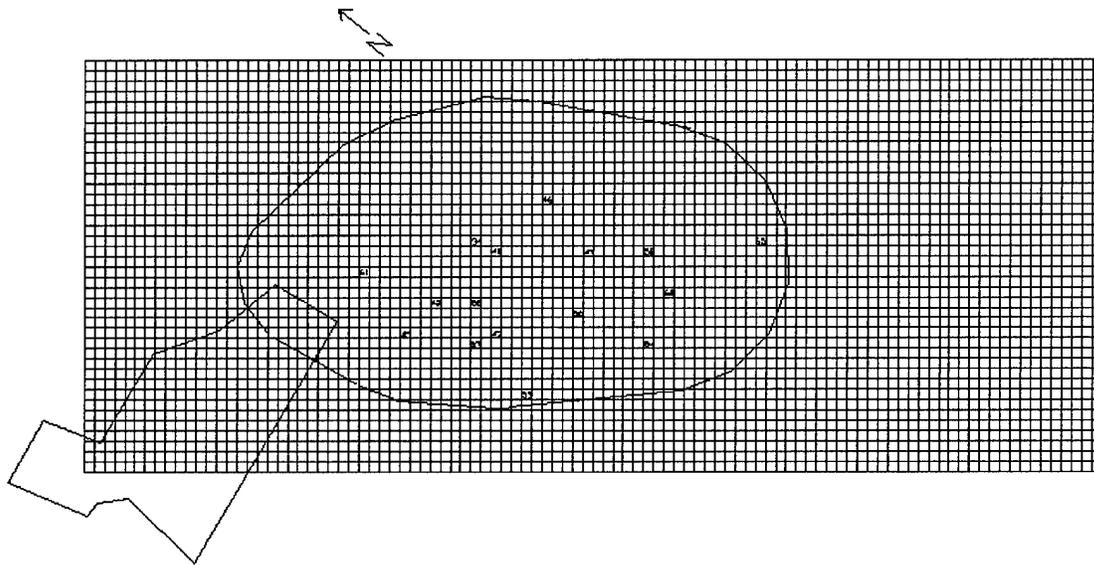
### 3.6 FIELD STUDY

Moody AFB Landfill #4 was chosen to illustrate a site that may be affected by the sequence of reactions hypothesized in this thesis. The Moody AFB landfill #4 study indicated the site had a hydraulic conductivity averaging 0.321 feet/day, the hydraulic gradient was 0.0094, porosity was 0.20 and the average groundwater linear velocity was therefore equal to 5.5 feet/year (Bourquin et al., 1997). Figure 3.2 illustrates how the plume was modeled by BioRedox.

Background concentrations for nitrate and sulfate were insignificant. The background oxygen concentration was 2.9 mg/L. When oxygen was less than 1.0 mg/L the area was assumed to be anaerobic. Fe(III) had a background concentration of 8.1 mg/L. Methane was present throughout the contaminant plume with the highest detected concentration of methane detected at a monitoring well 200 meters down gradient. Table 3.5 provides the concentrations of the various solutes measured at the monitoring well sites. We used the same values the Bourquin study used. The Bourquin study used conservative first-order degradation rates from the literature (Ellis, 1996). The rates used were TCE ( $1.59 \times 10^{-4} \text{ day}^{-1}$ ), DCE ( $1.81 \times 10^{-4} \text{ day}^{-1}$ ), and VC ( $1.56 \times 10^{-4} \text{ day}^{-1}$ ). The first-order degradation rate for

BTEX was assumed to be  $2.3e-2 \text{ day}^{-1}$ . BTEX was assumed to be added to the plume from the landfill at a concentration of 0.01 mg/L. The first order rate for direct oxidation of methane in the aerobic zone was estimated at  $1.14e-2 \text{ day}^{-1}$ .

The following picture illustrates the locations of the sampling points done for the study:



**Figure 3.2**

Well No	Cell Location x,y	TCE mg/L	DCE mg/L	VC mg/L	CH4 mg/L
DPT-42	35,24	0.34	0.615	1.034	5.39
DPT-43	41,27	0.087	0.29	3.103	10
DPT-45	32,27	0.016	0.063	0.215	3.9
DPT-46	46,14	0.0005	0.0005	0.0005	0.0178
DPT-47	50,19	0.011	0.0329	0.127	2.06
DPT-48	41,19	0.001	0.0013	0.0005	0.261
DPT-53	44,33	0.0031	0.0242	0.0005	3.06
DPT-54	56,28	0.0008	0.0045	0.0005	0.2289
DPT-55	39,24	0.306	0.415	0.869	0.673
DPT-56	49,25	0.34	0.1447	0.0438	0.702
DPT-57	39,28	0.035	0.2278	0.091	1.26
DPT-58	56,19	0.017	0.029	0.0005	0.2184
DPT-60	58,23	0.0005	0.0005	0.0005	0.752
DPT-61	28,21	0.025	0.043	0.14	2.05

DPT-65	69,18	0.0005	0.0005	0.0005	0.01
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**Table 3.5 Concentrations of Contaminants at Landfill Site**

## 4.0 ANALYSIS

### 4.1 INTRODUCTION

This chapter includes sensitivity analysis using BioRedox along with a model study of the Moody AFB site.

### 4.2 SENSITIVITY ANALYSIS

#### 4.2.1 Hydraulic Conductivity

Hydraulic conductivity is a coefficient of proportionality describing the rate at which water can move through a permeable medium. The purpose of testing varying rates of hydraulic conductivity is to analyze how the change in the water velocity will affect the fate and transport of the chlorinated solvents and therefore, the efficiency of natural attenuation. In this study the hydraulic conductivity was varied from 0.001 m/day to 10 m/day.

Figures presented in the sensitivity analysis are a 30 year time profile of a centerline cross section of the plume. As shown in Figure 4.1, at the slowest hydraulic conductivity TCE was completely degraded within 20 meters of the source. As the velocity of the water increased, the length of the plume increased. Using the oxygen concentration increase above the minimum level needed for microbial activity as an indication of the farthest down gradient point of the plume, the plume changed from 20 meters to 150 meters in length from the slowest velocity to the highest velocity. As shown in the figure 4.1, natural attenuation was insufficient to degrade TCE at the highest water velocity.

Although, DCE and VC were degraded completely (Figure 4.2 and 4.3) the TCE traveled too quickly through anaerobic zones to be sufficiently degraded. Once reaching the aerobic zone, the degradation of TCE by aerobic cometabolism didn't occur because the lack of methane available. The only decrease in TCE concentration in the aerobic zone occurred because of dispersion. Natural attenuation of CAHs is not conducive at high water velocities, although it is extremely rare that a soil matrix will allow a hydraulic conductivity of 10 m/day.

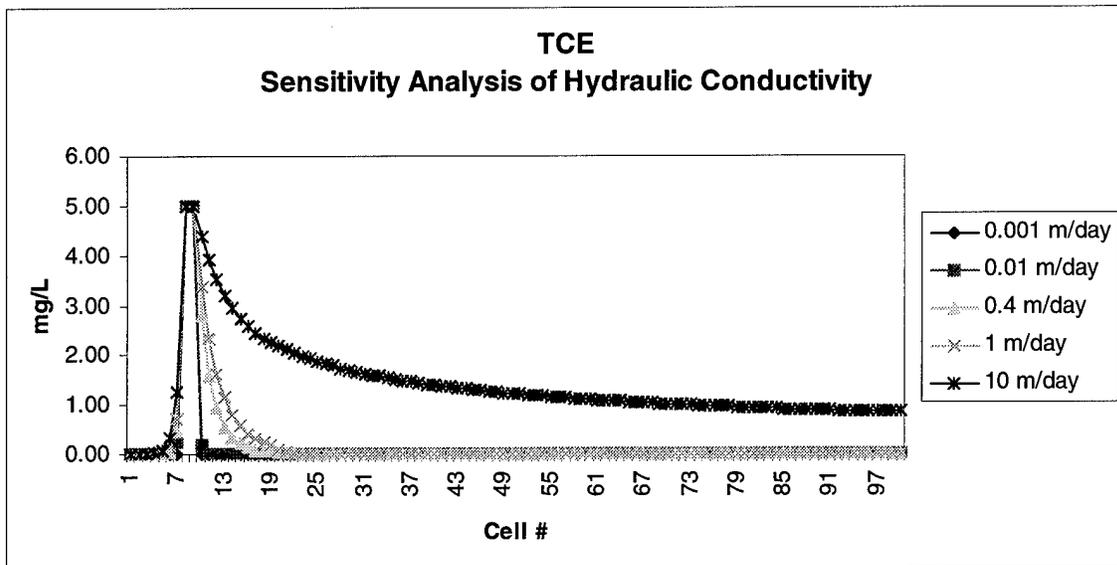


Figure 4.1

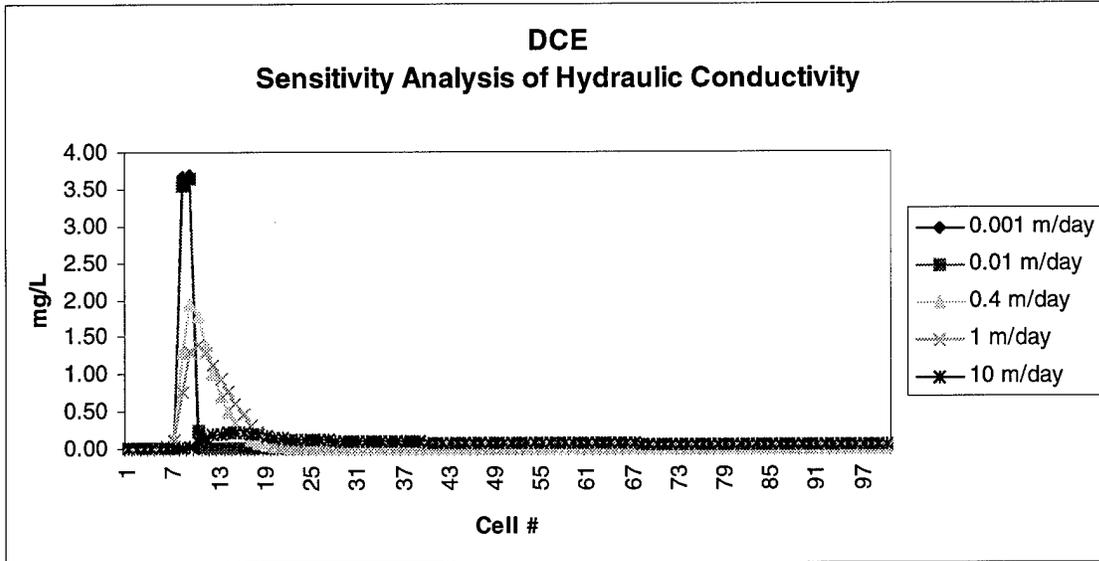


Figure 4.2

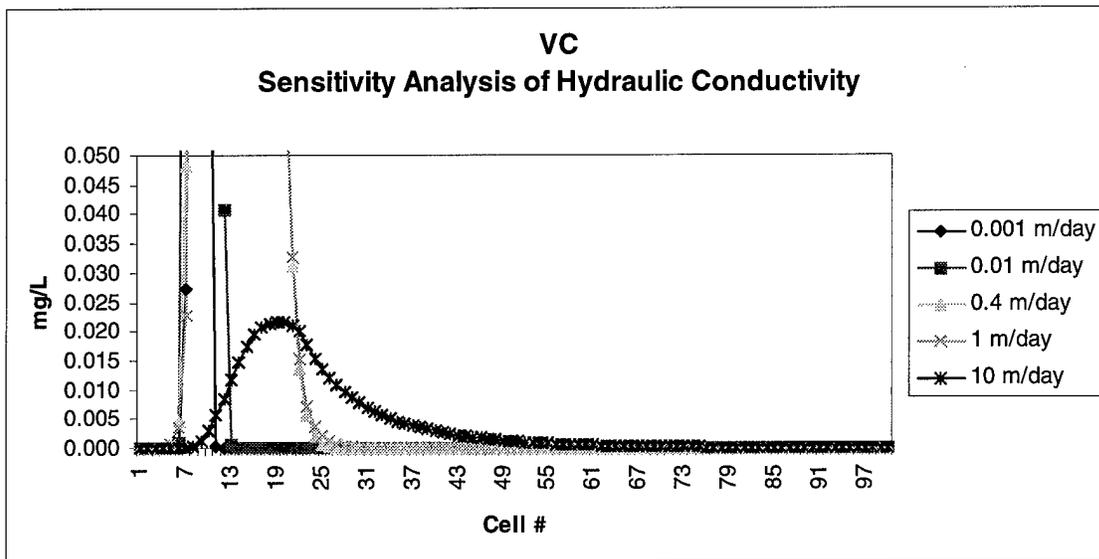


Figure 4.3

#### 4.2.2 Dispersion

Dispersion is the spreading of molecules along and away from the groundwater flow path due to pure advection as a result of mixing of groundwater in individual pores and

channels. Dispersion causes the contaminant concentration to reduce due to spreading of the contaminant mass. This study looked at the effects of dispersion on contaminant fate. The dispersivity was varied from 0.01 to 100 m. The value of dispersivity also allows the contaminant to travel up gradient from the source giving the appearance the source area may be larger than it actually is.

At the smallest dispersivity the CAHs were able to completely degrade. Only at the highest dispersion coefficient of 100 were TCE and DCE unable to degrade completely (Figure 4.4 and 4.5). It appears they are unable to degrade completely before they reach the aerobic zone. VC does not have this same difficulty (Figure 4.6) because it can degrade as a primary substrate in the aerobic zone.

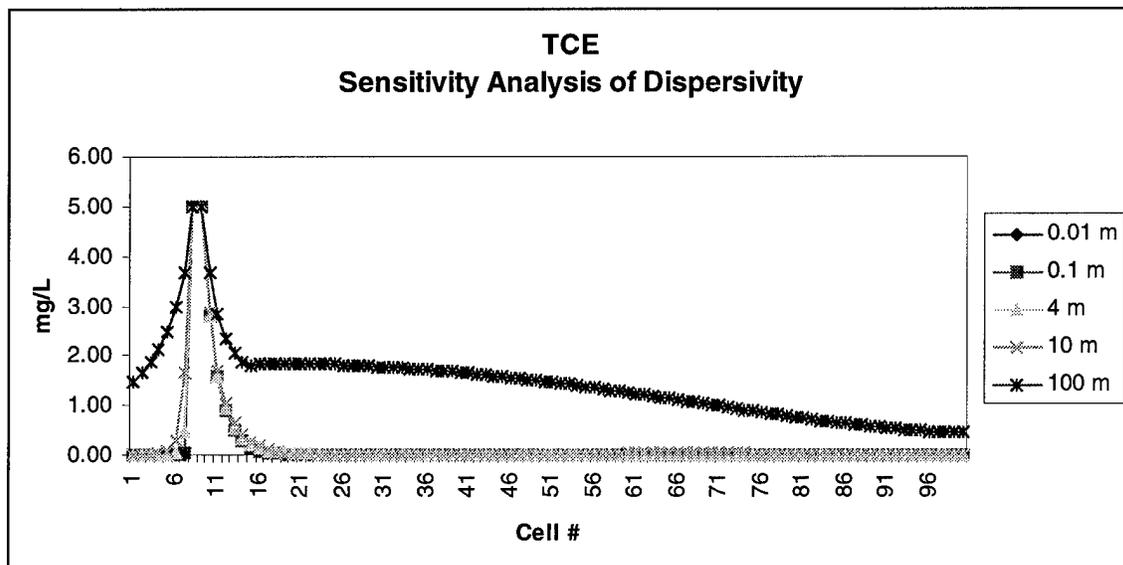


Figure 4.4

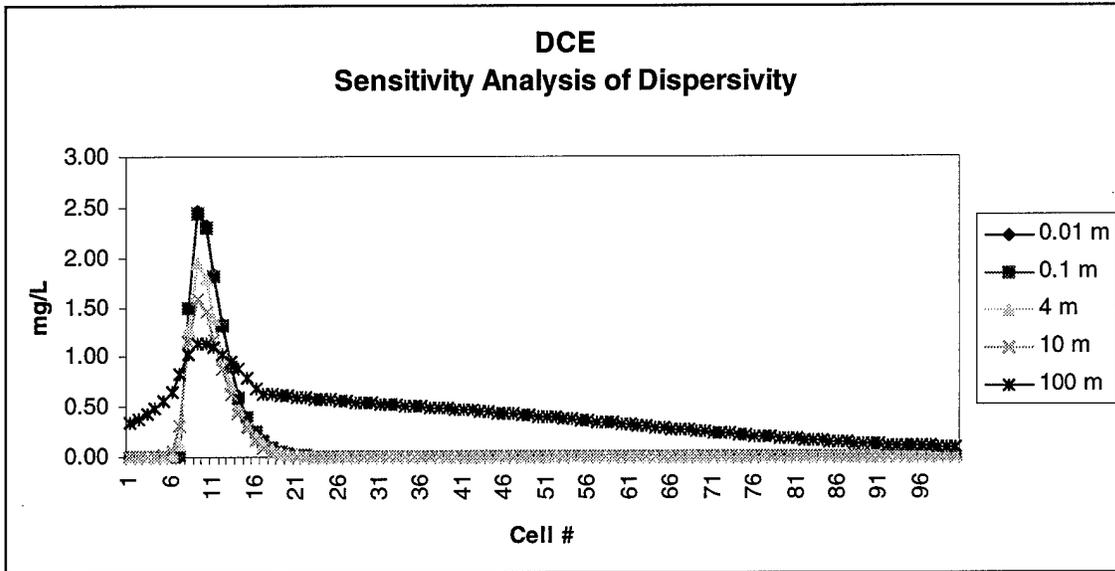


Figure 4.5

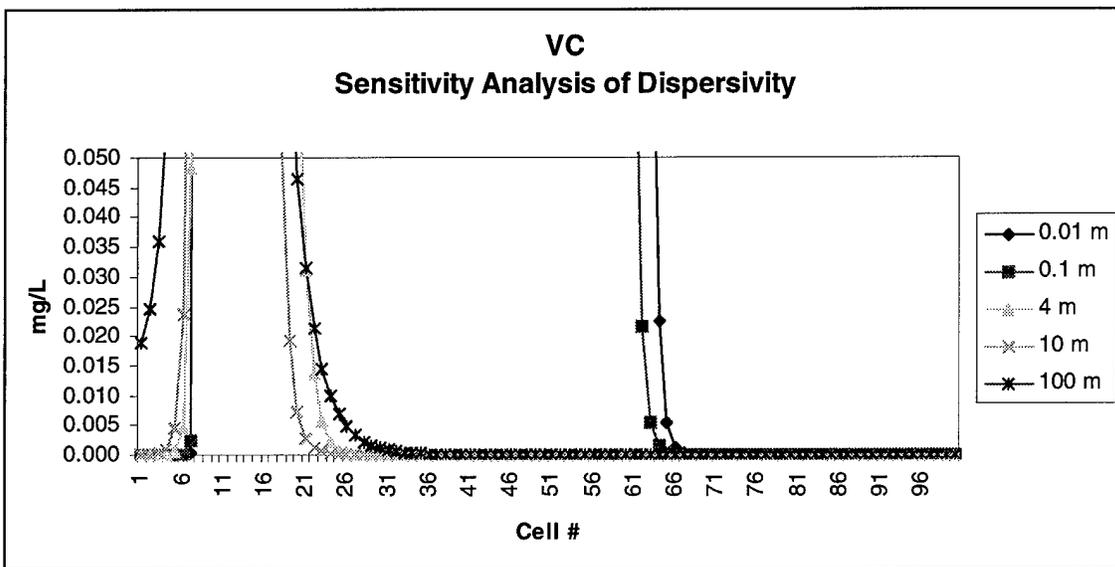


Figure 4.6

### 4.2.3 Contaminant Concentration

#### 4.2.3.1 BTEX

The BTEX concentration is an important parameter because it is the source of methane which is needed down gradient for the cometabolic degradation of the chlorinated solvents. The anaerobic source zone is critical, as TCE needs methanogenic or sulfidogenic conditions to reductively dechlorinate. BTEX is an arbitrary chemical because any hydrocarbon or related chemical that can be a source of organic carbon and will deplete the electron acceptors in the aquifer will have the same significance. BTEX was introduced into the aquifer as a constant concentration source that varied from 0 mg/L to 70 mg/L.

When BTEX was set at 0 mg/L the aquifer never became anaerobic. Therefore, TCE was unable to degrade anaerobically and there was no methane produced to degrade TCE cometabolically in the aerobic area (Figure 4.7). Also note that when BTEX was less than or equal to 0.007 mg/L, no DCE was produced (Figure 4.8). The source zone did not become anaerobic until the BTEX concentration was 0.7 mg/L. The TCE was degrading when the BTEX concentration was at 0.7 mg/L but DCE would not degrade. At a BTEX concentration of 3 mg/L a noticeable level of methane was produced (1 mg/L). At this minimum BTEX concentration the chlorinated solvent was able to completely degrade, as methane was available to support cometabolism in the aerobic zone. When the BTEX was introduced at a concentration of 70 mg/L, the TCE degraded anaerobically. However, because of the low rate VC anaerobic degradation, the VC traveled a significant distance down gradient before it degraded (Figure 4.9). This was because the high BTEX levels created a very long anaerobic zone. Only when VC reached the aerobic zone was it able to degrade. From these simulations, it appears the successful

degradation of CAHs requires a minimum concentration of BTEX. There is no apparent upper limit on the concentration BTEX can be at for the complete degradation of TCE.

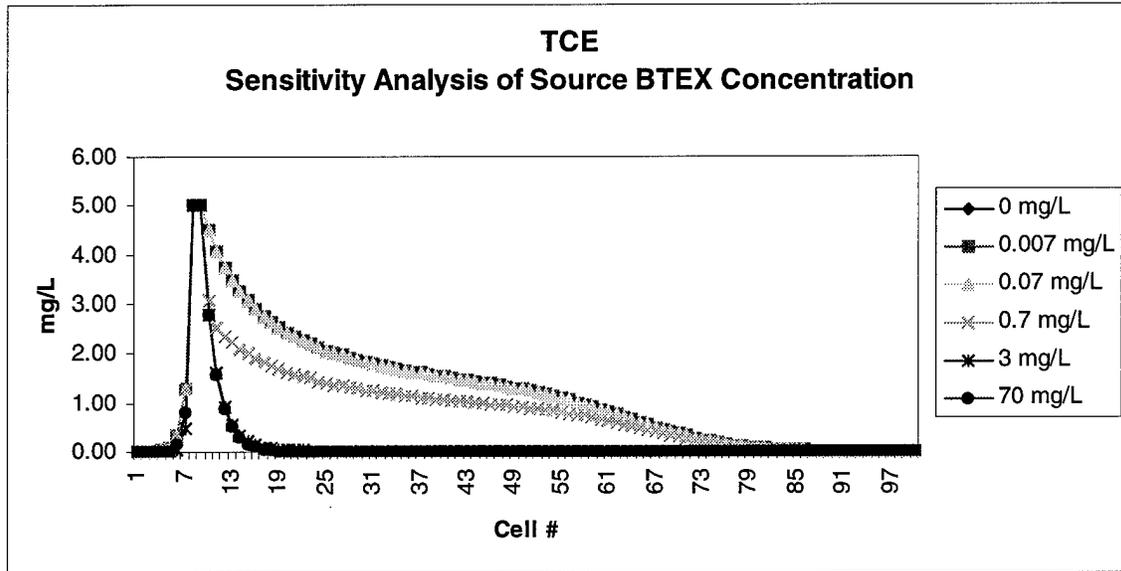


Figure 4.7

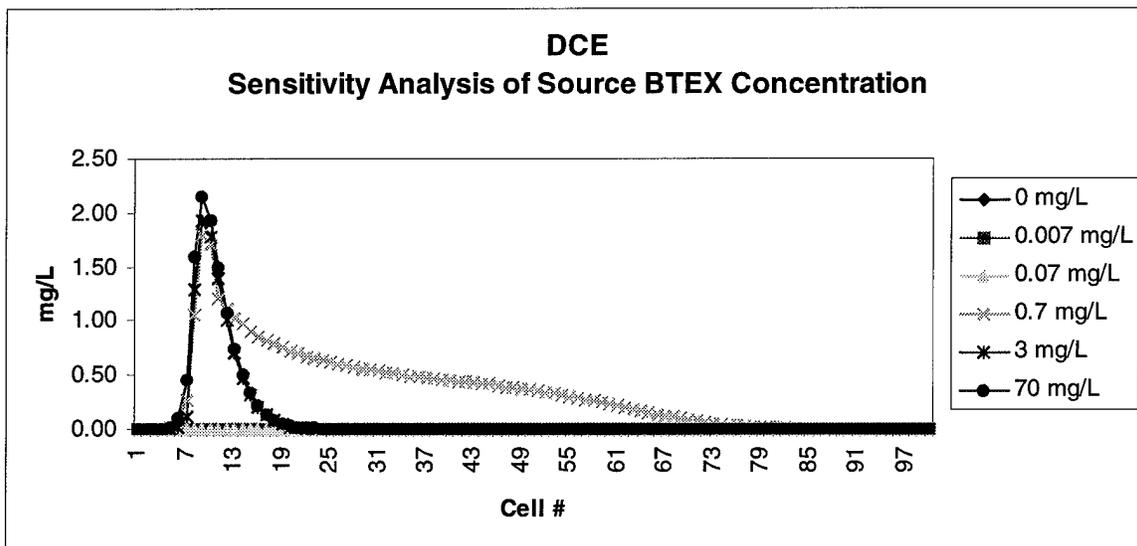
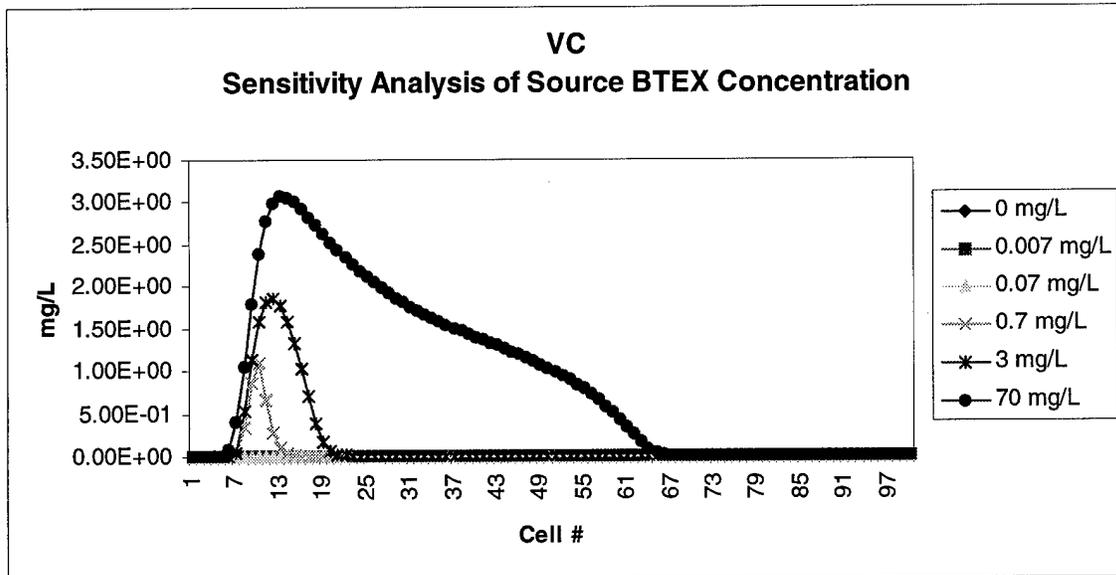


Figure 4.8



**Figure 4.9**

#### 4.2.3.2 TCE

The TCE source concentration needs to be studied to find if the concentration of TCE will adversely affect its degradation. High concentrations of TCE may overwhelm the electron acceptors to degrade the TCE. There is excessive supply of TCE that reductive dechlorination and cometabolism combined can not degrade all of the TCE. TCE was placed as a constant concentration source and was varied from 0.005 mg/L (Safe Drinking Water Act established maximum contaminant level) to 100 mg/L.

TCE was degraded completely under all source concentration levels. The redox zones remained constant for all concentration tests of TCE. When TCE was placed at 100 mg/L, VC reached a high value of 38 mg/L. Even at this high concentration, VC was able to be completely degraded once the chemical reached the aerobic zone. This information combined with the information from the tests from the BTEX source concentration tests,

makes it clearly apparent the importance of the creation of the anaerobic and aerobic zones to degrade the chlorinated solvent and how the concentration of BTEX is the primary influence on the creation of the redox reducing zones.

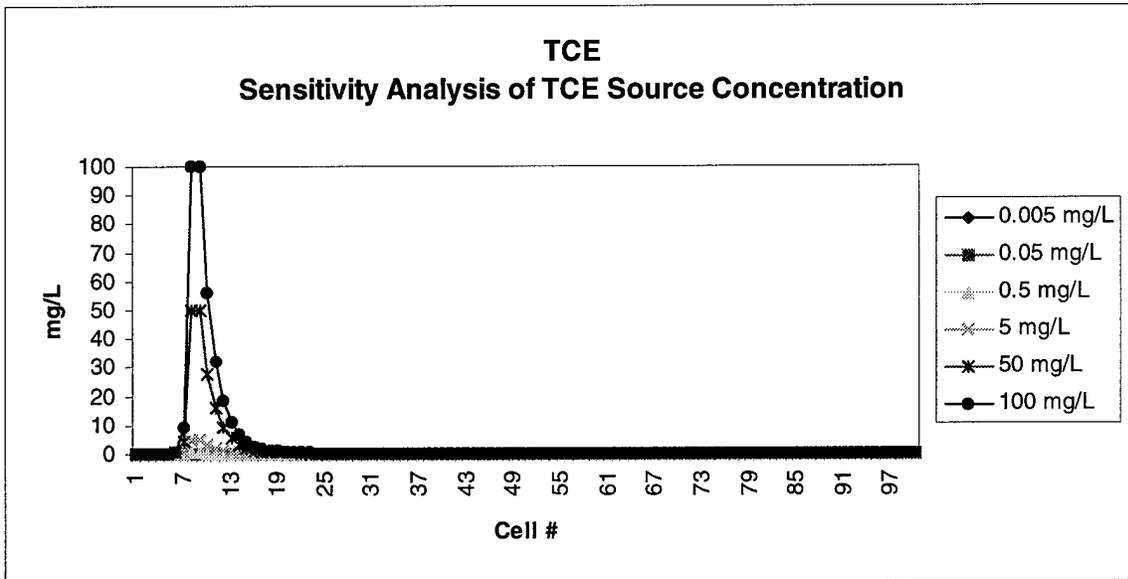


Figure 4.10

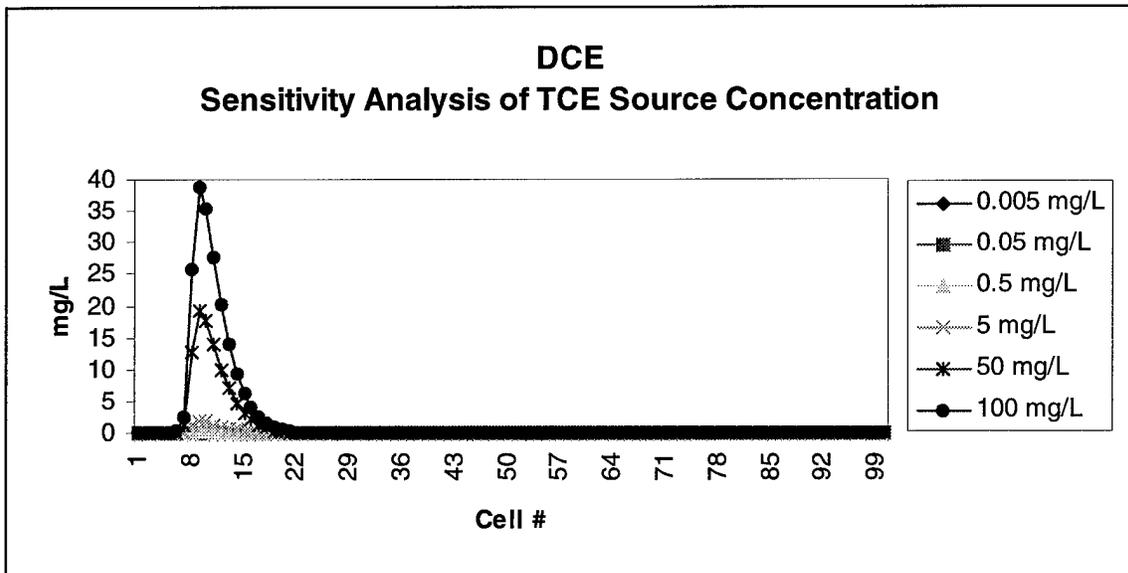
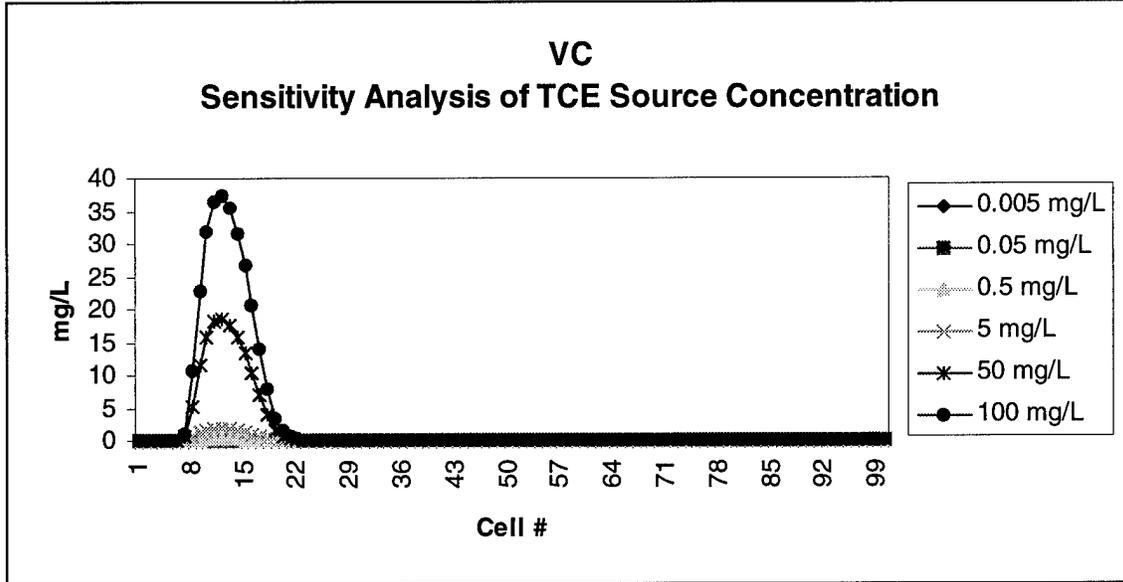


Figure 4.11



**Figure 4.12**

#### 4.2.4 Electron Acceptor Background Concentration

##### 4.2.4.1 O<sub>2</sub>

Initial oxygen concentration flowing into the aquifer from the western boundary was varied between 0.005 mg/L and 10 mg/L. The difference in the background concentration of oxygen had no net effect difference on the complete mineralization of TCE because for all concentrations TCE completely mineralized. The only effect the oxygen concentration was on the length of the plume. This result seems reasonable because a higher concentration will simply make more electron acceptors available to degrade the electron donors (BTEX, CAHs, methane). An oxygen concentration of 10 mg/L produced a plume length of 90 meters while a oxygen concentration of 0.5 mg/L produced a plume length of 550 meters. As the plume increased so did the distance the VC traveled before it was finally degraded under aerobic conditions (Figure 4.13).

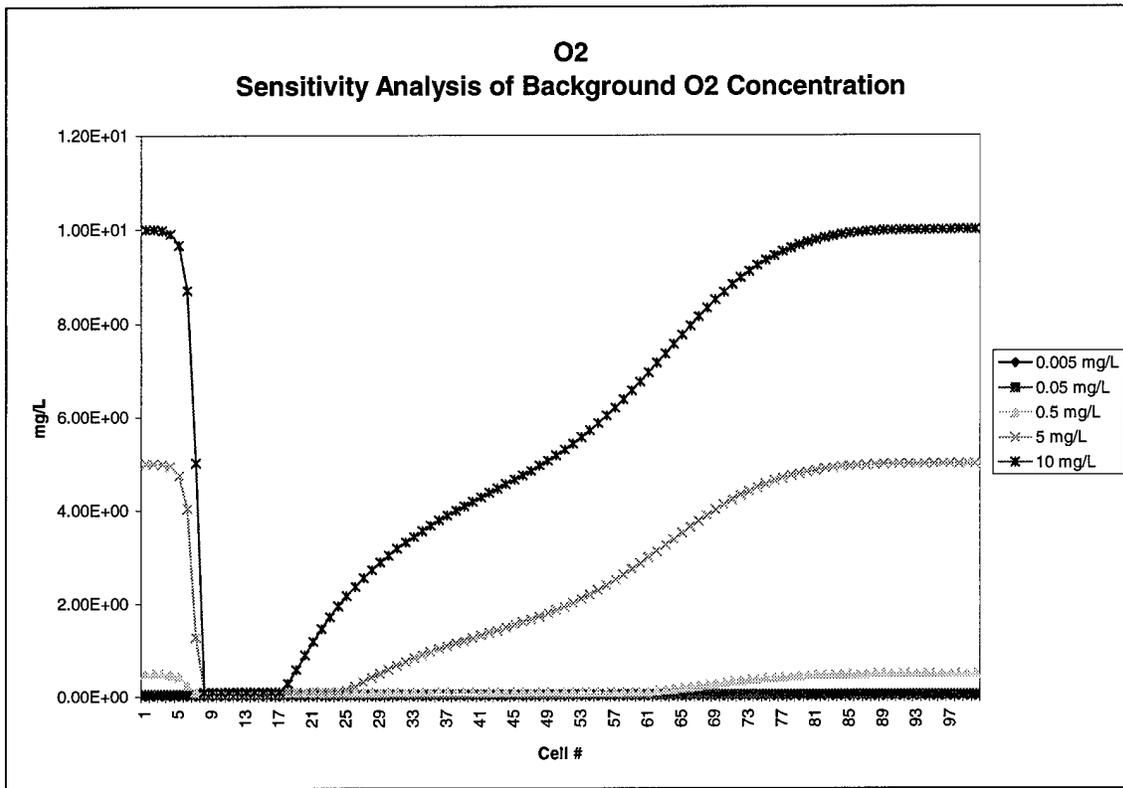


Figure 4.13

#### 4.2.4.2 SO4

Initial western boundary sulfate concentration was varied between 0.005 mg/L and 100 mg/L. The difference in the background concentration of sulfate had no net effect difference on the complete mineralization of TCE except at very high concentrations. At 100 mg/L sulfate TCE and DCE were not able to degrade completely. An explanation is the high concentration of sulfate prevented the creation of a methanogenic zone. The explanation is supported by the fact that simulations of methane should that there was no methane produced when sulfate was set at 100 mg/L.

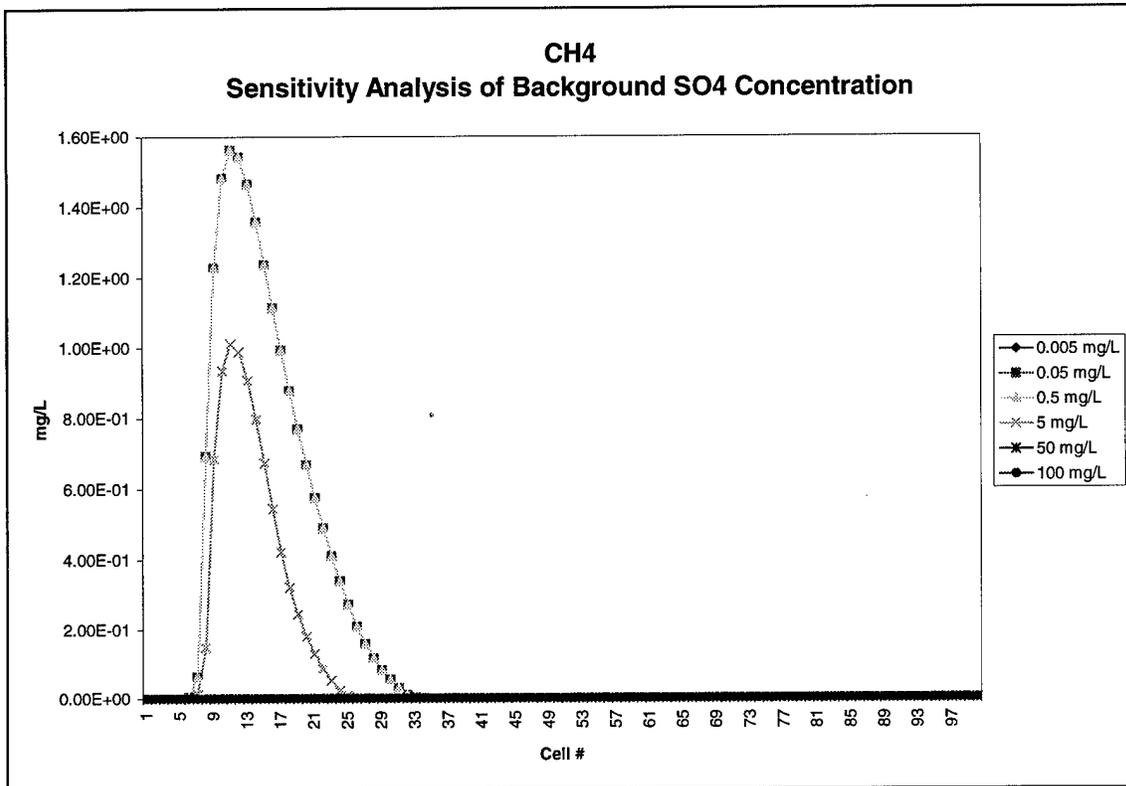


Figure 4.14

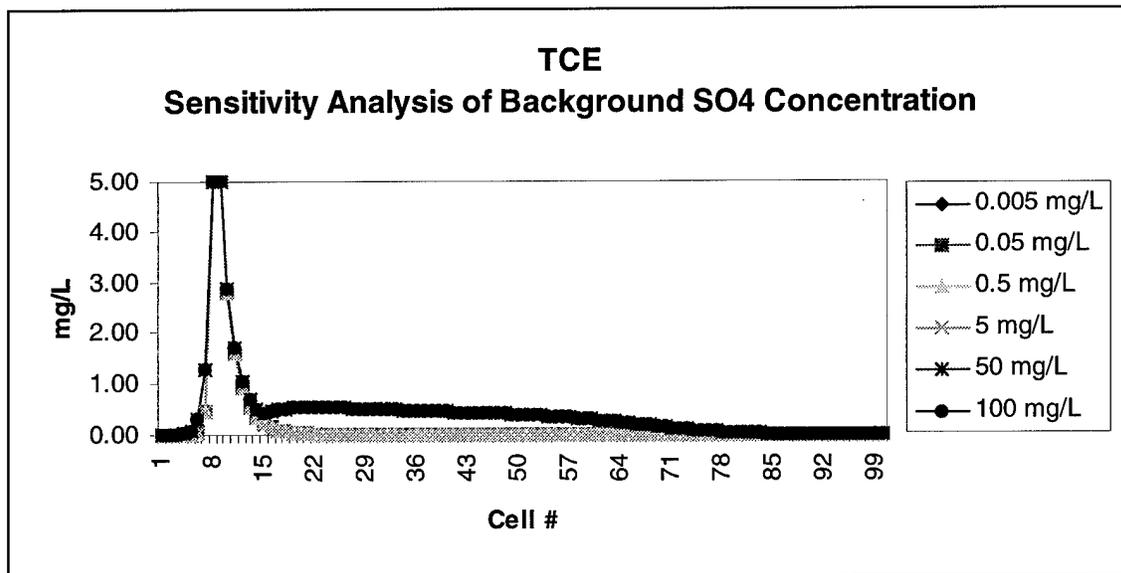


Figure 4.15

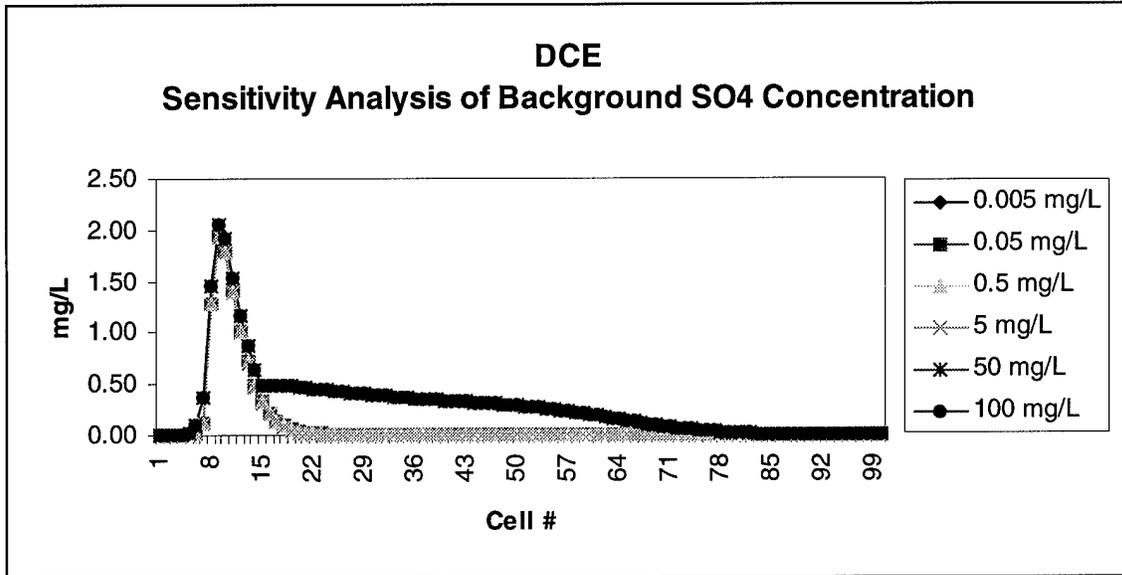


Figure 4.16

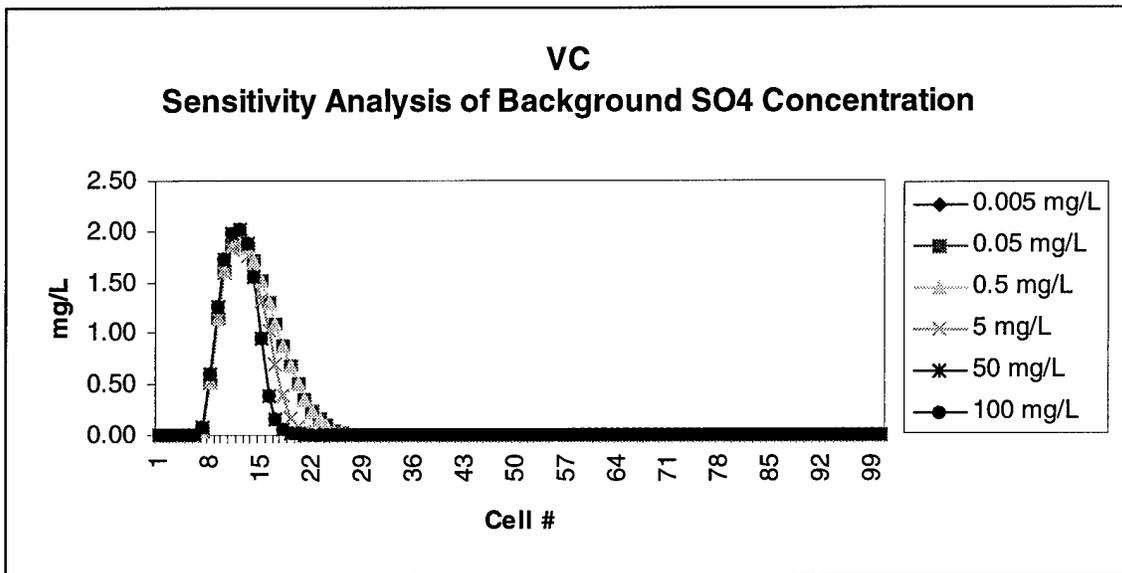


Figure 4.17

#### 4.2.4.3 Fe<sup>3</sup>

Iron (III) was varied between 0.005 mg/L and 100 mg/L. The difference in the background concentration of iron (III) had no net effect difference on the complete

mineralization of TCE because for all concentrations TCE completely mineralized. The only effect iron (III) concentration had was on the length of the plume which slightly shortened with the higher concentrations. The ability of TCE to mineralize was extremely insensitive for various background concentration of iron (III).

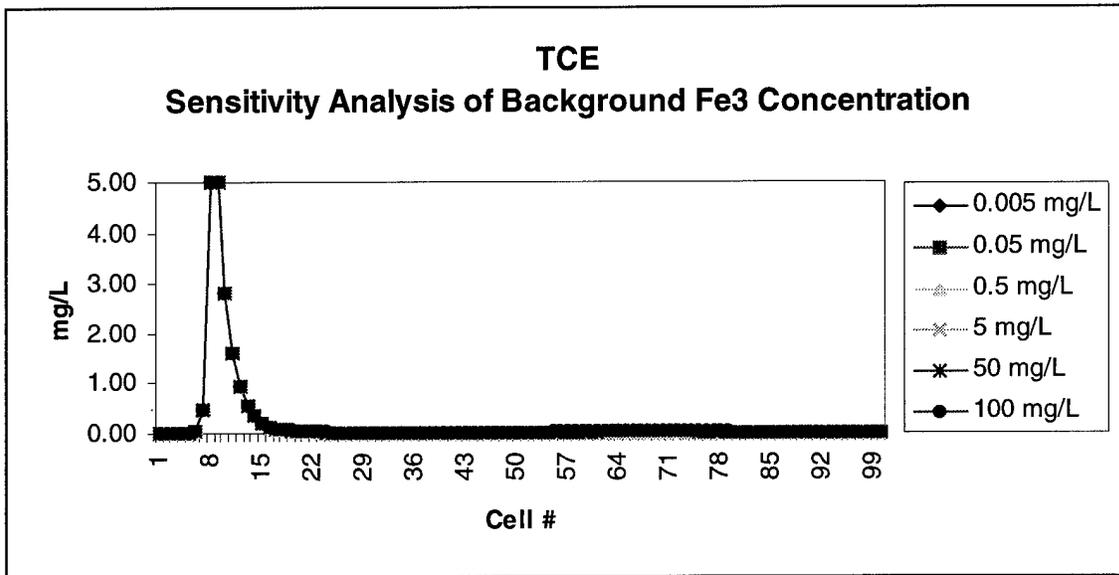


Figure 4.18

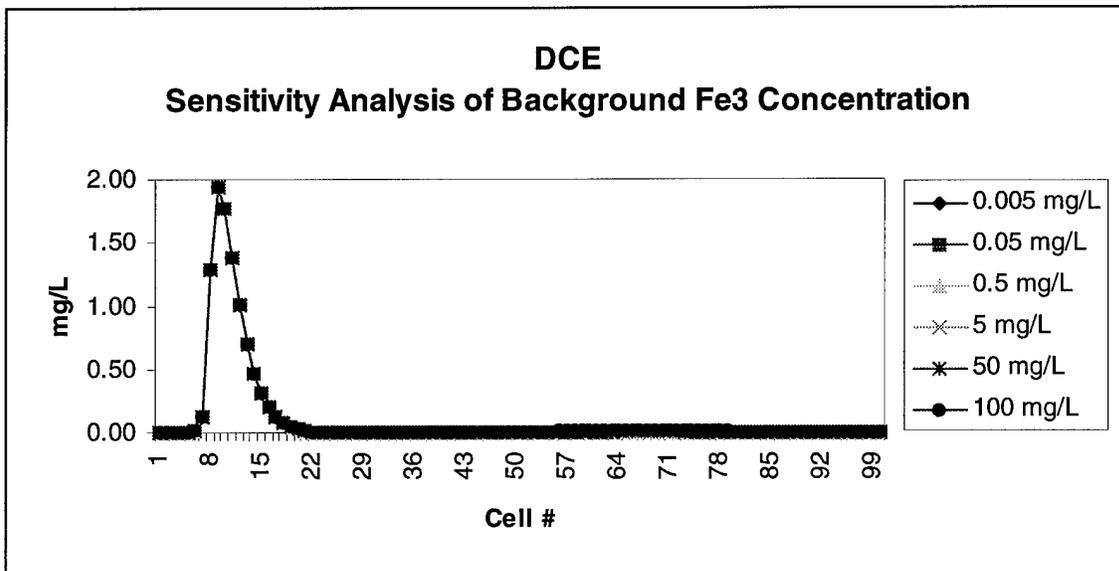
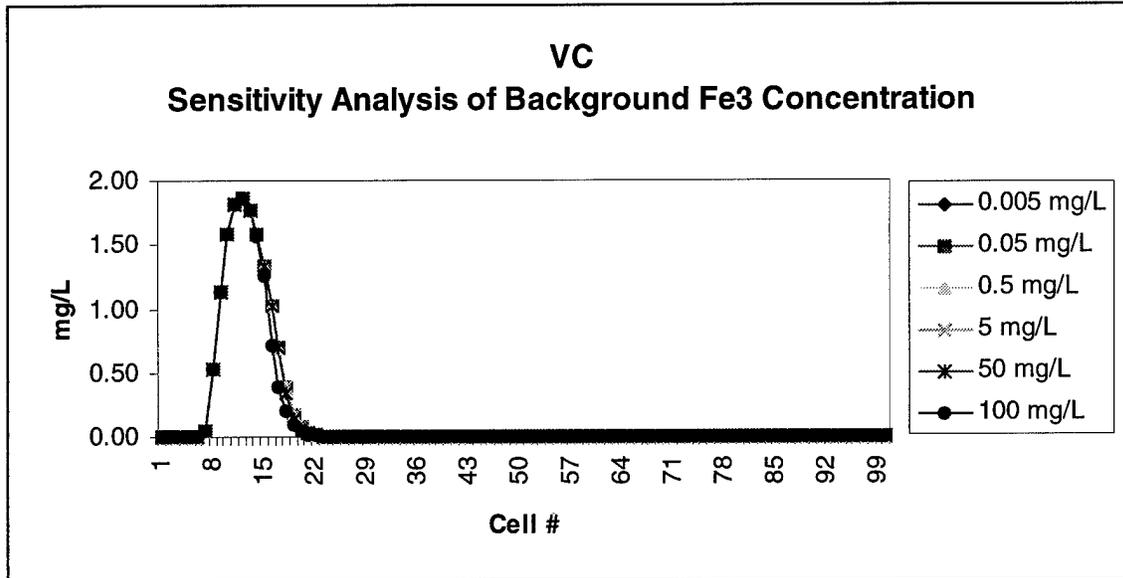


Figure 4.19



**Figure 4.20**

#### 4.2.4.4 NO<sub>3</sub>

Initial and western boundary nitrate concentration was varied between 0.005 mg/L and 100 mg/L. The difference in the concentration of nitrate had no net effect on the complete mineralization of TCE except at very high concentrations. Nitrate background concentrations above 5 mg/L significantly shortened the plume length and also marked the point at which TCE could not completely degrade. Similar to the effects of high concentrations of sulfate, one explanation of the inability of TCE and DCE to degrade is the high concentration of nitrate prevented the creation of a methanogenic zone. This explanation is supported by the fact that simulation of methane showed there was no methane produced when sulfate was set at 100 mg/L. TCE cannot degrade under nitrate reducing conditions (table 3.3). Thus, TCE degradation can't begin until all the NO<sub>3</sub> is used during the BTEX oxidation. This appears to be the reason why Figure 4.22 has

more TCE than Figure 4.15. Also, since TCE isn't degrading in the presence of NO<sub>3</sub>, daughter products such as DCE is less in Figure 4.23 than DCE in Figure 4.16. Another explanation is the high sulfate made the anaerobic zones too short to degrade TCE and DCE before they reached the aerobic zone.

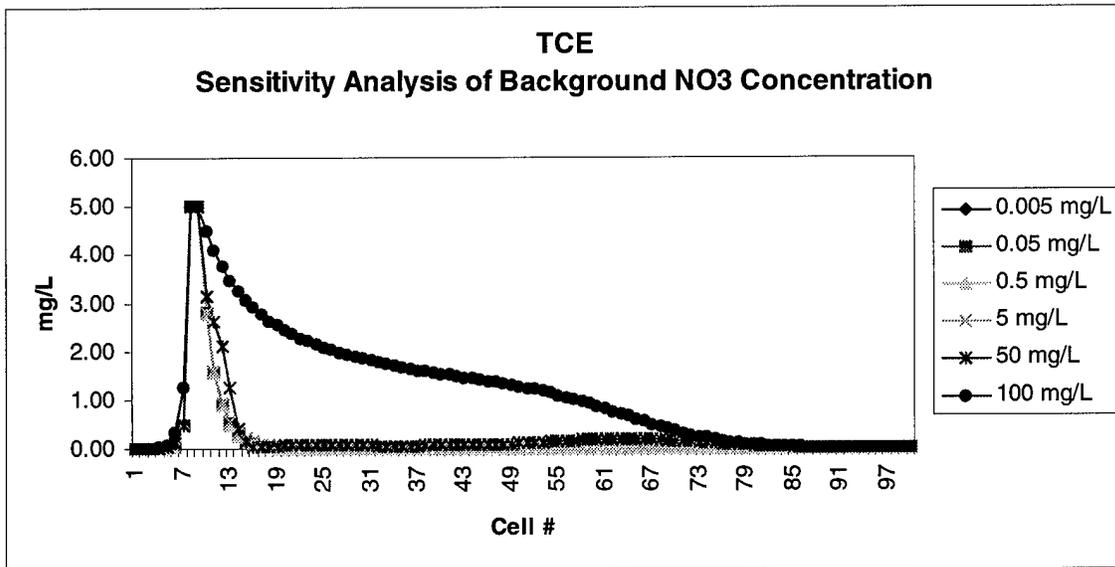
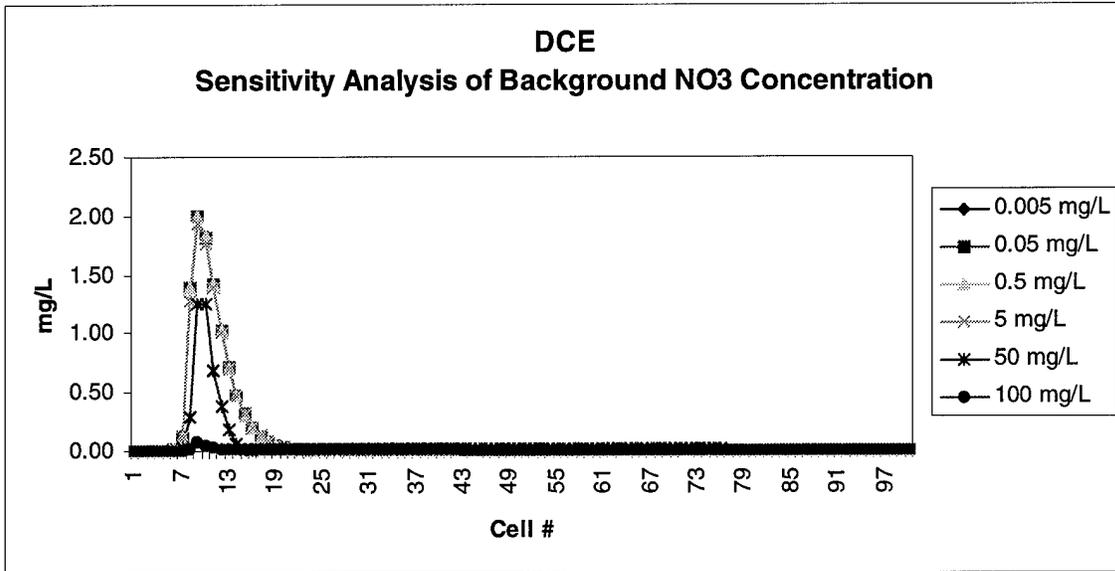
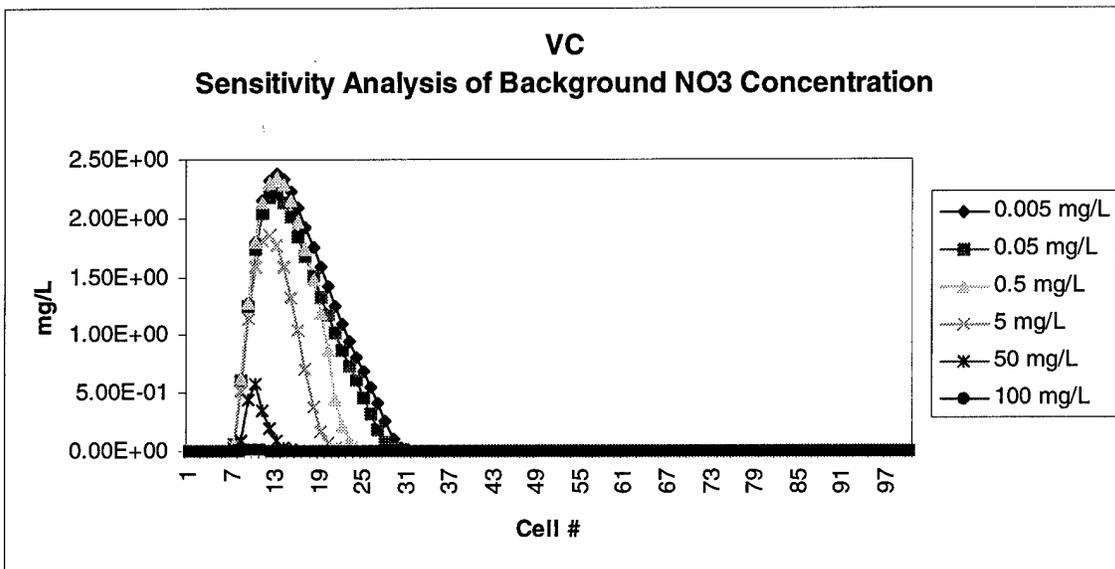


Figure 4.21



**Figure 4.22**



**Figure 4.23**

#### 4.2.4 First Order Degradation Rate Coefficient

##### 4.2.4.1 BTEX

The BTEX first order degradation rate coefficient was varied from  $6.0 \times 10^{-5}$  per day to  $1.0 \times 10^{-1}$  per day. The BTEX first order rate was assumed constant for the all redox zones including the aerobic zone. TCE was unable to be degraded when the BTEX first order degradation rate constant dropped below  $1.0 \times 10^{-3}$  per day or lower. As the first order rate of BTEX degradation becomes smaller, the longer the BTEX plume becomes, but the shorter the redox zones become. At low rates methane production is inhibited (Figure 4.25) because methanogenic conditions are not created, therefore reductive dechlorination and cometabolism of TCE does not occur (Figure 4.24).

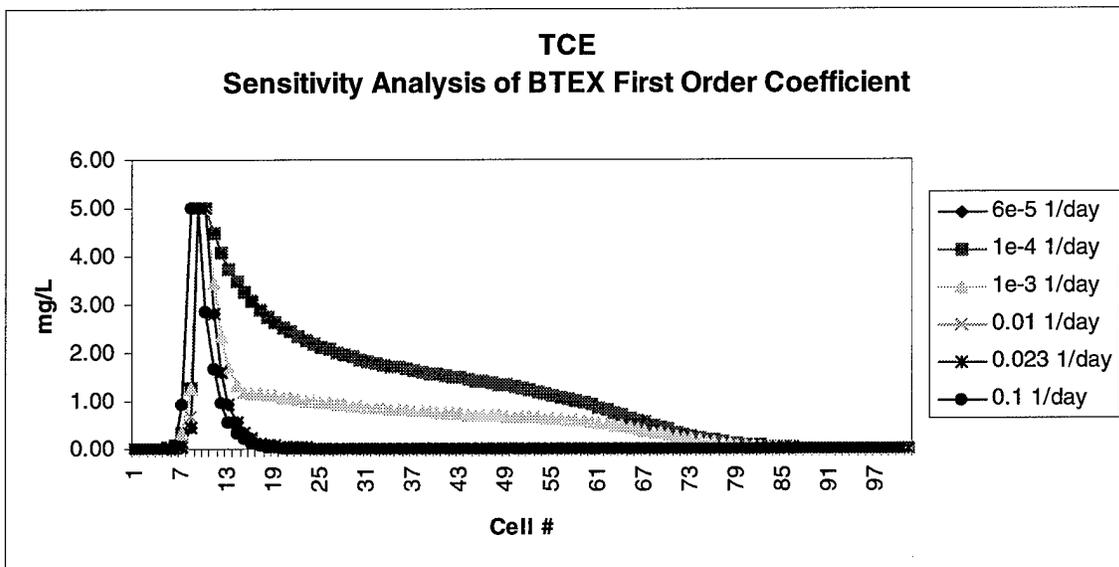
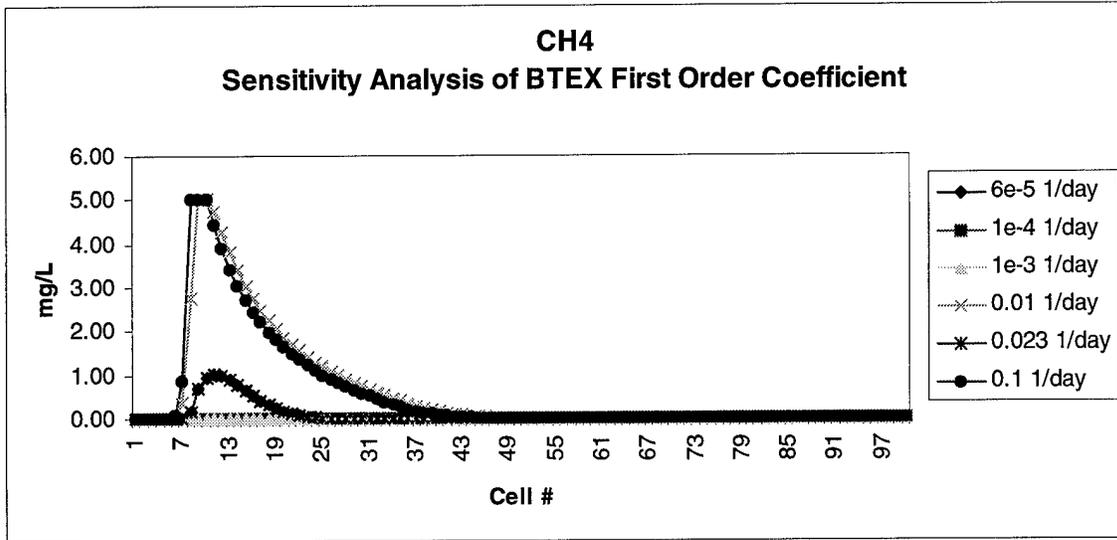


Figure 4.24



**Figure 4.25**

#### 4.2.4.2 TCE

The study of TCE first order rate coefficient looked at aerobic and anaerobic coefficients separately. The aerobic degradation rate was examined first. The TCE first order rate coefficient was varied from  $4.5e-4$  per day to  $3.0e-1$  per day. TCE was unable to be completely degraded at the smallest rate of  $4.5e-4$ . The cometabolic degradation of TCE that occurs in the aerobic zone appears to be an important component to successfully degrade TCE completely. From the Figure 4.26 there appears to be a “bump” of TCE concentration at the down gradient location in the aquifer. This is caused by the aquifer profile being taken at 30 years. The model had not reached steady state yet. This artifact of the model was created because the TCE passed down gradient before the BTEX had time to create anaerobic conditions.

The anaerobic degradation rate constant was varied ranging from  $4.5e-4$  per day to  $3e-1$  per day. The TCE was able to completely mineralize in all cases. The slower the first

order rate constant, the longer the TCE plume, but ultimately the TCE was degraded when it reached the aerobic zone.

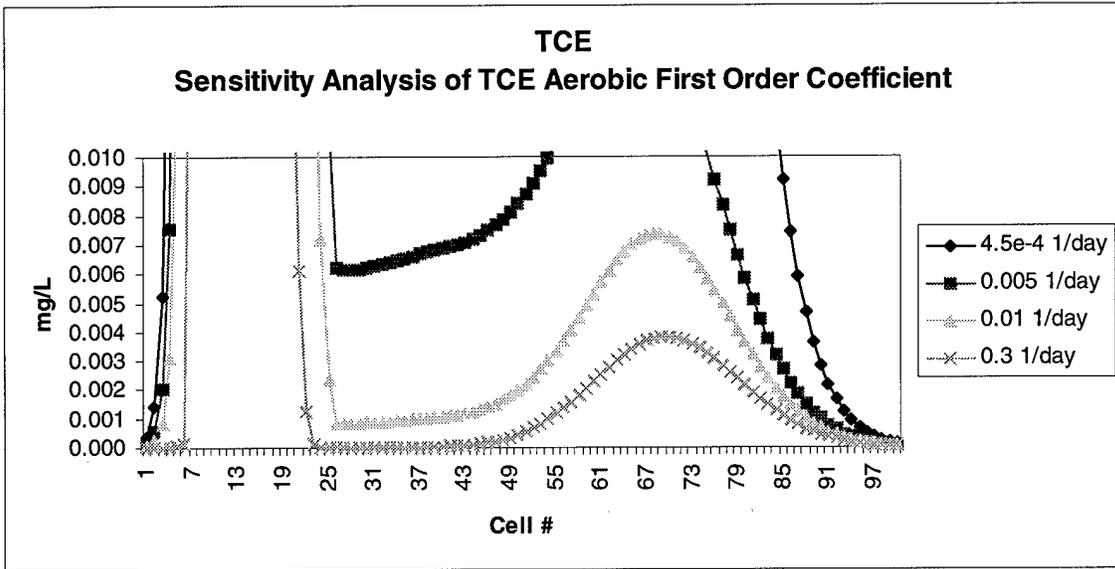


Figure 4.26

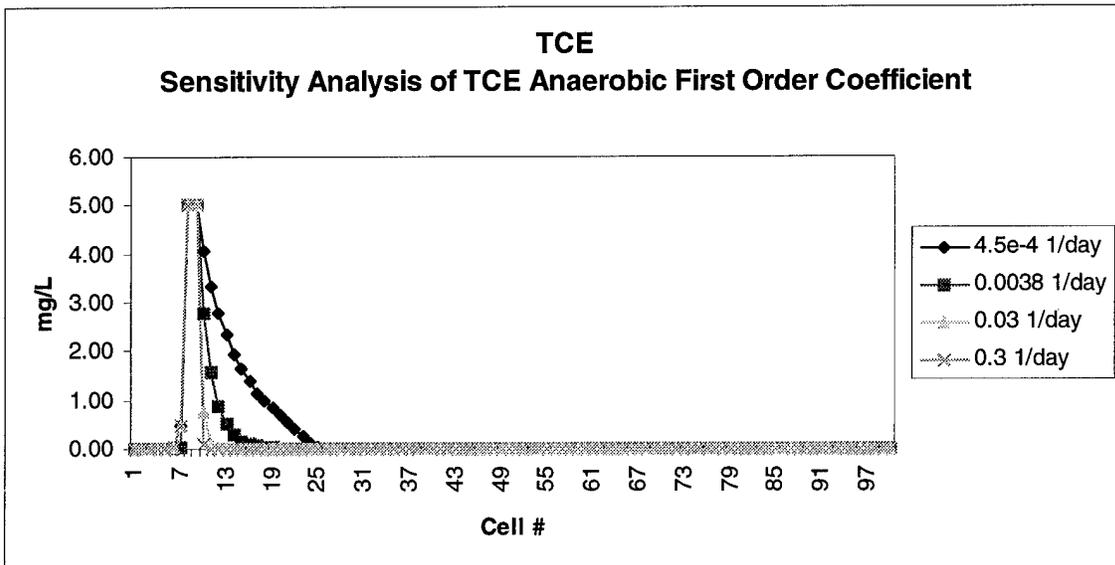


Figure 4.27

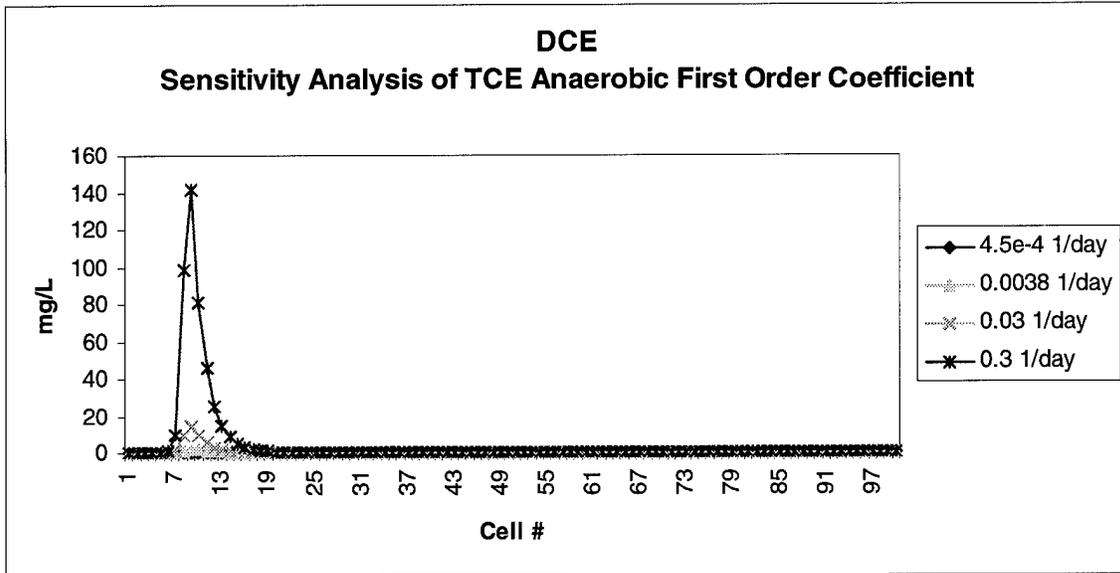


Figure 4.28

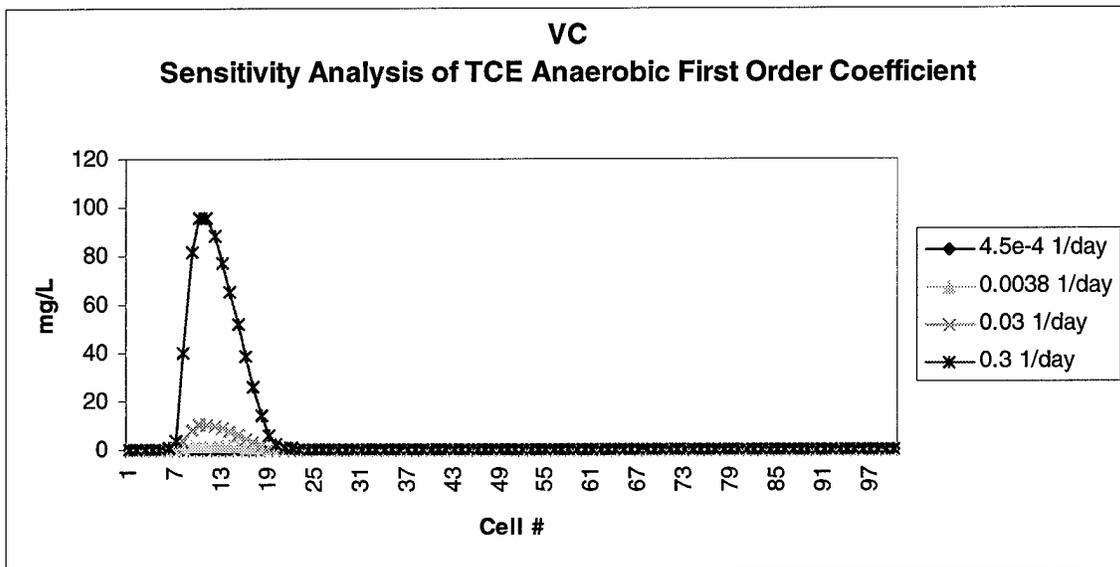


Figure 4.29

#### 4.2.4.3 DCE

The study of the DCE first order rate coefficient also looked at the aerobic and anaerobic coefficients separately. The aerobic degradation rate was studied first. The TCE first

order rate coefficient was varied from  $7.1e-4$  per day to  $2.6e-2$  per day. TCE and DCE were degraded for all values of the first order rate coefficient.

The anaerobic degradation rate constant for DCE varied from  $7.1e-4$  per day to  $2.6e-2$  per day. The DCE was able to completely degrade in all cases. The slower the first order rate, the longer the DCE plume, however, DCE was ultimately degraded when it reached the aerobic zone. Under all rates TCE was able to completely degrade.

#### **4.2.4.4 VC**

The study of the VC first order rate coefficient looked at the aerobic and anaerobic coefficients separately. The aerobic degradation rate was studied first. VC first order rate coefficient was varied from  $3.0e-5$  per day to  $1.2e-2$  per day. TCE, DCE, and VC were degraded for all values of the first order rate coefficient.

The anaerobic degradation rate constant for VC was varied ranging from  $3.0e-5$  per day to  $1.2e-2$  per day. The VC was able to completely degrade in all cases. The slower the first order rate become the longer the VC plume, however, VC ultimately degraded when it reached the aerobic zone. Under all rates all contaminants were able to completely mineralize.

### **4.3 CASE STUDY**

The former landfill site located at Moody AFB, Georgia was characterized using the information provided in the study done by CDM (Bourquin et al., 1997). The aquifer was

modeled with a constant head boundary on the East and West side of the aquifer similar to how the aquifer was modeled for the sensitivity analysis. The head values were in good agreement with the head lines from the study. The maximum deviation for any gradient line was .4 cm.

The monitoring study lacked any guess as to the location of the source. Because of this, we placed the source at six up gradient positions in the plume. We also placed four sources of the BTEX co-contaminant. The monitoring study lacked information on redox zones. This information could have been determined by hydrogen concentrations, electron acceptor concentrations, and electron equivalents. The only significant electron acceptors were oxygen and iron (III). Due to uncertainties of location and source concentration of the contaminants it was impossible to calibrate the Bioredox model against the measured contaminant concentrations at various data points. Instead, a qualitative study was completed to illustrate that the processes presented in this thesis can explain apparent degradation occurring at this site.

Based on the input values, Bioredox over estimated the ability of the aquifer to naturally attenuate the TCE. Because the source location and concentrations were not known, we used a conservative approach and placed a constant source concentrations of TCE at 9 mg/L. The BTEX was placed as a constant source concentration of 0.3 mg/L. Figure 4.33 and 4.34 show the TCE concentrations much higher than the measured concentrations. Because of the high simulated TCE concentrations, this also made the daughter products of TCE higher too. DCE and VC comparisons can be seen in Figure

4.35 through 4.38. The source concentration for BTEX of 0.3 mg/L closely matched the measured values as can be seen in the production of methane in Figure 4.39 and Figure 4.40. Figure 4.30 illustrate how the BTEX established the anaerobic region in the aerobic aquifer. The area with methane is the anaerobic region with the aerobic region starting when the oxygen concentration increases. Figure 4.31 demonstrates the methanogenic and ferrogenic redox zones of the anaerobic zone. Despite the low concentration of BTEX used and the high concentration of TCE, the aquifer proved its ability successfully mineralize TCE.

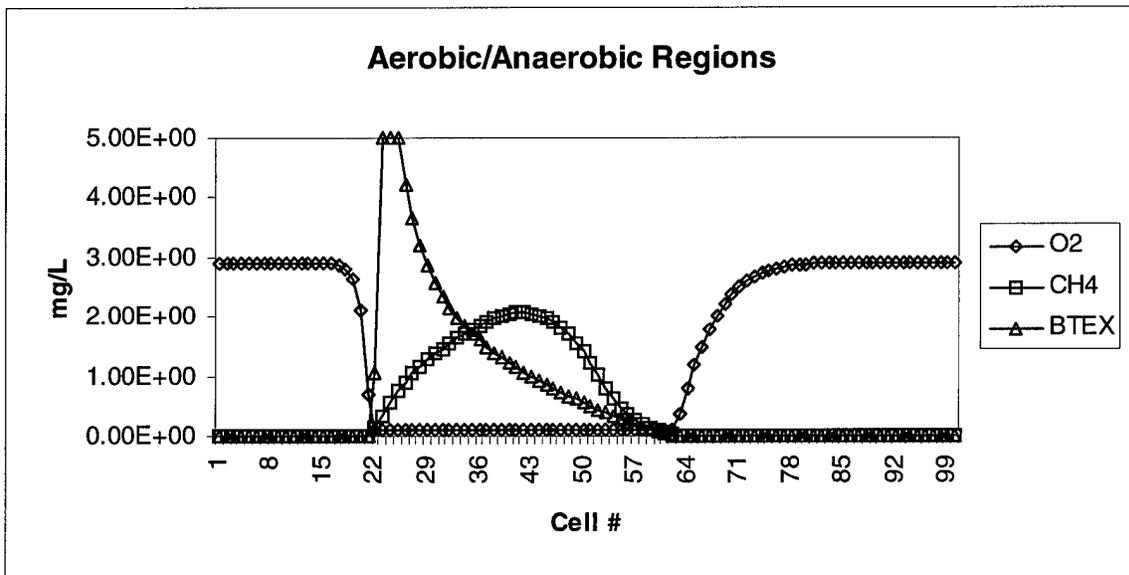


Figure 4.30

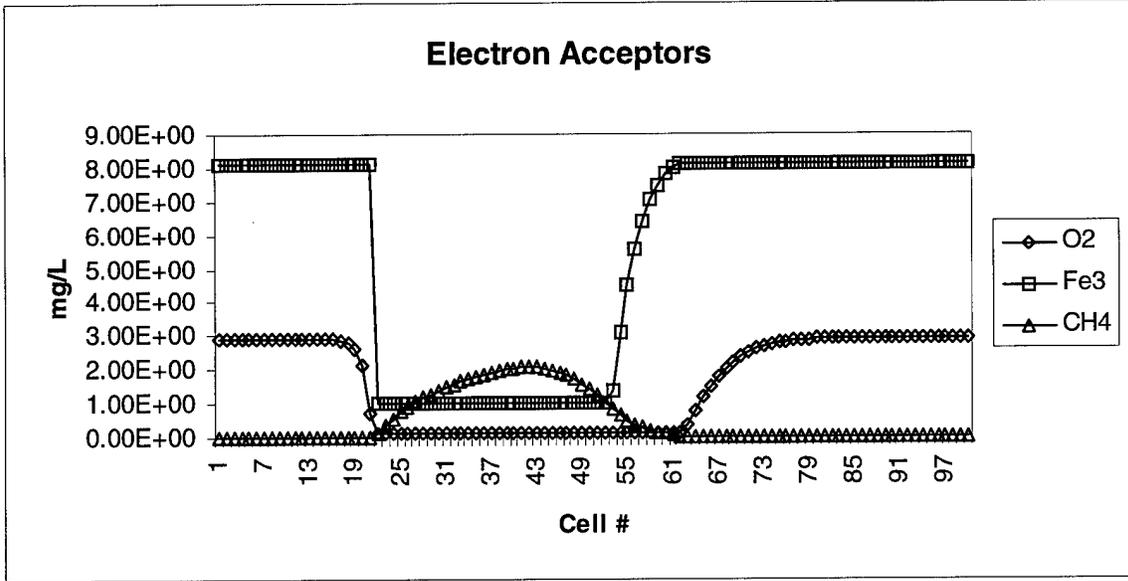


Figure 4.31

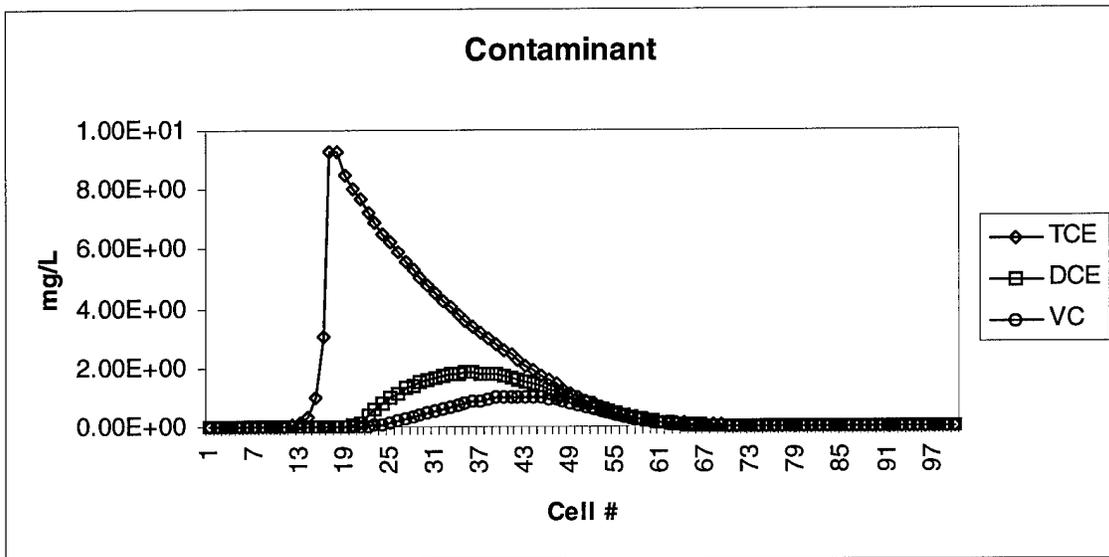


Figure 4.32

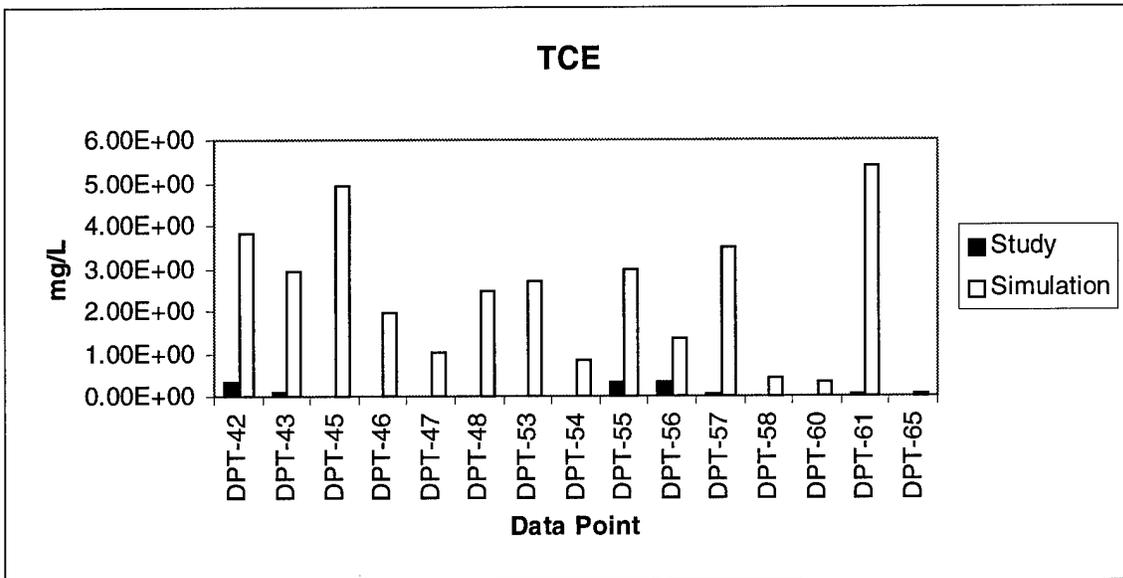


Figure 4.33

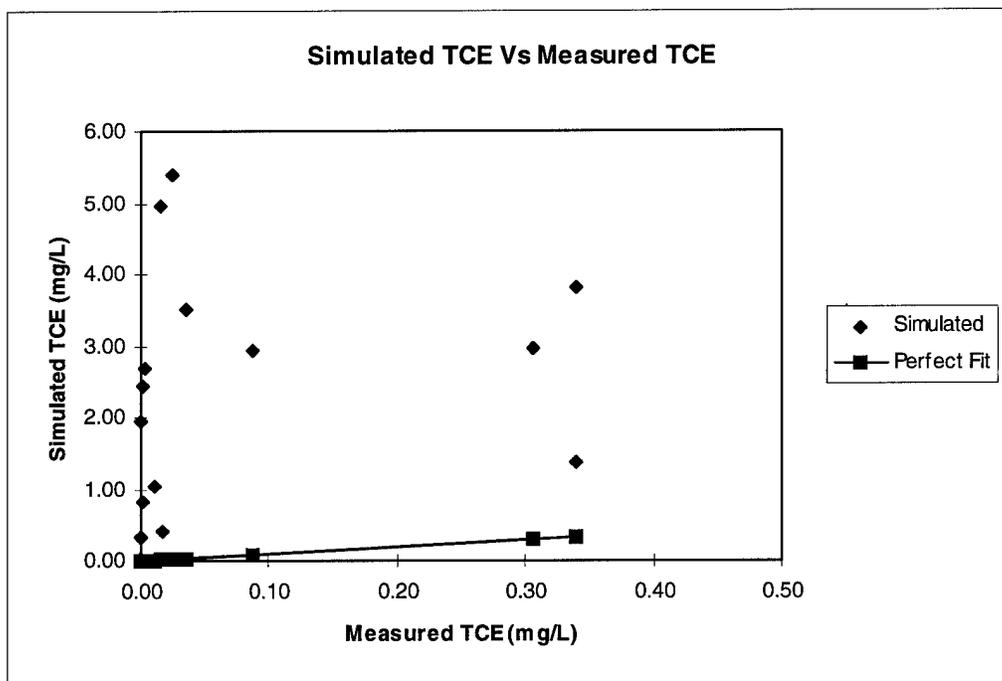


Figure 4.34

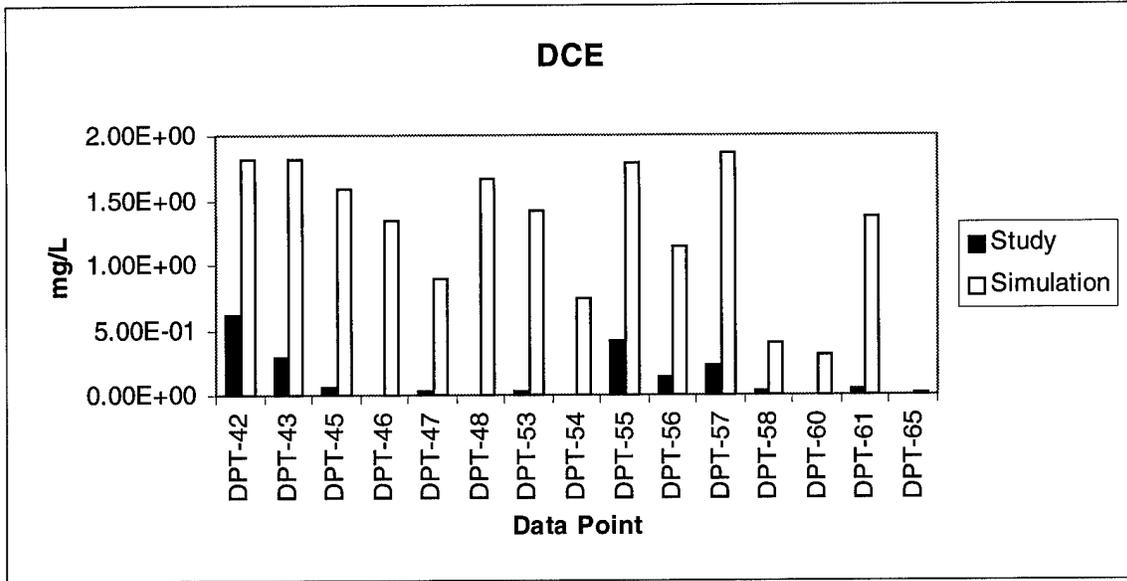


Figure 4.35

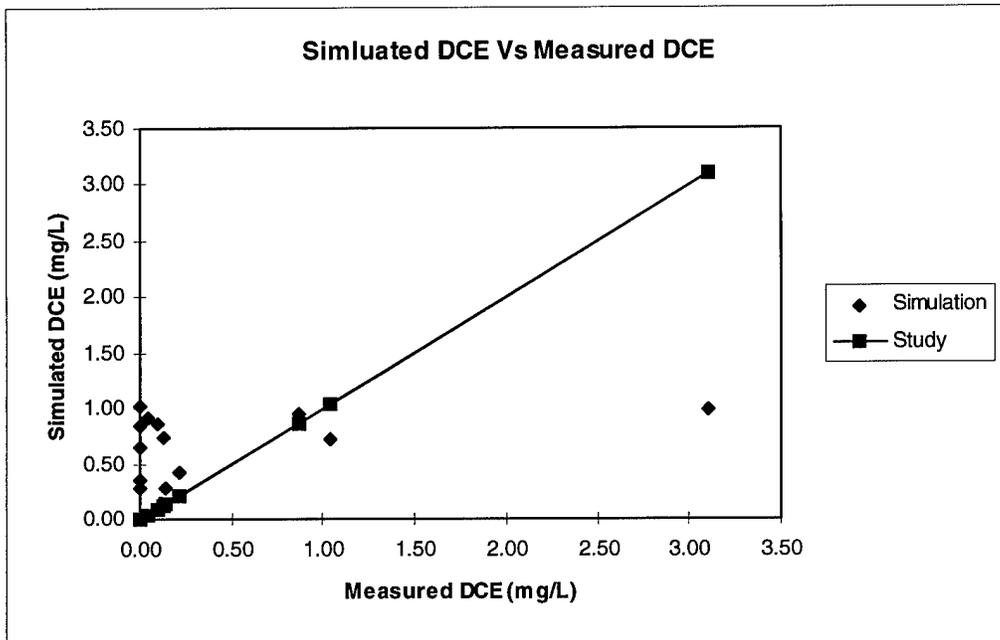


Figure 4.36

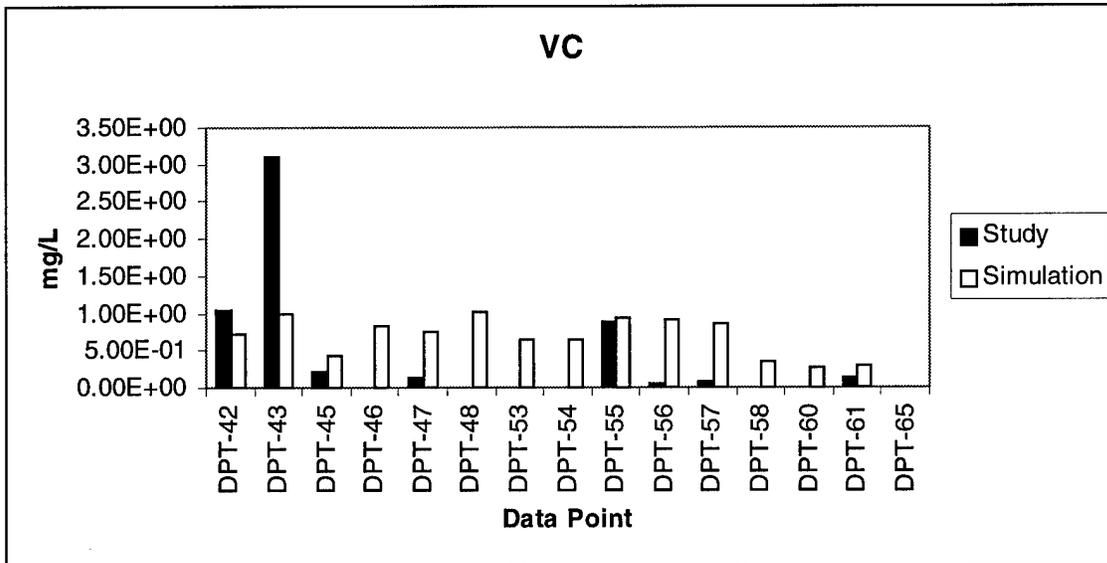


Figure 4.37

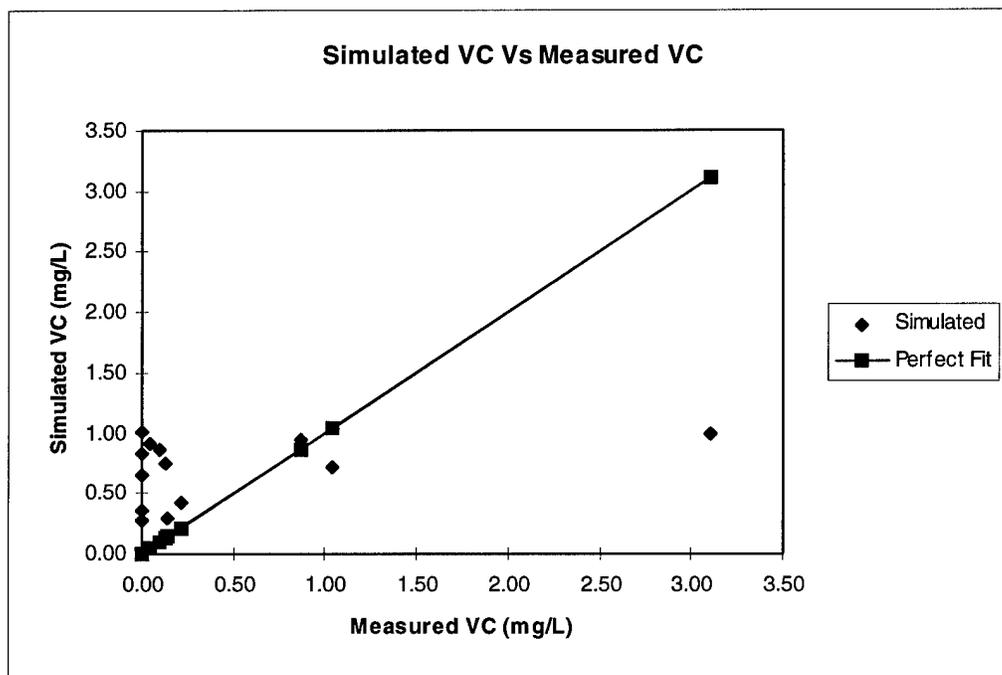


Figure 4.38

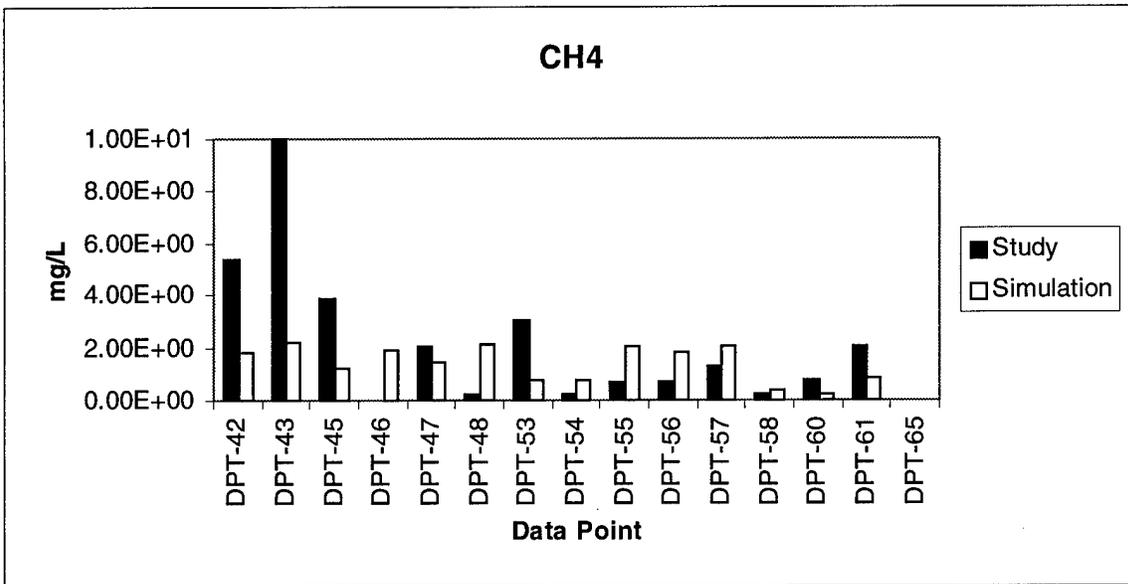


Figure 4.39

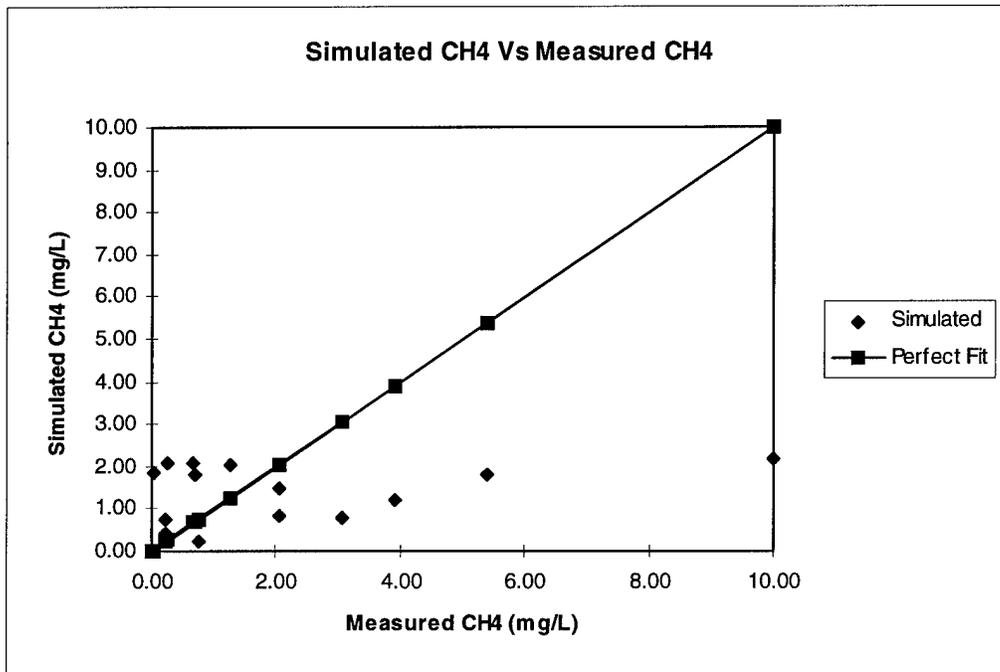


Figure 4.40

## **5.0 CONCLUSIONS**

### **5.1 SUMMARY**

In this thesis a model was developed that can explain the natural attenuation of TCE that has been observed at various sites. The hypothetical process combines the property of highly chlorinated CAHs to be reductively dechlorinated with the ability of methanotrophic bacteria to under aerobic conditions to cometabolically degrade less chlorinated CAHs, using methane as a primary substrate. The methane can be created by the degradation of hydrocarbons and other co-contaminants that may be present in a source area by methanogenesis. Using Bioredox we were able to conduct a sensitivity analysis in a hypothetical aquifer to evaluate the parameters having the most influence on the natural attenuation of TCE. We also looked at a case study and applied the model to it as an illustration of how these processes may occur at an actual site.

### **5.2 CONCLUSIONS**

#### **5.2.1 Sensitivity Analysis**

TCE was unable to completely degrade when the advective or dispersive flow of the ground water was unusually high. It was also unable to completely mineralize when the dispersion coefficient was very large. It appears under these circumstances the TCE traveled too quickly through the more favorable redox zones for degradation. When the TCE reached the aerobic front, there were not sufficient levels of methane produced for cometabolic degradation either. Although TCE was unable to degrade under these conditions, its daughter products were able to completely mineralize. These conditions of

either extremely high flow velocities or extremely high dispersions are rare and should not be of concern.

The destruction of TCE was very sensitive to the concentrations of BTEX, SO<sub>4</sub>, and NO<sub>3</sub>. Sufficient levels of a commingled hydrocarbon is essential to the degradation of TCE because it creates the anaerobic zones necessary for the degradation of TCE, as well as producing conditions for methanogenesis. Very high concentrations of SO<sub>4</sub> and NO<sub>3</sub> inhibit the ability of TCE to degrade. High concentrations of electron acceptors inhibits the creation of methanogenic conditions because these electron acceptors are never depleted. If methanogenic conditions are not created, more halogenated CAHs will not degrade as easily because methanogenic conditions are necessary for higher rates of reductive dechlorination. Methanogenic conditions also produce methane for use as a primary substrate in the cometabolic degradation in the aerobic zone.

Changes in the first order rate coefficient were very insensitive to the successful mineralization of TCE. Under all conditions, TCE was successfully degraded. The first order rate coefficient only changed the length of the plume.

### **5.2.2 Case Study**

The case study at Moody AFB indicated the site may be using the sequence of reactions studied in this report. The results of BioRedox proved the aquifer was robust in its ability to degrade the contaminant by natural attenuation. The lack of knowledge for the source and concentration of the contaminants hampered efforts to closely simulate the measured

values. The results of BioRedox show the aquifer is quite robust in degrading TCE even at a higher source concentration than what the site may actually have. A complete evaluation and calibration was not possible because of the lack of data.

### **5.3 RECOMMENDATIONS FOR FURTHER STUDY**

1. Examine sites that contain characteristics identified in this thesis for potential natural attenuation in Air Force or DoD inventory.
2. Conduct sensitivity analysis including rate limited sorption kinetics, monod model of cometabolism with competitive inhibition. New version of RT3D may included these processes within it.

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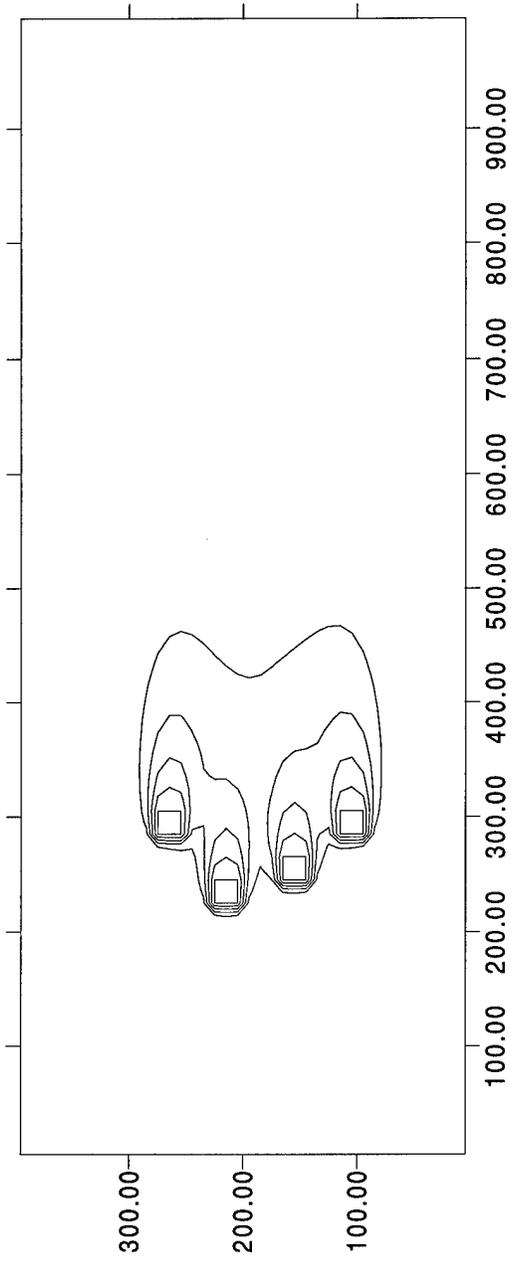
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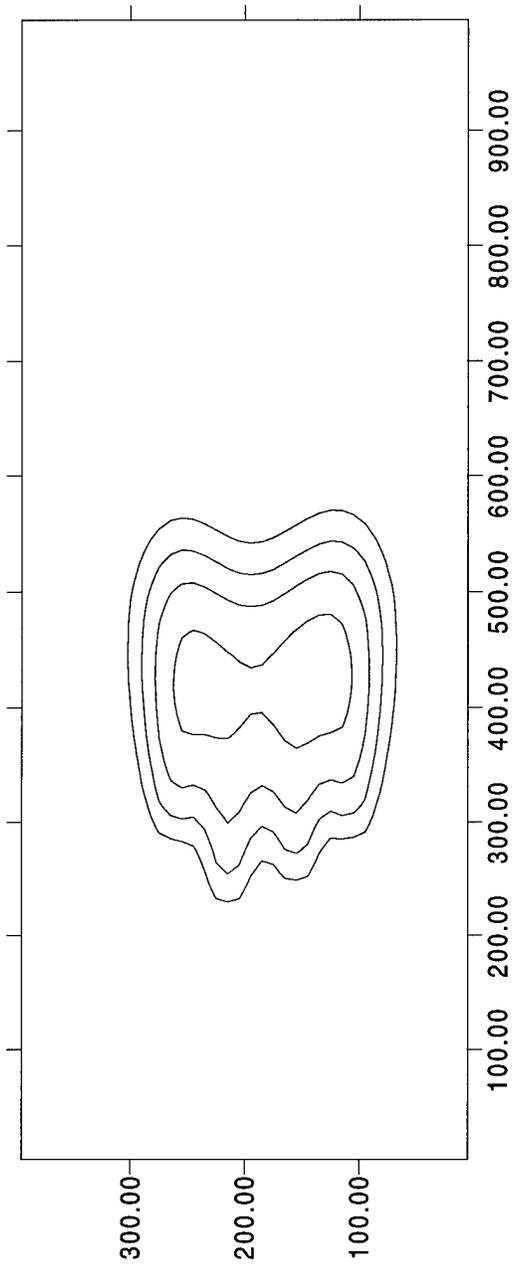
## **APPENDIX A**

### **Case Study**

**BTEX**  
**Contour lines for 1, 2, 3, 4, 5 mg/L**

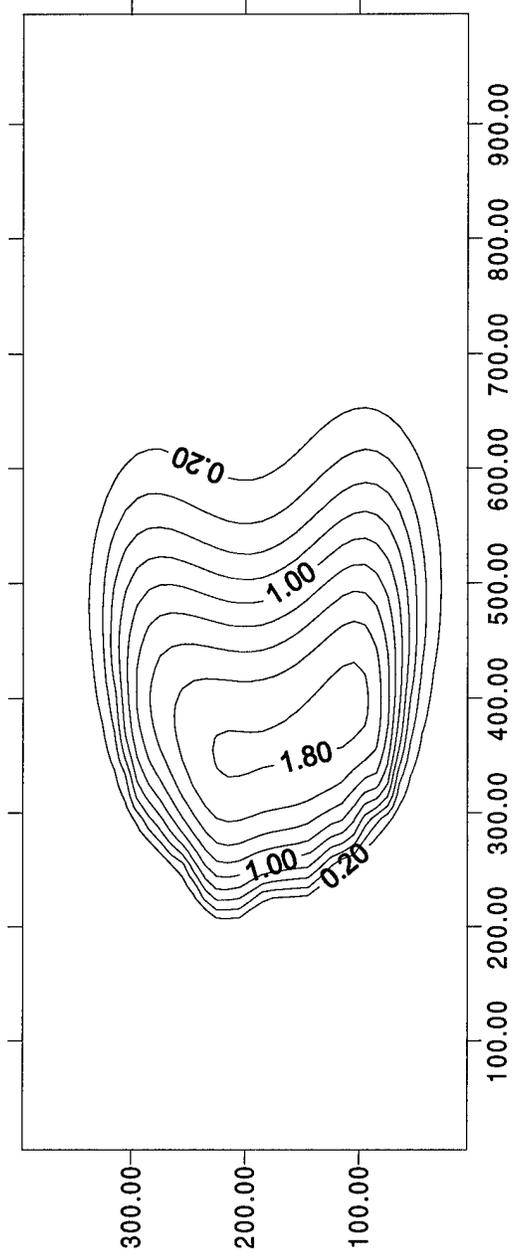


**CH4**  
**Contour lines for 0.5, 1.0, 1.5, 2.0 mg/L**

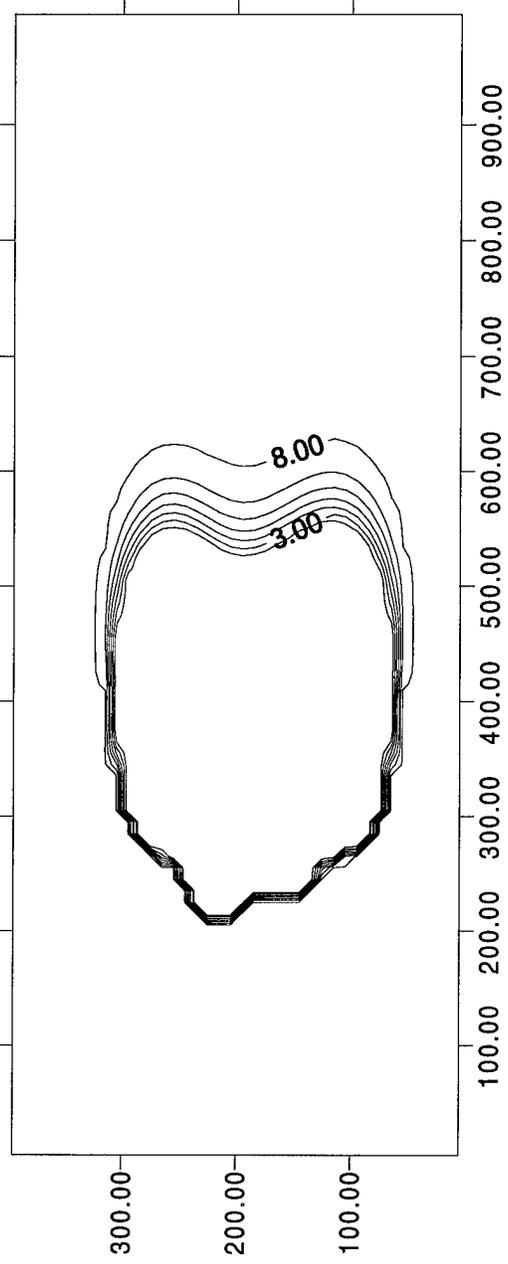


# DCE

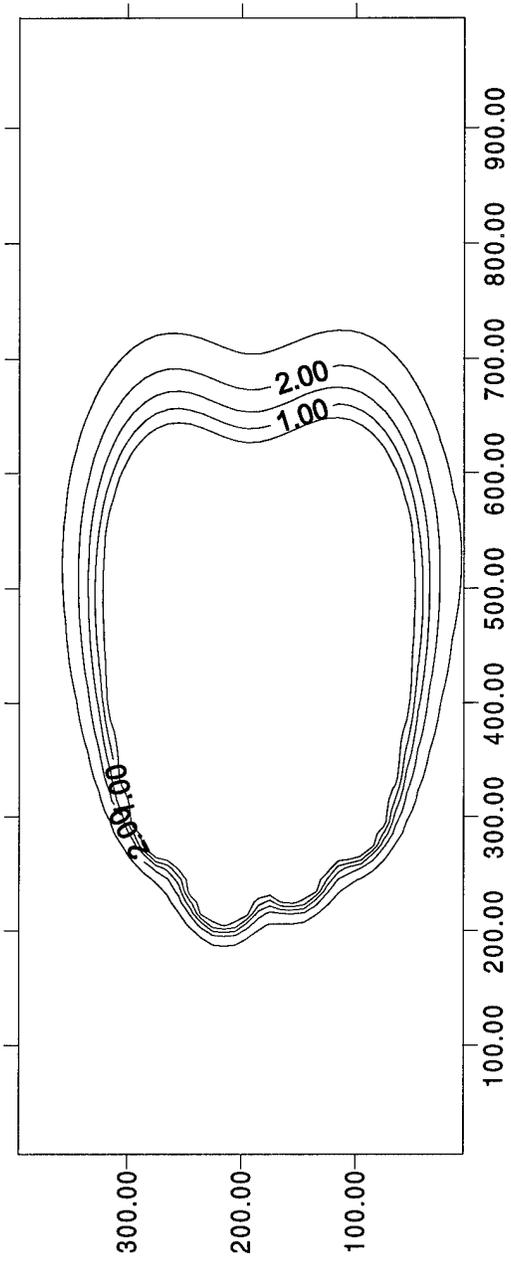
Contour lines for 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 mg/L



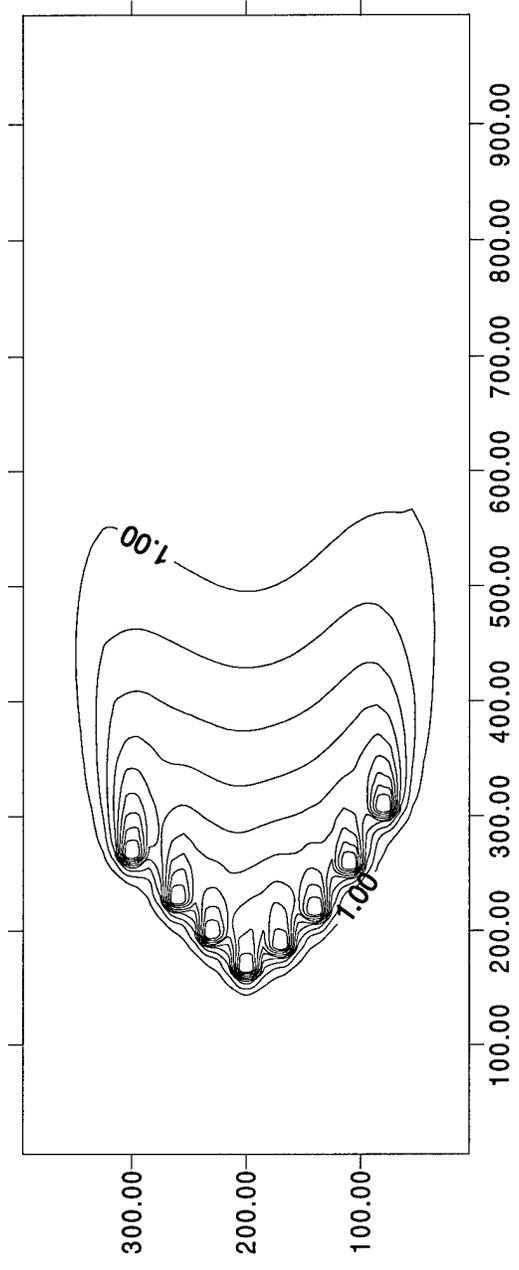
**Fe3**  
**Contour lines for 1, 2, 3, 4, 5, 6, 7, 8, mg/L**



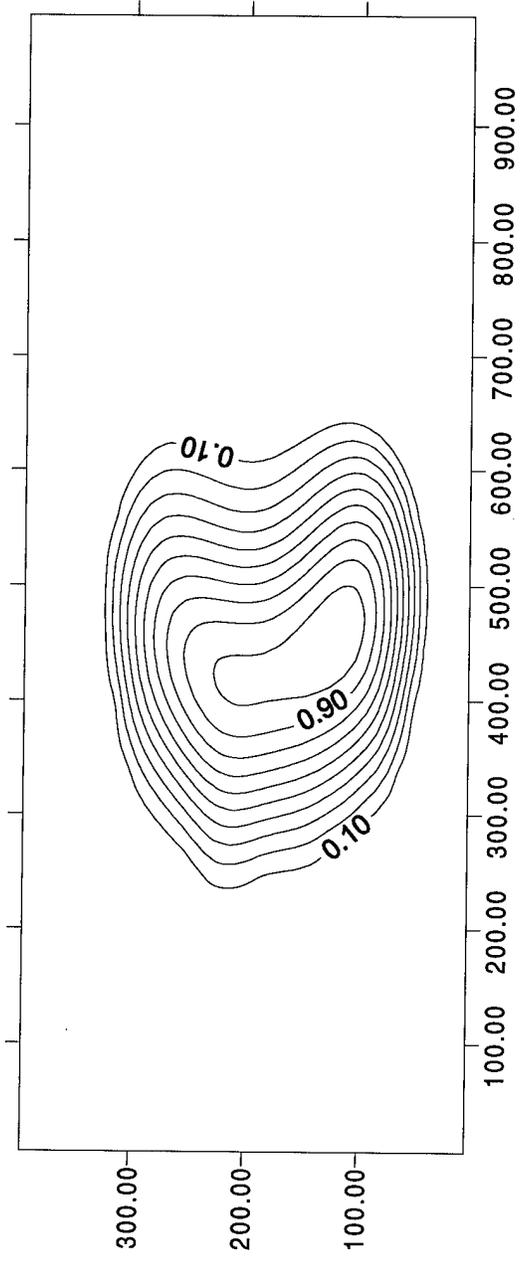
**O<sub>2</sub>**  
**Contour lines for 0.5, 1.0, 1.5, 2.0, 2.5, mg/L**



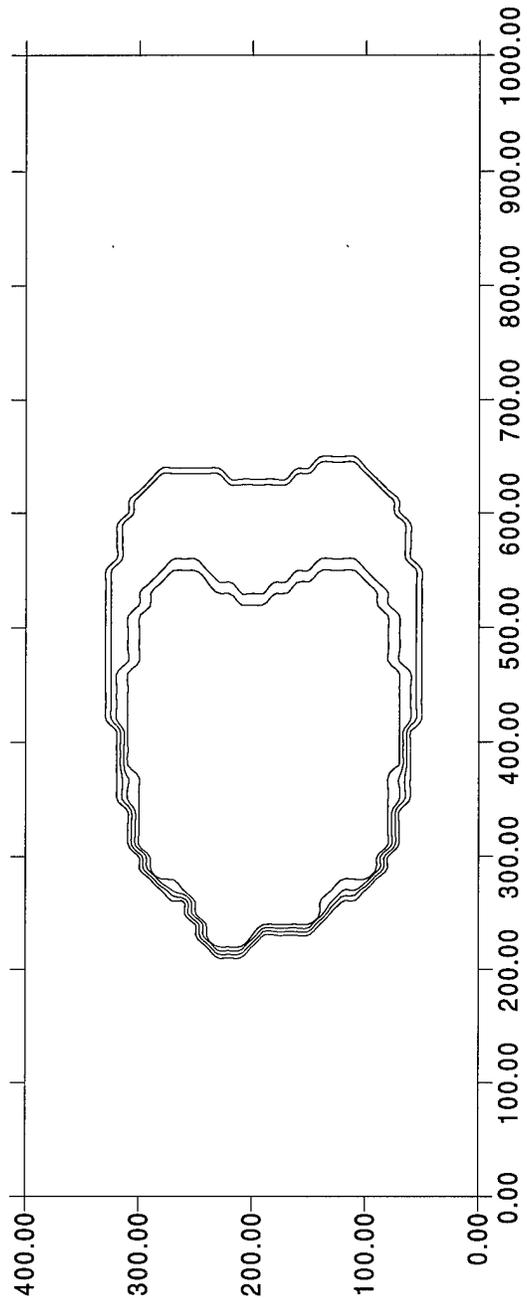
**TCE**  
**Contour lines for 1, 2, 3, 4, 5, 6, 7, 8 mg/L**



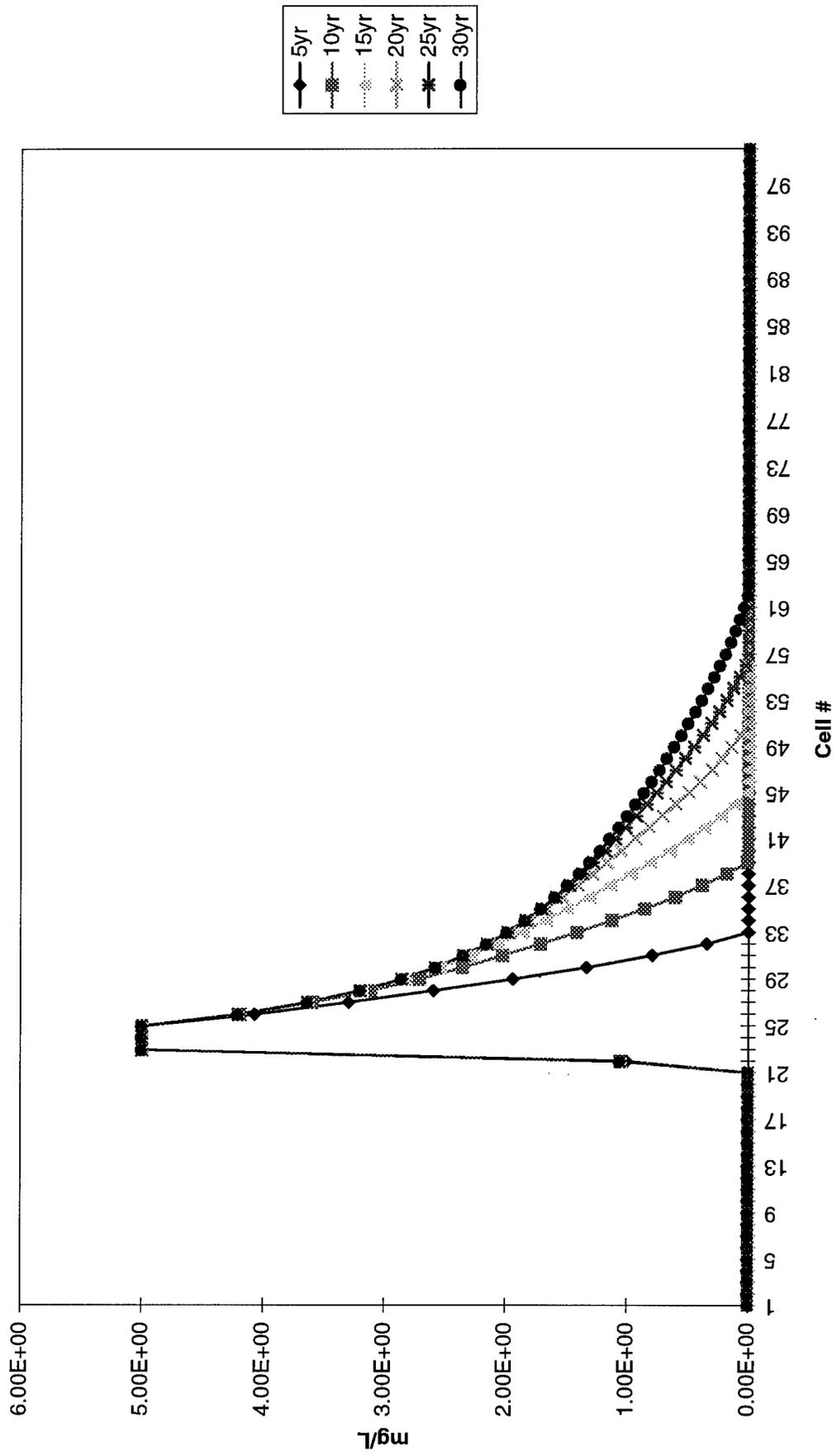
**VC**  
**Contour lines for 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 mg/L**



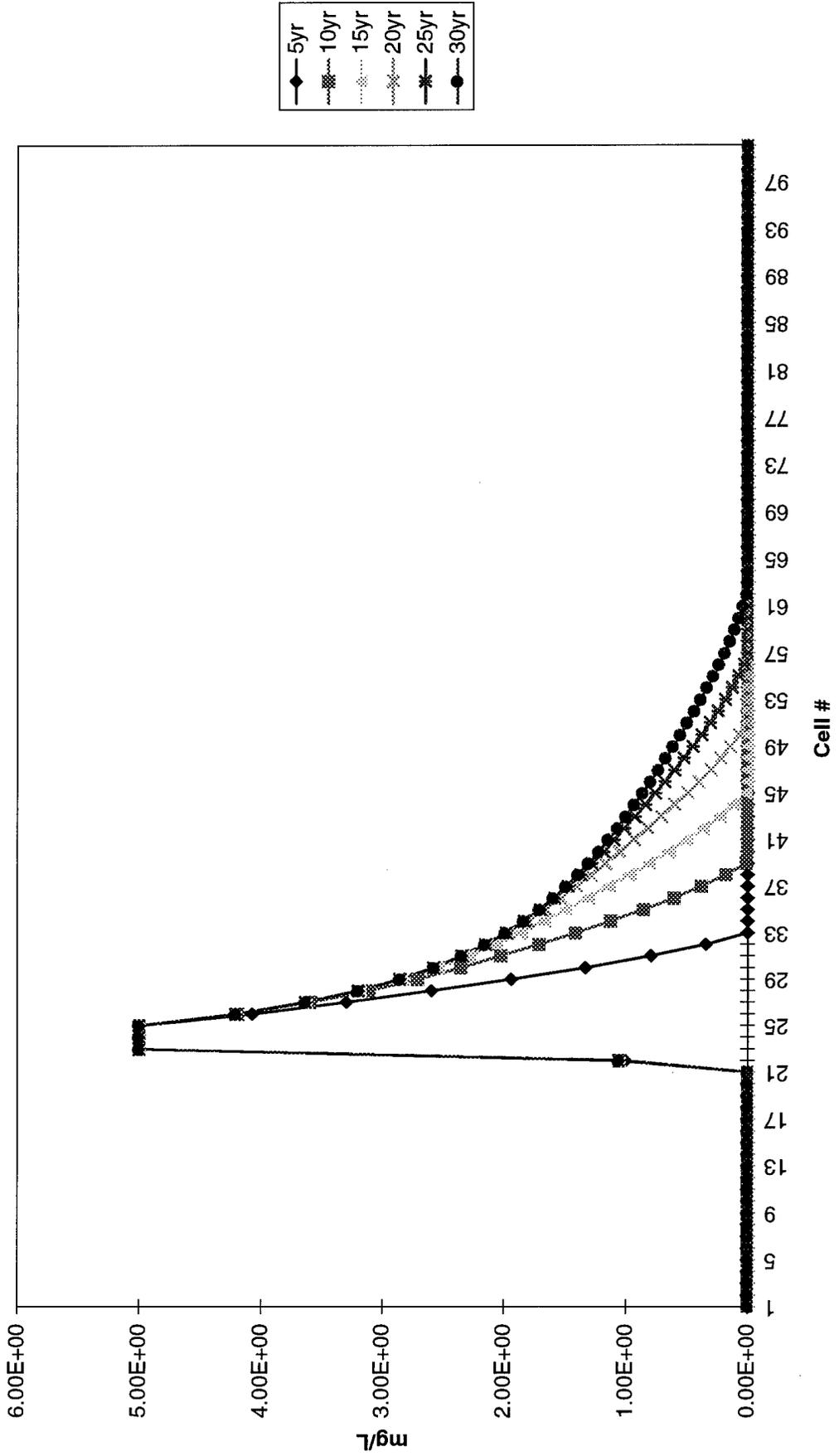
**Redox Zones**  
**Contour lines for Methanogenic, Ferrogenic, Aerobic**



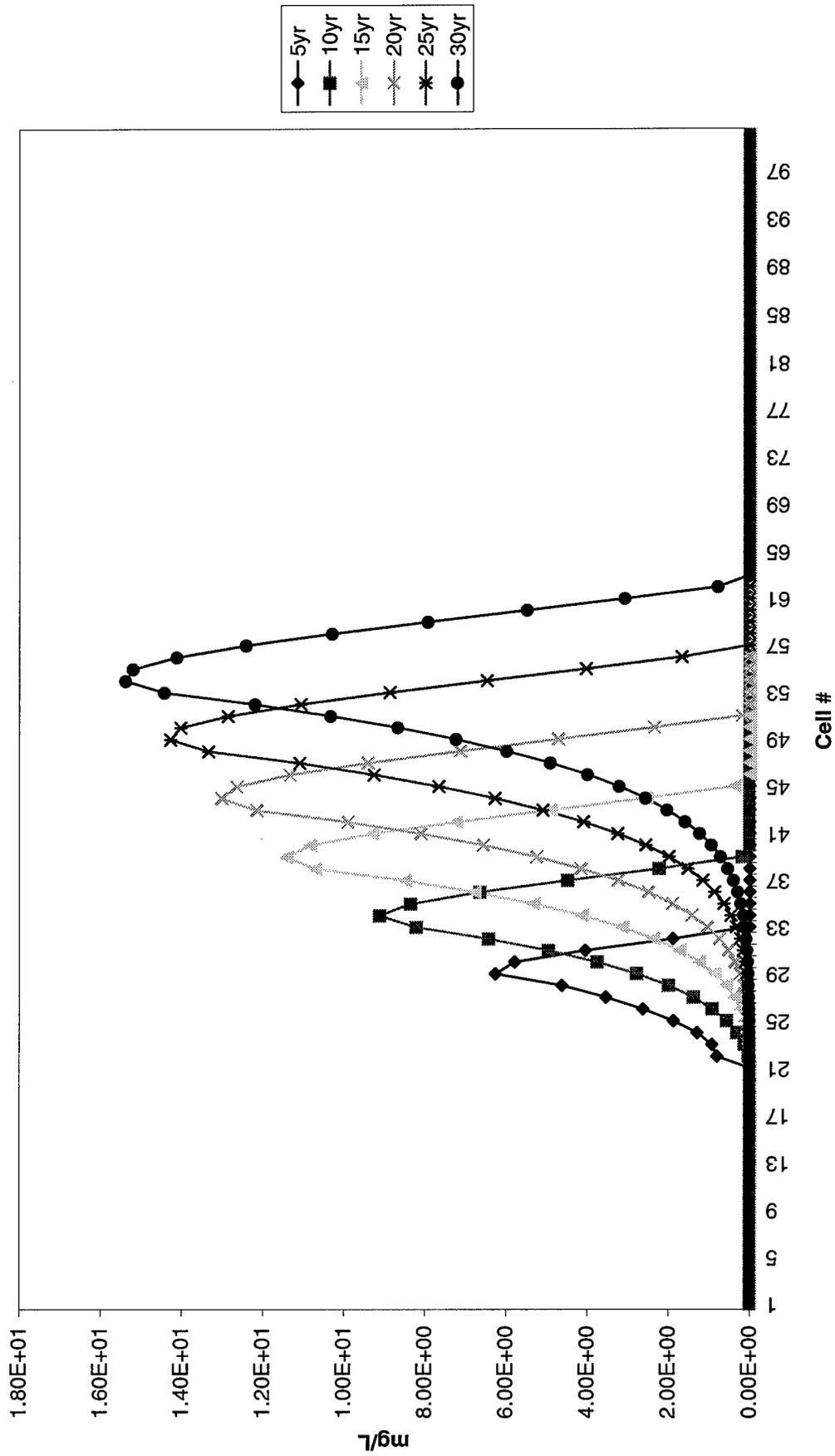
# BTEX Casestudy



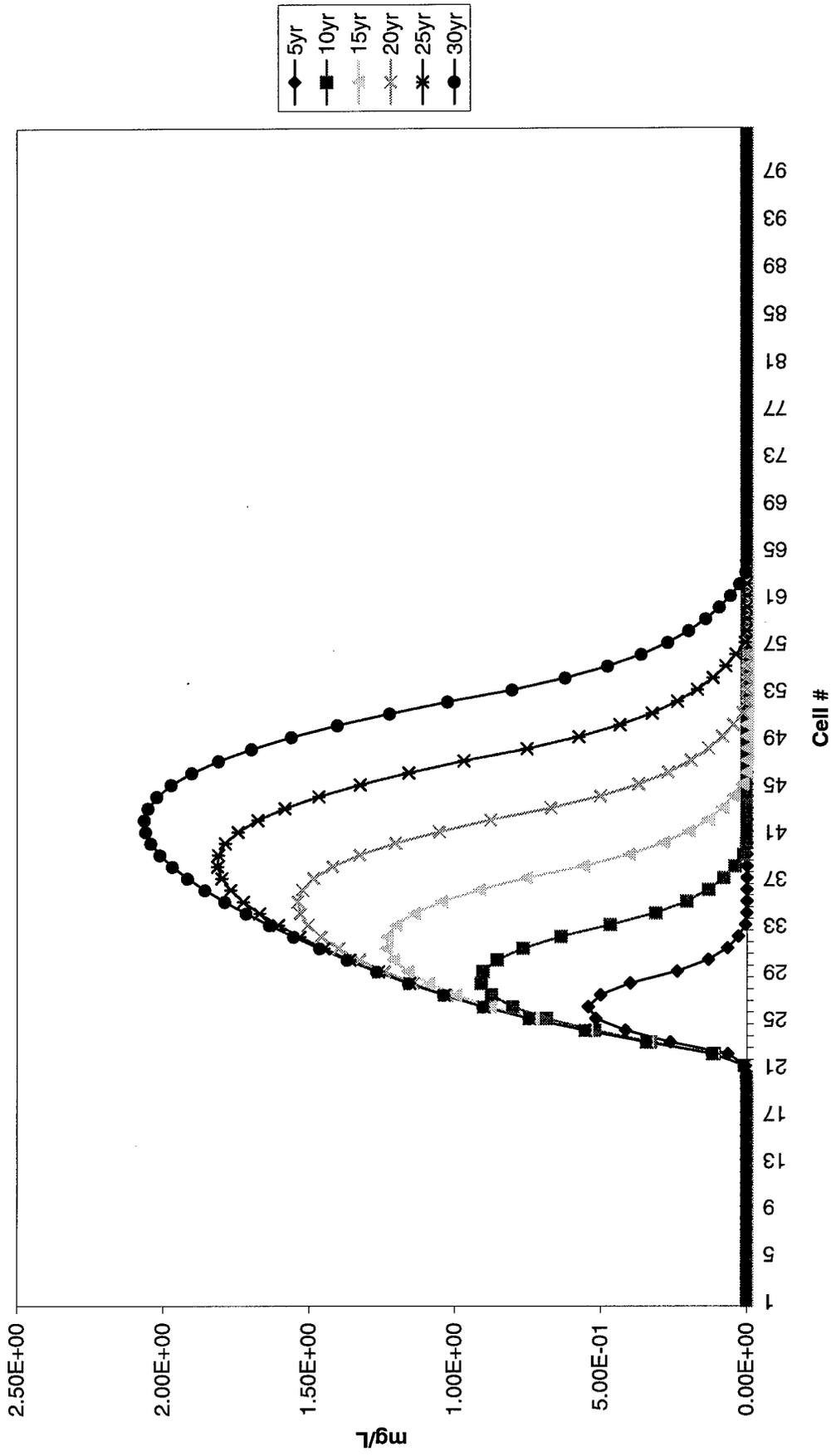
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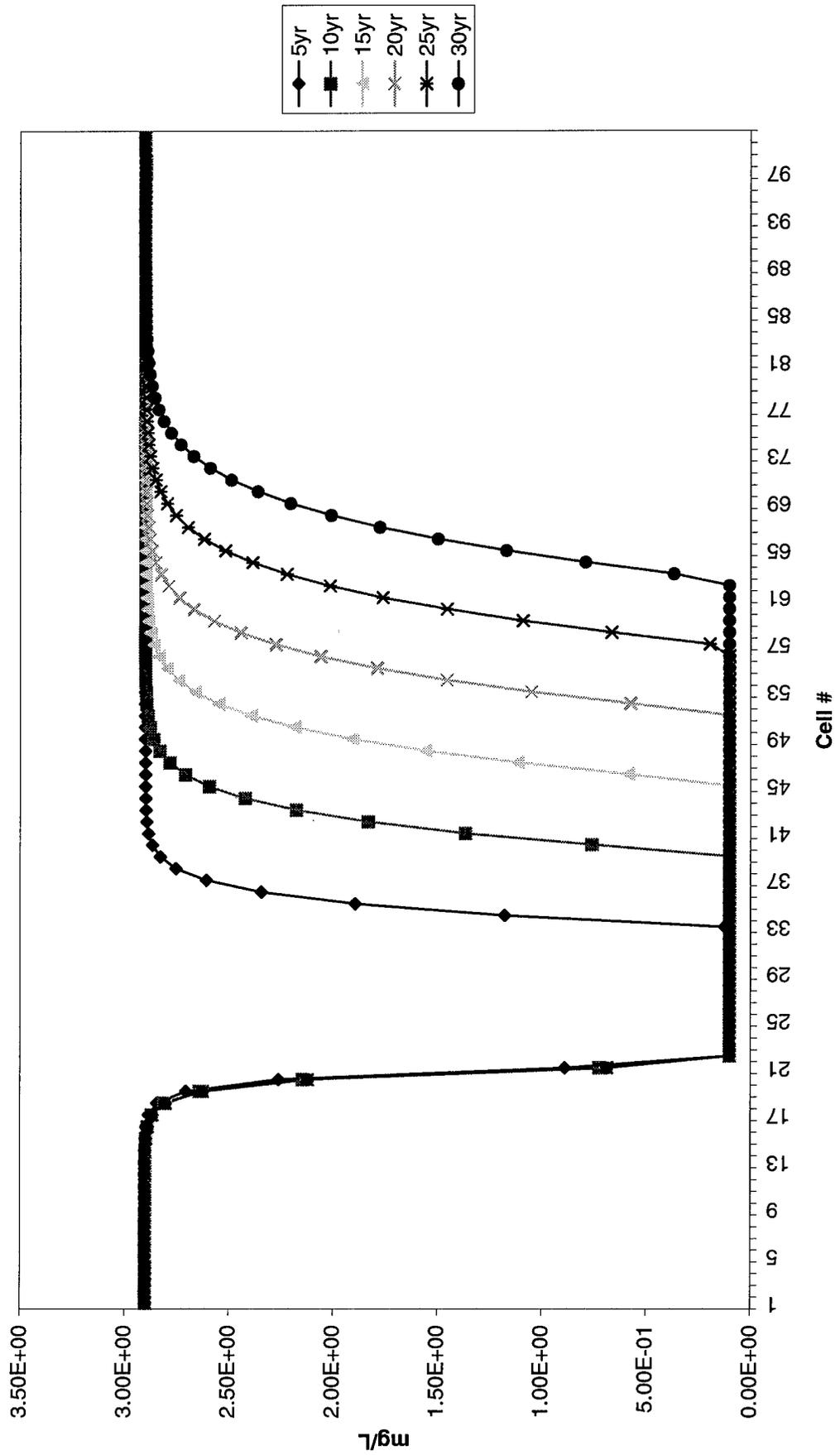
# Fe2 Casestudy



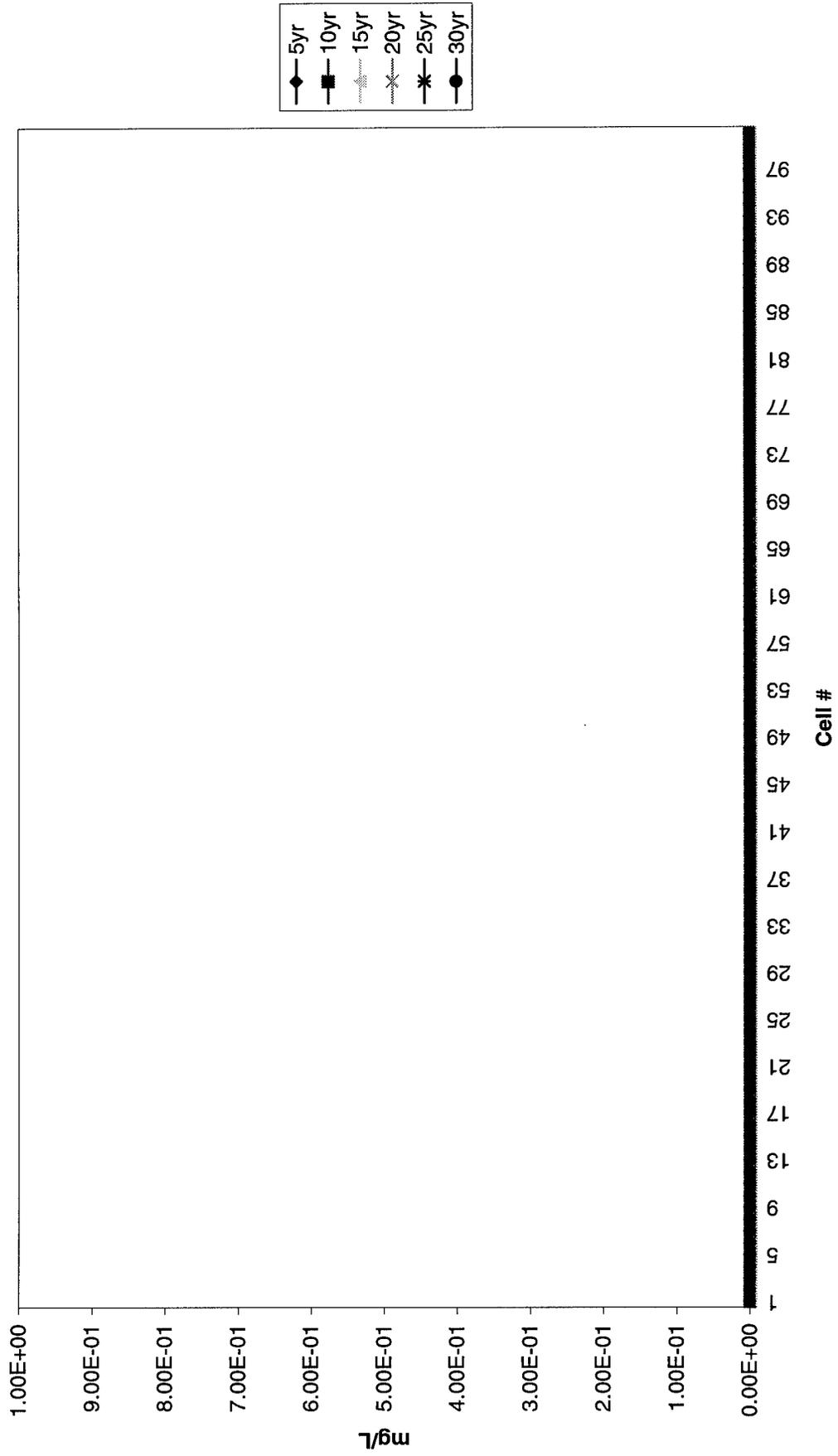
# CH4 Casestudy



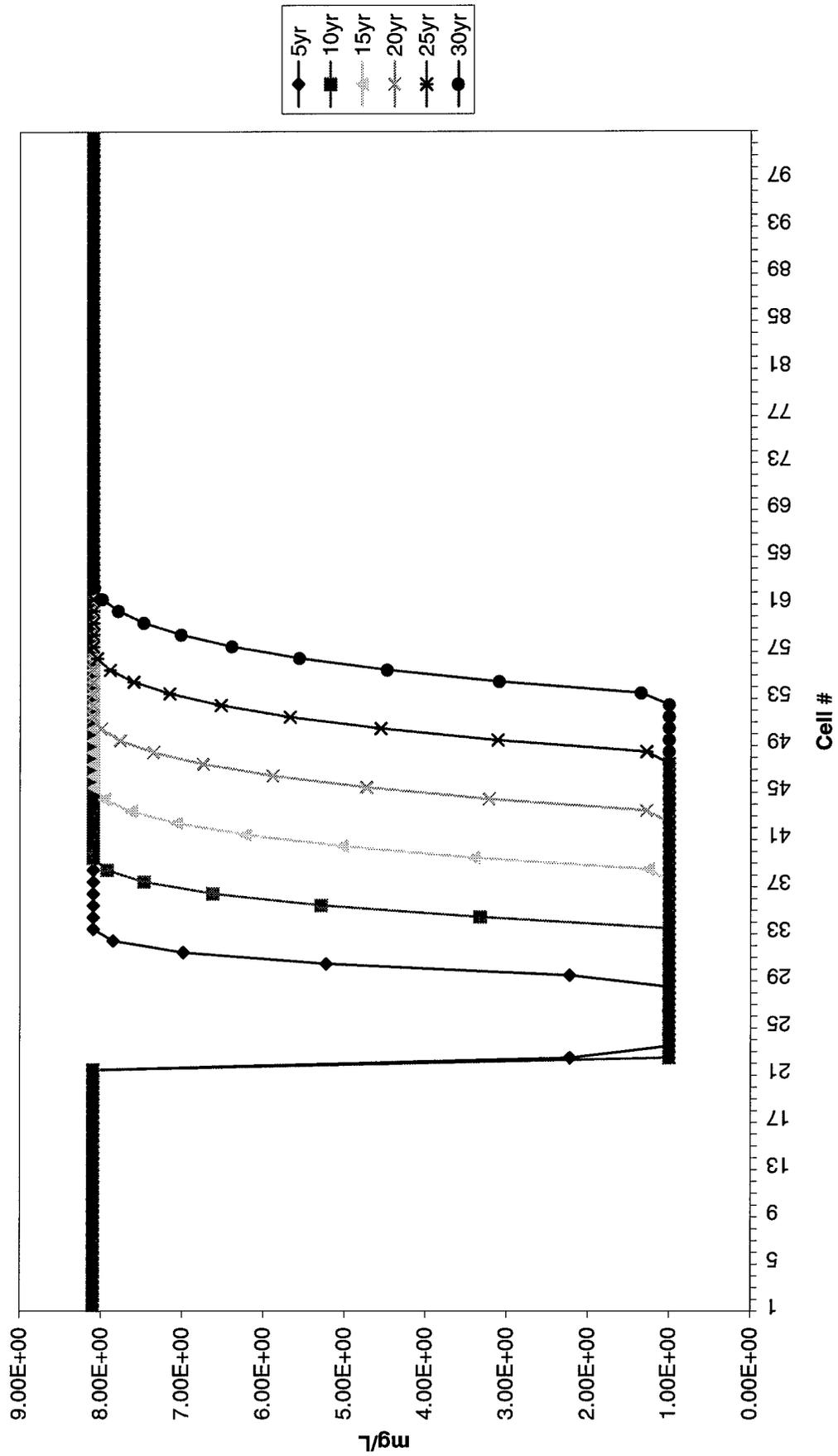
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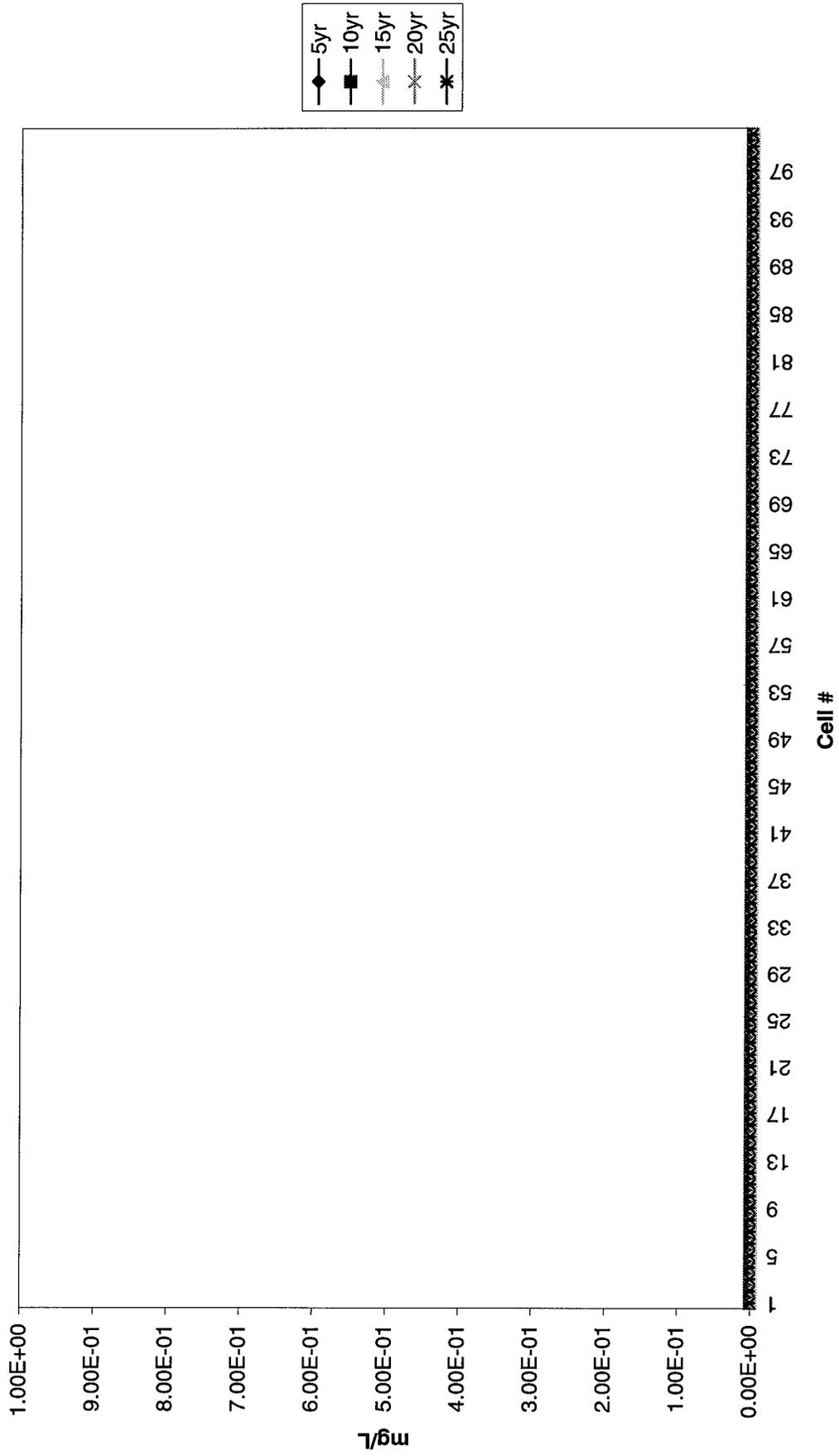
# NO3 Casestudy



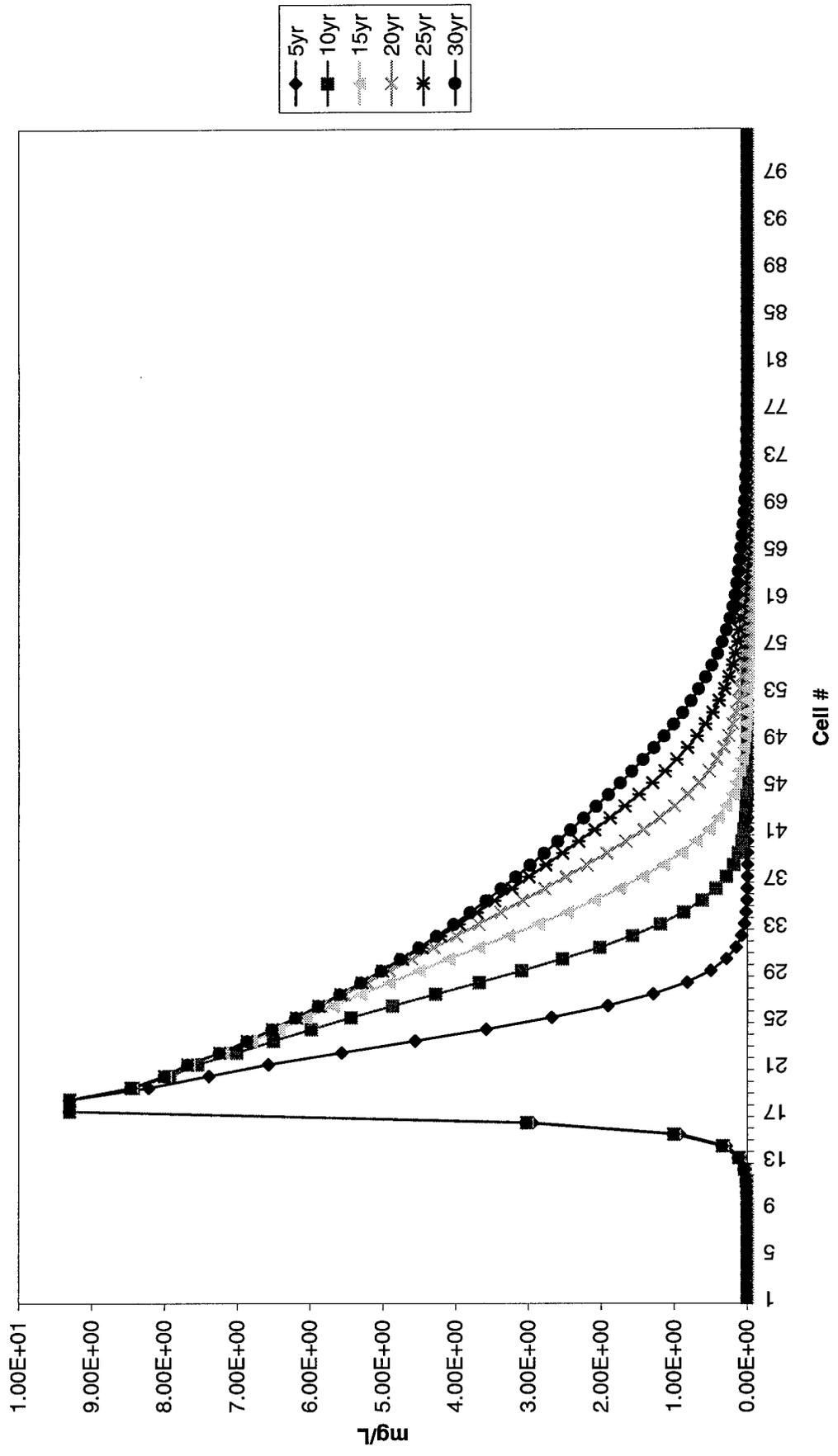
FE3  
Casestudy



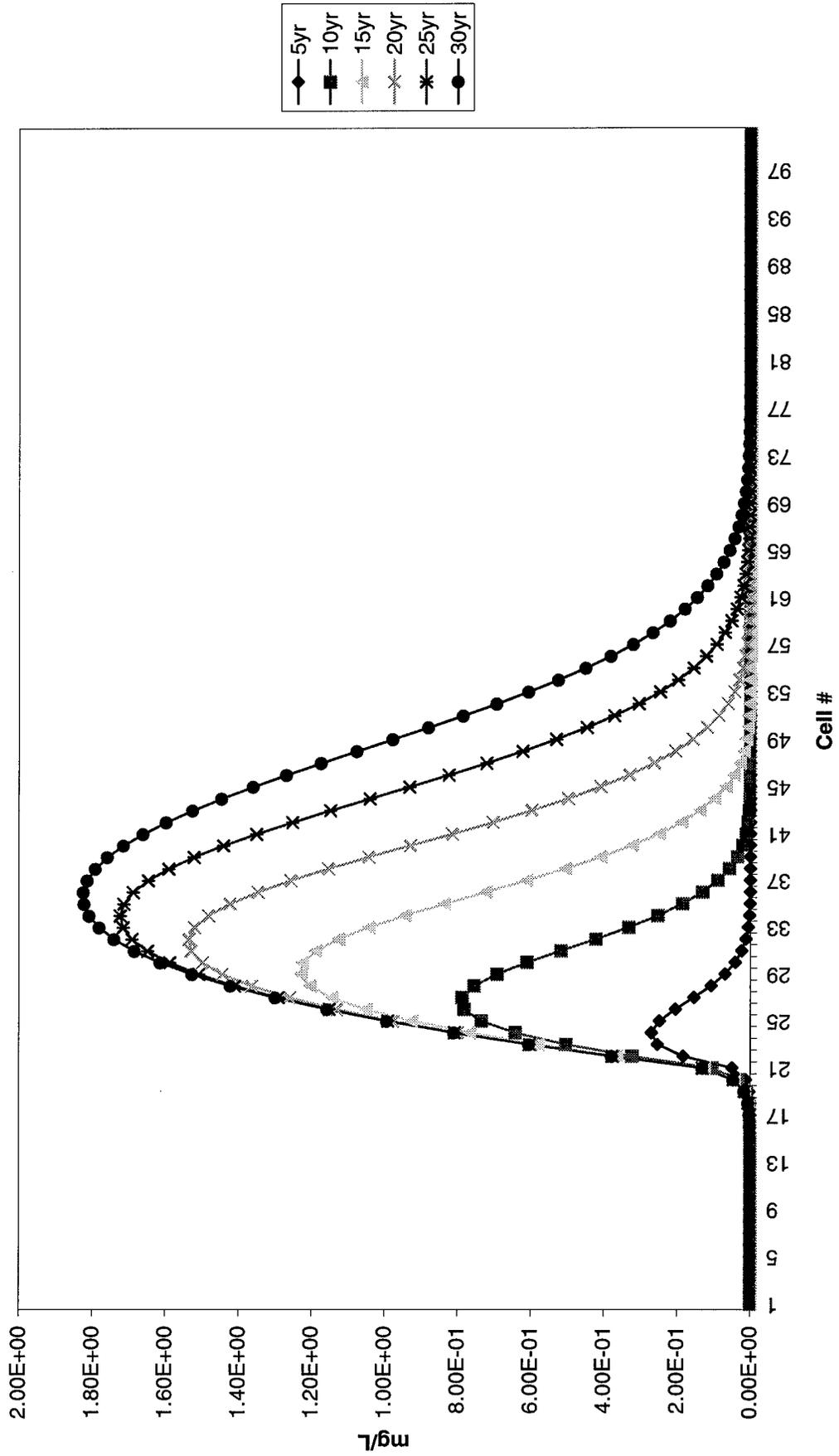
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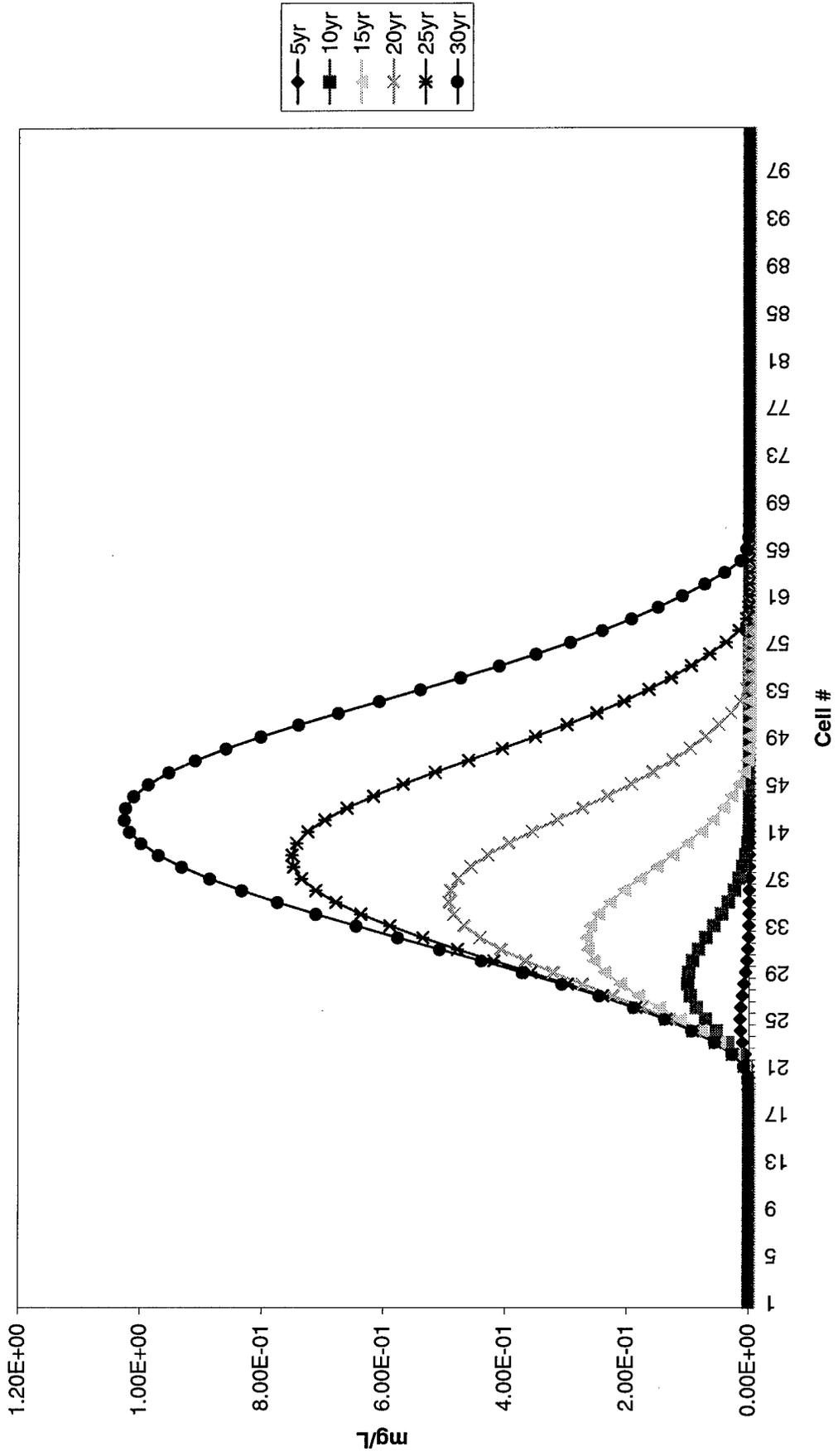
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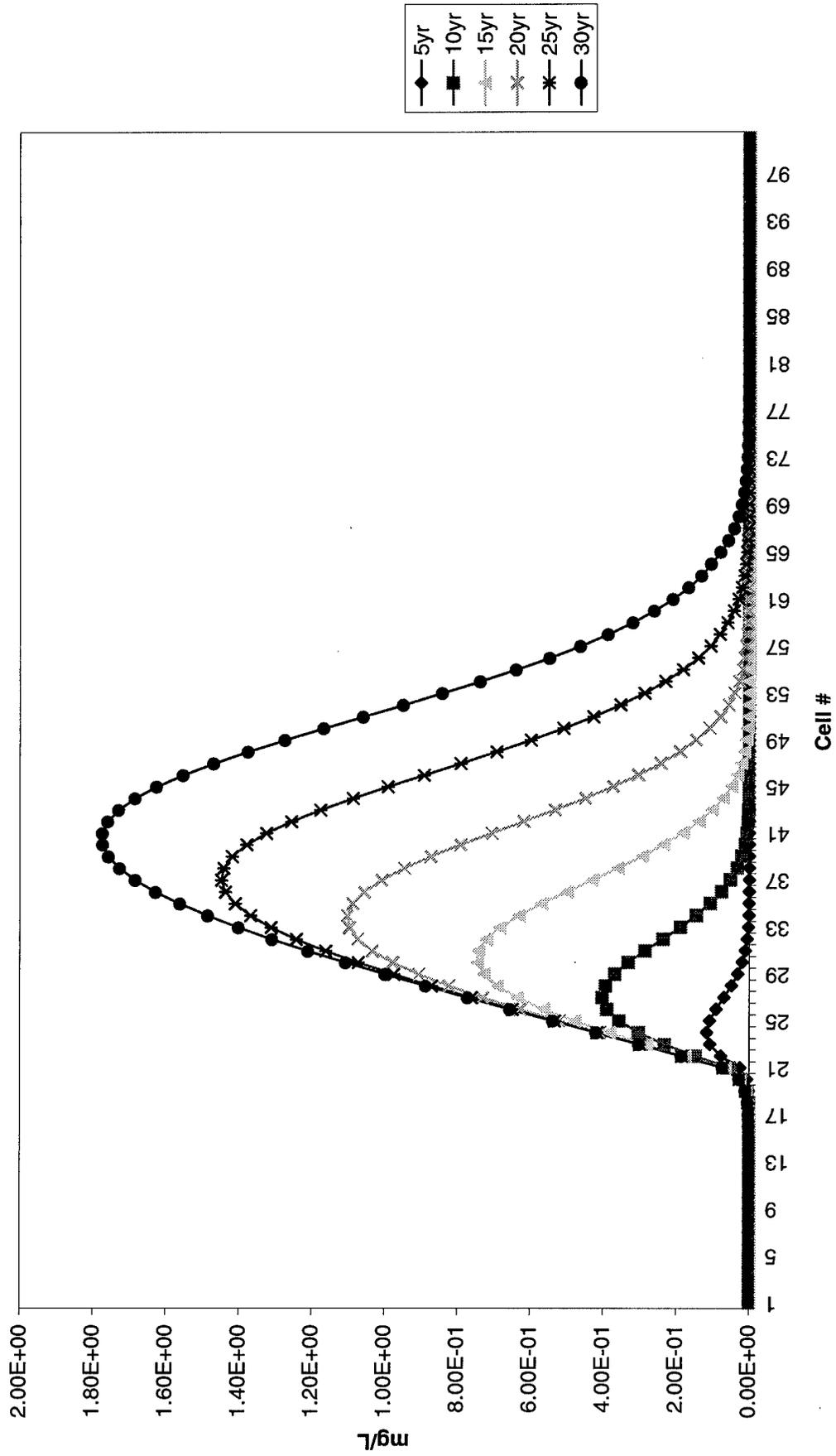
# DCE Casestudy



VC  
Casestudy



Cl  
Casestudy



## Vita

Derek D. Veerkamp was commissioned as an officer in the United States Air Force June 1995. He was assigned to the 17<sup>th</sup> Civil Engineer Squadron at Goodfellow AFB, TX. His second assignment was at the Air Force Institute of Technology to pursue his Master's degree. His next assignment is to 82<sup>nd</sup> Civil Engineer Squadron at Sheppard AFB, TX.

Permanent address:

1530 Highland Ct. Apt B

Fairborn, OH 45324-6579

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