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AN ANALYSIS OF SITE PARAMETERS AFFECTING
NATURAL ATTENUATION IN SATURATED SOIL

THESIS

William H. Potts, Captain, USAF

AFIT/GEE/ENV/93S-12

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ATTENUATION IN SATURATED SOIL

THESIS

Presented to the Faculty of the School of Engineering
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In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Environmental and Engineering Management

William H. Potts

Captain, USAF

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Preface

This research was performed to investigate site parameters affecting natural attenuation of JP-4 in groundwater in the saturated zone and to suggest general site conditions which favor natural attenuation. If this evaluation is of some assistance from either a methodological or results standpoint, my efforts will have been worthwhile.

I was attracted to the study of natural attenuation because I have an affinity toward the natural - - natural foods, natural energy sources, natural healing, etc. This remediation alternative provided a natural, common sense approach to a serious problem. Although it may take more time than technologically based alternatives, natural attenuation promises to be a reasonable solution to the escalating costs of site remediation. In becoming more familiar with the process, I found that many authors have recognized the advantages of this option and ongoing research is being done to better understand the process.

I wish to express my gratitude to Lt Col Michael Shelley, my thesis advisor, and Lt Col Mark Goltz, member of the thesis committee, for their aid , encouragement, and assistance in unraveling the sometimes confusing jargon and mechanisms involved in the natural attenuation process. Thanks are also due to Lt Col Ross Miller of AFCEE for his suggesting the research topic and for his input to the early development of the research project.

Finally, I wish to thank my wife, Kathy, and my children, Micole, John, Aubrey, Ruthanne, and Shannon for the sacrifice they made by giving up much of the time they would have liked to spend with daddy. I am truly grateful for their patience, encouragement, and understanding throughout this course of study.

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Abstract

This study investigated the natural attenuation mechanisms and some of the parameters affecting those mechanisms in the saturated zone. A literature search revealed numerous studies of various attenuation mechanisms and the associated parameters. Much of the literature emphasized biodegradation as the most promising attenuation mechanism. BIOPLUME IITM, a fate and transport model, developed by researchers at Rice University and North Carolina State University, was used to simulate the fate and transport of contaminant plume. The effects of the model parameters were investigated by observing the distance a contaminant plume was expected to migrate over a fifty year period. The investigation was limited by the model which excludes chemical reactions and some physical and physiochemical reactions. The model simulations indicated that parameters which exhibited significant influence on natural attenuation include hydraulic conductivity, reaeration, and coefficient of anaerobic biodegradation. These three parameters were investigated further to observe how they affected natural attenuation in concert. Results from the model simulations indicated that the lower the value of hydraulic conductivity and the higher the value of aerobic and anaerobic coefficients, the more favorable are conditions for natural attenuation. A regression analysis was performed on the data to generate a mathematical relationship between site parameters and natural attenuation.

AN ANALYSIS OF SITE PARAMETERS AFFECTING NATURAL ATTENUATION OF JP-4 IN THE SATURATED ZONE

I. Introduction

General Issue

The mission of the Air Force is "to defend the United States through control and exploitation of air and space" (General Merrill A. McPeak, Air Force Chief of Staff). To meet this mission, the Air Force must be able to fly its weapon systems. One essential requirement to getting these airplanes off the ground and fulfilling the mission is fuel for the aircraft. Therefore, the Air Force purchases, transports, stores, and otherwise handles vast quantities of jet fuel to support their fundamental mission. One problem with possessing and handling jet fuel is that, occasionally, the fuel finds its way into the soil by one means or another. This contamination can occur from leaking fuel storage tanks (underground or above ground), accidental fuel spills, intentional fuel jettisons, or some other means. Once this fuel has found its way into the soil, it presents a potential health hazard to the environment or to humans. To the extent this spent fuel poses a hazard, it must be cleaned up and the affected area restored to a nonhazardous condition.

Background

Several techniques have been used in the past to clean up or remediate the sites where jet fuel has made its way into the soil. General remediation methods include excavation and landfill or incineration and ex-situ and in-situ chemical and biological treatments (6:248-254). These remediation methods have met with varying degrees of success and each has

advantages and disadvantages (31:228-229). Some newer technologies include in-situ heating of soil by electrical energy, migration barrier technology, air sparging of organic compounds in soils and groundwater, biological filters, and bioventing (13:Sessions 1-3). These newer technologies exhibit varying degrees of promise. Both the tried and tested methods and the newer technologies can be costly and regulatory compliance is often difficult to achieve (20:preface). Because of the magnitude of the problem and current budget considerations, it is prudent to find the least costly method of remediation. If it could be shown that no remedial action was required to eliminate the problem, that alternative would be a very attractive option because it would cost much less to comply with site closure criteria. Money saved could be used to clean up other sites.

According to Major Ross Miller of the Air Force Center for Environmental Excellence (AFCEE), natural attenuation could be a cost effective mechanism for remediation of JP-4 at certain sites. He states that from \$1 million to \$5 million per site could be saved for a total savings to the Air Force of \$500 million to \$2.5 billion (23:4).

Specific Problem

The hydrocarbons which reach the soil are expected to attenuate over time. Many organic compounds, including hydrocarbons found in petroleum products, such as JP-4, are broken down by naturally occurring bacteria in the soils (8:482). The hazardous constituents of JP-4 are the BTEX compounds (13:Session 3), which are also broken down aerobically. Under aerobic biodegradation, the nonhazardous end products of organic breakdown are water and carbon dioxide (1:144). Hydrocarbons, contaminating the unsaturated zone, well above the water table, will be subject to long-term aerobic conditions. Oxygen is all that is needed

in the unsaturated zone to stimulate biodegradation of the dissolved fuel components. Due to the oxygen content of the air in the unsaturated zone, the hydrocarbons are expected to biodegrade over time (8:482). Biological clean up of hydrocarbon contaminated soils can be enhanced by providing oxygen to the local microorganisms through forced aeration of the soil. However, it is unnecessary to add oxygen, other organisms, or nutrients, in order for the attenuation process to proceed in the unsaturated zone (23:4).

Due to limited oxygen concentrations, attenuation in the saturated zone is less certain. Because groundwater is the most likely exposure pathway for spilled or leaking JP-4, it would be beneficial to be able to predict the fate and transport of the contaminant plume in the saturated zone. Knowing the expected behavior of the contaminant plume would allow one to choose appropriate remediation actions.

Objective

Several models have been developed to predict degradation of various contaminants in certain environments. There are ongoing studies to validate, calibrate, and improve these models. The model chosen for use in this study is the BIOPLUME II model.

The focus of this research is to investigate, through the use of the BIOPLUME II model, the conditions and parameters which favor natural attenuation, to examine the plume characteristics for these conditions and parameters, and to theoretically estimate whether the contaminant concentrations will fall within established risk and contamination limits before reaching a potential exposure point and becoming a hazard to human health or to the environment. If risk and contaminant levels fall within established guidelines, the natural attenuation alternative may be the appropriate remediation elective.

This research project proposes to use BIOPLUME II, software developed by Rice University, to assess the site conditions and parameters which enhance or optimize natural attenuation of JP-4. Theoretical data will be input to the model to analyze how the value of various parameters affect the contaminant plume. A sensitivity analysis will be accomplished to explore critical ranges and variations in parameters and to explore which parameters may be the most critical. General site conditions will be proposed for which natural attenuation should be considered the primary remediation option.

Scope

Natural attenuation includes several mechanisms by which contaminant concentrations are reduced. These mechanisms include volatilization, sorption, dilution, dispersion, advection, hydrolysis, biodegradation, and others. These processes occur in distinct zones, three of which are the atmosphere, the vadose or unsaturated zone, and the saturated zone. This research will focus on natural attenuation in the saturated zone which includes natural biotransformation of hazardous organic compounds in the subsurface (37:1). The investigation will be limited to the analysis of results generated by the BIOPLUME II™ software.

Overview

This chapter has given a brief background to set the stage for the subsequent discussion of natural attenuation and associated parameters. These parameters will be examined with the aid of BIOPLUME II™, a two-dimensional model which will simulate the natural attenuation process in the saturated zone. Chapter 2 of the thesis consists of a discussion of the relevant literature on this topic. Chapter 3 includes the research design and

the methodology employed for this research effort. Chapter 4 contains the data description and analysis and chapter 5 presents discussion of findings, conclusion, and recommendations.

II. Literature Review

In the last decade or two, the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) have prompted a frenzy of activity in the environmental restoration arena. Because of the increased attention given to the environment, a great deal of research has been done in the field of hazardous waste remediation. Due to the increasing costs of environmental restoration, researchers have been looking for effective remediation technologies which are also cost effective. The search has led to few promising technologies which are effective yet inexpensive. One of the least costly methods of restoration is natural attenuation. Even where naturally occurring mechanisms are at work degrading hazardous substances into harmless byproducts, one must verify that this activity is taking place and that the natural process will be sufficient to bring the hazard within acceptable limits. This verification is accomplished by monitoring the contaminant plume at a hazardous waste site through the use of monitoring wells. Even with extensive monitoring requirements, cost savings can be significant. Natural attenuation has become a very promising remediation option due to its low cost. Wherever possible, the Air Force would like to take advantage of this natural degradation process because of the attractive low cost advantage (23:4).

This chapter will take a closer look at the natural attenuation alternative. The chapter will begin with some background followed by a definition of some of the terms associated with natural attenuation and a brief description of each of the principle mechanisms comprising the natural attenuation process. Following the discussion of natural attenuation

mechanisms, the soil parameters or aquifer parameters affecting these natural mechanisms will be addressed. The discussion will be limited to activity in the saturated zone. Next, factors to be considered in selecting natural attenuation as a remediation option will be reviewed. A brief overview of BIOPLUME II™, the model chosen to analyze the natural attenuation parameters, will be presented followed by a final summary.

Background

Early studies of contaminant transport indicated that contaminant plumes did not migrate as fast and as far as initially predicted (27:208). Figures 1 and 2 show the differences between predicted [theoretical] contaminant plumes and actual [measured] contaminant plumes for two specific compounds at one site. Observations like this led to the discovery of various naturally occurring attenuation mechanisms. More recent studies have been conducted to better understand the natural attenuation mechanisms. An aerobic biodegradation study of water supply wells in California, conducted by Hadley and Armstrong in 1991, compared the presence of benzene, an easily biodegraded contaminant, with two solvents, trichloroethylene (TCE) and tetrachloroethylene (PCE), which are not as easily degraded. The study indicated that far less benzene enters the subsurface groundwater than expected. Table 1 shows the relative occurrence of benzene as compared to the other two solvents in the California wells. The results from these studies suggest that naturally occurring mechanisms are at work removing contaminants from groundwater under certain conditions (38:2).

Much has been written concerning the possible mechanisms, including volatilization, sorption, chemical and biological degradation, and others, that come into play in the

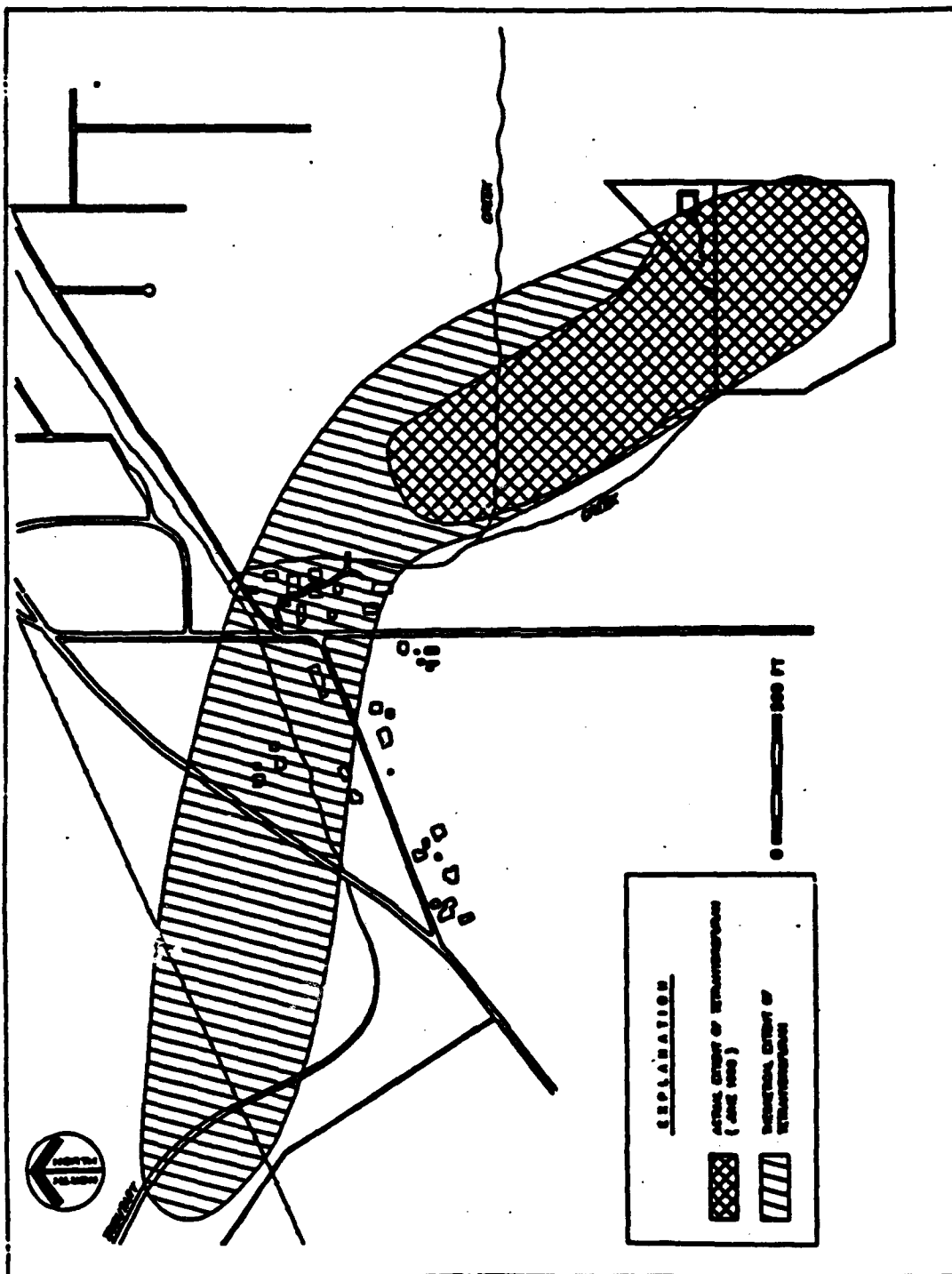


Figure 1. Theoretical and actual distributions of tetrahydrofuran (27:211)

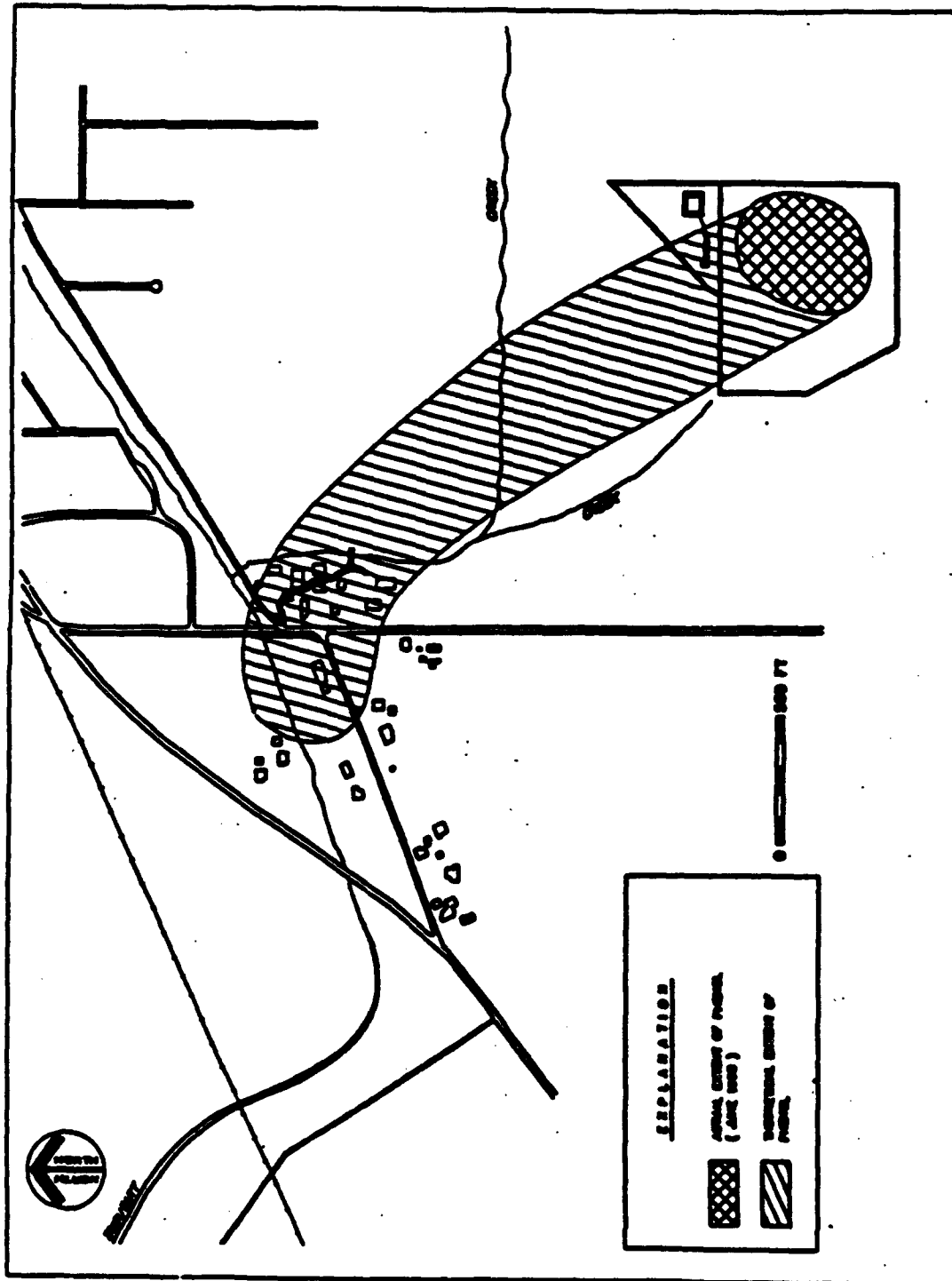


Figure 2. Theoretical and actual distributions of phenol (27:213)

Table 1. Relative occurrence of benzene, trichloroethylene, and tetrachloroethylene in water supply wells in California. (38:2)

Compound	Number of Wells	Median Concentration (mg/liter)	Maximum Concentration (mg/liter)	Minimum Reported Conc. (mg/liter)
Benzene	9	0.2	1.1	0.1
TCE	188	3.2	538	0.1
PCE	199	1.9	166	0.1

attenuation of chemical contaminants. Research has shown that under varying site conditions, great differences occur between attenuation efficiencies observed in the laboratory and those encountered in the field (24:830). This variation may be attributable to the complexity of the field environment and the many parameters that affect expected attenuation efficiencies (20:205).

Definition of Terms

In the following discussion, the principle mechanisms associated with natural attenuation will be defined and discussed. Many of the terms associated with natural attenuation not defined here may be found in a glossary of often-encountered terms in Appendix A.

Attenuation

Attenuation of chemical constituents in soil and rock is a well recognized phenomenon. The concept has been and is currently being used by state and federal regulators for the following actions (20:215):

- 1) establishing general standards
- 2) determining cleanup criteria for polluted sites on a case by case basis
- 3) providing variances for the disposal of waste into landfills
- 4) regulating the disposal of treated waste water sludge to land
- 5) regulating ground water recharge projects.

"Attenuation is defined as the reduction in quantity or toxicity of a chemical constituent in liquids that may be released to the environment (20:205)." Attenuation can be accelerated through various remediation technologies; however, this study is concerned with the natural, rather than anthropogenic, processes.

Natural Attenuation

Natural attenuation is the naturally occurring attenuation of a chemical constituent without artificial stimulation or augmentation. Natural attenuation occurs because of several mechanisms. These mechanisms have been delineated into physical, physiochemical, chemical, and biological categories. These mechanisms operate along the contaminant plume migration pathway and begin almost immediately when a contaminant is released to the environment (20:217).

Natural attenuation is the preferred method of remediation in the Air Force as shown in Figure 3. This matrix presents a hierarchy of preferred remediation alternatives. As shown, natural attenuation is the preferred method in all situations except vapor treatment for which natural remediation is not applicable.

	PCL-Vadose Zone (ft., per foot, depth)	PCL-Exhausted Soil	Feeding Product Depth (ft.)	Feeding Product Shallow (<50 ft)	Feeding Product High Permeability	Desired Result in Ground Water (GTEQ)	Observed Saturated in Vadose Zone (ft., TCE)	Desired Chlor- inated Saturated in Ground Water	Heavy Metals in Vadose Zone	Heavy Metals in Exhausted Soil	PCL Vapor Threshold	Observed Saturated Vapor Threshold
Natural Attenuation/Assimilation	1	1	1	1	1	1	1	1	1	1	1	1
Blowtilling	2	4					2	1				
Soil Vapor Extraction	3	5					3					
Heat Enhanced Vapor Extraction	4						4					
Low Permeability Cover/Cap	5						5					
Excavate and/or Heat	6	6					6					
Composting (no filling)		2										
Land Farming		3										
Low Temp Thermal Desorp		6										
Induration (High Temp)		7										
Apparent vs Actual Studies			2	2	2							
Passive Extraction Wells			4	5	4							
Hard Soil			3	3	3							
Vacuum Assisted Pumping				4	5							
Soil Pump System			5									
Air Sparging						2		2				
Passive Treatment Well						3		3				
Conventional Pump and Treat						4		4				
Slurry Wall						5		5				
Stabilization							5		2	3		
Permitted Direct Evaporation											1	1
Pave											2	
Biological Filter											3	2
Catalytic Induration											4	3
On-site Regenerated Polymer											5	4
Carbon Adsorption											6	5

This matrix is for rating technologies for use at various Air Force sites. Managers should use this hierarchy for screening technologies; however, not justify why a particular technology was selected. For instance, if soil vapor extraction (5) is the selected technology for PCL in the vadose zone, then managers should be able to justify why neither natural attenuation (1) nor blowtilling (2) was selected. The natural attenuation alternative should always be considered first and, if selected, should be based on a scientifically defensible risk assessment. Selection of this technology should be accompanied by field sampling and modeling to quantify and predict natural attenuation rates. A long term monitoring program should be implemented to verify natural attenuation model predictions.

Figure 3. AFCEE remediation technology matrix (24:4)

Physical Mechanisms

The physical mechanisms to be discussed include advection, filtration, volatilization, dispersion, and diffusion. These physical mechanisms attenuate a contaminant primarily by reducing the concentration of contaminant rather than reducing the toxicity of the contaminant. Frequently, the physical mechanisms simply transfer the contaminant from one medium to another (21:5).

Advection

In permeable aquifers, such as, sand and gravel aquifers, advection is the primary mechanism affecting contaminant migration (9:159). Advection is a result of the bulk motion of flowing groundwater (29:1-6). The flowing groundwater transports a contaminant through the substrate from a region of high hydraulic head to a region of lower hydraulic head (9:159). The difference in hydraulic head causes a pressure differential termed the hydraulic gradient. The velocity at which groundwater flows through a substrate is a function of the hydraulic gradient and the substrate's inherent capability to transport groundwater. This inherent capability is a function of the soil or aquifer characteristics which will be discussed later. Calabresi and Kostecki report that "Groundwater velocities in uniform sand and gravel aquifers, under natural gradient conditions, are typically between 10 and 100 m/yr, with a potential range between 1 and 1000 m/yr (9:159)."

Filtration

Filtration is defined as the simple obstruction of particulates migrating through a permeable soil. The particulates may be insoluble minerals or chemical precipitates. Physical filtration is the process of suspended solids being captured in the soil matrix because they are

too large to flow through the pore spaces (20:222) Filtration attenuates contaminants by obstructing their movement through the substrate. A change in groundwater pH or other environmental conditions may cause a chemical precipitate or insoluble mineral to dissolve and be released to the groundwater. For this reason, filtration should not be relied on as an attenuation mechanism.

Volatilization

Volatilization is defined as the process whereby a contaminant is transferred from the soil or water phase to air or vapor phase. Volatilization is a form of diffusion, that is, molecular movement of chemicals or ions from a high concentration region to a low concentration region. Volatilization is an extremely important attenuation mechanism for many organic compounds; however, rates of volatilization can vary over a large range (9:160).

In the saturated zone, there is no air in the soil pores, therefore, only the surface of the groundwater table or capillary fringe is in contact with air. Also, the aquifer is not a well-mixed system. Lyman reports that these two conditions eliminate volatilization from being a significant attenuation mechanism in the saturated zone (23:209).

Dispersion

Dispersion refers to the spreading out of a dissolved contaminant as it is transported by the groundwater through the soil matrix. Dispersion occurs because of two fundamental processes, molecular diffusion in solution due to a concentration gradient and mechanical mixing (or mechanical dispersion) caused by the groundwater flow through the soil. The molecular diffusion process is a result of the contaminant seeking chemical equilibrium. The

overall result is a transfer of solutes from a high concentration zone to a lower concentration zone (9: 159).

Molecular diffusion is a process, whereby ionic or molecular constituents move under the influence of their kinetic activity causing a net directional movement opposite the direction of their concentration gradient. The mass of a contaminant is diffused as it passes through a specified cross section of a given medium per unit of time. According to Fick's first law, the diffusion of a contaminant is proportional to the concentration gradient.

The rate at which a chemical contaminant is diffused is a function of the chemical properties of both the pollutant and the soil through which it passes. In the saturated zone, the effect of mechanical dispersion is generally much greater than that of molecular diffusion, because mechanical dispersion is proportional to the groundwater flow velocity. Therefore, diffusion is often neglected in the saturated zone. Diffusion is generally not significant unless the aquifer has a very low flow rate. Tucker and Nelken suggest that molecular diffusion can be ignored at groundwater velocities exceeding .002 cm/sec (9:159-160).

Dispersion can have a significant effect on natural attenuation in the saturated zone because it exposes the chemical contaminant to a larger volume of soil and pore water at a reduced concentration, increasing the potential for attenuation by sorption or degradation by chemical reactions and microbial activity (20:223). Figure 4 illustrates the dispersion processes on a molecular scale.

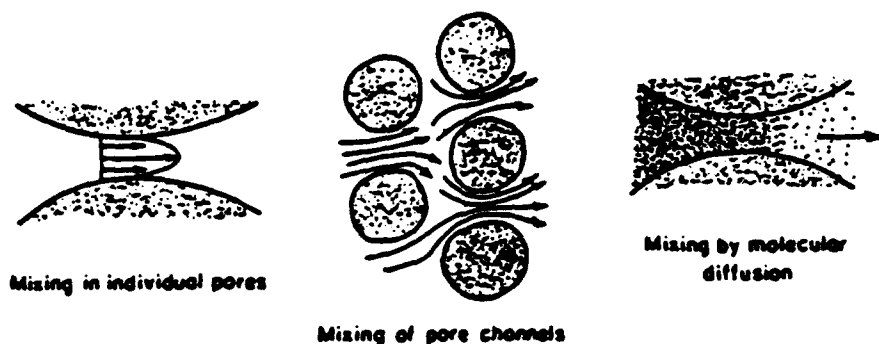


Figure 4: Processes of Dispersion on a Microscopic Scale (30:1 - 8)

Physiochemical Mechanisms

The mechanisms included in this category are neither purely physical nor purely chemical but depend on both. The primary mechanism included in this category is sorption.

Sorption

Sorption consists of absorption, adsorption, and desorption. Absorption, or solid state diffusion, is the accumulation of a contaminant within the soil particle pores. Absorption results in a decrease in the amount of an element available for transport in the groundwater, effectively reducing the concentration of contaminant in the groundwater. Adsorption is the accumulation of the pollutant at the surface of the soil particle. The bonding which causes this accumulation can be either physical or chemical. The chemical bonding is also referred to as chemisorption and is usually irreversible, rendering the chemical immobile. Adsorption can decrease the concentration of an element in the groundwater. Desorption is transfer of the contaminant from the soil particle pores to the soil particle surface or from the soil particle surface back into the groundwater (9:160-163, 20:228).

One significant effect sorption has in the attenuation of contaminants is that it can drastically retard the migration of pollutants in soils. Sorption and subsequent migration retardation are dependent upon the type of chemical and the type of soil through which a contaminant is moving (9:163).

Sorption, like filtration, should not be relied upon as an attenuation mechanism. Because of the retardation effect, sorption can aid in controlling the migration of a contaminant plume; however, post remediation monitoring for certain remediation techniques has shown that sorption may be reversible after a site has been restored (28:42-44). The low contaminant concentrations, resulting from remediation, cause subsequent desorption of the contaminant from the soil particles back into the groundwater resulting in elevated contaminant concentrations.

Chemical Mechanisms

Chemical mechanisms can result in transformation of the contaminant from a hazardous chemical species to a nonhazardous species (20:233). These mechanisms are considered equilibrium processes and may be reversed if the physiochemical conditions of the pore water change (20:222). The reversibility of the chemical reactions is one reason certain chemical mechanisms should not be relied upon as attenuation mechanisms. Chemical mechanisms include precipitation, hydrolysis, complexation, oxidation, and reduction.

Precipitation

Precipitation occurs when the contaminant exceeds its solubility limits and forms an insoluble solid compound which becomes suspended in solution. The solid particles are then subject to the filtering mechanism discussed earlier. Filtration actually "captures" the

constituent in the soil matrix, preventing it from migrating. These suspended particles can remain insoluble indefinitely; however, a change in environmental conditions, such as redox potential, pH, or ion concentration, may cause the precipitate to dissolve and be released back into the groundwater. Because of the reversibility of these chemical reactions, precipitation should not be relied upon as an attenuation mechanism (20:231-232).

Hydrolysis

A hydrolysis reaction results in the transformation of contaminants from one chemical species to another. Hydrolysis reactions primarily affect organic compounds. Organic compounds are transformed as they react with water, forming new compounds. The process typically consists of the breaking of the carbon-halogen bond in the original molecule and the formation of a new carbon-oxygen bond (9:166-168).

Depending on the chemical compound and the environmental conditions, the rate of hydrolysis can vary widely. Hydrolysis is site dependent and may or may not be a significant attenuation mechanism in the saturated zone. Fourteen orders of magnitude and associated half-lives as low as a few seconds to as high as 10^6 years can be expected (9:167). Because of this variability, hydrolysis is often excluded from models or, if included, it is often not corrected for environmental conditions (9:167). In either case, model results should be evaluated cautiously. The BIOPLUME II™ model used in this study excludes hydrolysis from consideration, therefore, for some conditions, the model may yield conservative results.

Complexation

Complexation, or chelation, occurs when a chemical complex is formed by the union of a metal ion with nonmetallic ions. The resultant metal-ligand complex will generally

prevent the metal from further chemical reactions (9:169). The complex may also be less toxic than either of the complexed chemicals (20:234). Because it is primarily an attenuation mechanism for metals, complexation is probably not a significant attenuation mechanism for jet fuel in the saturated zone. Due to limited understanding and available information about the process, complexation reactions have not been modeled (9:169).

Oxidation-Reduction

For some organic compounds, chemical oxidation is an important degradation process. The process is dependent upon environmental conditions and usually involves reactions between the organic compound and free radicals already in solution (9:166). Oxidation occurs when an element undergoes a change in valence state, from a lower valence state to a higher valence state, by the loss of valence electrons. The change in valence often transforms the element from a solid state to a soluble ion. Reduction occurs when the chemical contaminant gains valence electrons. Either process may result in reduced toxicity of a chemical contaminant. Reduction in toxicity occurs when the valence electron state of a contaminant causes the chemical species to become less toxic than the original chemical species. This electron valence change can also alter the mobility of the contaminant (20:234).

Biological Mechanisms

By far, the majority of literature pertaining to natural attenuation emphasizes bioattenuation. Several studies have shown that naturally occurring microorganisms can degrade or oxidize hazardous substances such as jet fuel into harmless substances such as water and carbon dioxide (13:Sessions 2 - 4, 37:380, 9:115). This process, known as natural biodegradation, is fast becoming a preferred remediation alternative. One author states that

"Bioremediation, or enhanced microbiological treatment, of environments contaminated with a variety of organic and inorganic compounds is one of the most effective innovative technologies to come along this century" (21:preface).

In reality, bioremediation is merely a new application of a technology used in ancient times for wastewater treatment. "Romans and others built intricate networks of sewers as early as 600 B.C. for collecting wastewater which underwent subsequent biological treatment" (21:1). Natural biodegradation, however, existed long before these manmade uses of microorganisms.

Biodegradation

Biodegradation in the subsurface includes three patterns of biotransformation: aerobic respiration, anaerobic respiration, and fermentation (37:368, 38:1,9:115). The best understood and most developed bioremediation technologies rely on aerobic microbial activity. Aerobic degradation is considered the most attractive degradation pattern due to its rapid rate of transformation and the absence of noxious by-products which may result from anaerobic microbial degradation (37:368). In aerobic respiration, microorganisms consume oxygen while decomposing organic hydrocarbons (26:73). The basic requirements for aerobic biodegradation include: the abundance of local microorganisms; the availability of an energy source, a carbon source, oxygen and nutrients; and the presence of acceptable environmental conditions (6:Rifai). Dissolved oxygen concentration in the groundwater is usually the limiting factor for aerobic respiration (23:296). Natural aerobic biodegradation can account for significant mass loss of dissolved contaminants in a plume (13:Rifai).

Anaerobic decomposition of hazardous chemicals occurs in the absence of oxygen. In an oxygen depleted environment, other electron acceptors include nitrate, sulfate, carbonate, and iron III (9:115). The effectiveness of anaerobic degradation is somewhat more controversial than aerobic degradation. Calabresi and Kostecki state that "convincing proof of significant anaerobic hydrocarbon biodegradation is still outstanding. Sulfates are a potential electron acceptor, but are not abundant in soils. Nitrate is not energetically favorable for this purpose in soils (8:224)." Although this process is not yet well understood, recent studies show that certain chemical compounds are biodegradable in groundwater under anaerobic conditions. Anaerobic degradation is a slower process than aerobic degradation, sometimes requiring months to years for the process to begin (38:4).

In the fermentation process, the organic compound serves as an electron acceptor, instead of the more common roles of electron donor or carbon source. In essence, the chemical contaminant becomes something for the microorganism to breath rather than a food source. In this process, the degradation rate is limited by the electron acceptor demand from other organic compounds and by competition from other more conventional electron acceptors (38:1-4).

Aquifer Parameters

The substrate properties and characteristics which are considered important to physical transport in the saturated zone include composition of the soil, storage capacity of the soil, porosity, hydraulic conductivity, and dispersivity parameters.

Porosity

Porosity is defined as the ratio of the volume of the void space between soil particles to the total volume by the relationship:

$$n = \frac{V_{\text{voids}}}{V_{\text{total}}}$$

Figure 5 illustrates the relationship between the soil texture and porosity.

Typical values for porosity are given in Table 2. A common misconception is that the more porous the soil, the greater the ability to transport groundwater. However, one can see that porosity varies over a wide range for different soil types, such as well sorted sand and gravel or clay. Clay soils can have a greater porosity than sand and gravel, yet are less permeable, that is, less able to transport groundwater.

Dispersivity

Dispersion has been discussed previously as an attenuation mechanism. The mechanism, however, is a function of soil structure and composition. The spreading of contaminant in the same direction as groundwater flow is termed longitudinal dispersion. Dispersion perpendicular to the direction of flow is termed transverse dispersion (29:1-8).

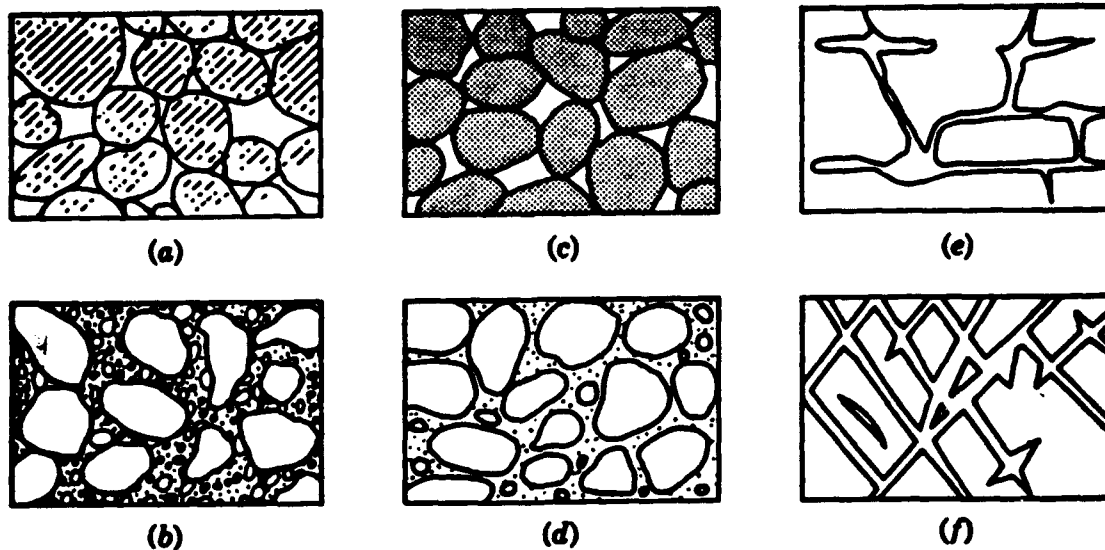


Figure 5. Relation between texture and porosity. (a) Well-sorted sedimentary deposit having high porosity; (b) poorly sorted sedimentary deposit having high porosity; (c) well-sorted sedimentary deposit consisting of pebbles that are themselves porous, so that the deposit as a whole has a very high porosity; (d) well-sorted sedimentary deposit whose porosity has been diminished by the deposition of mineral matter in the interstices; (e) rock rendered porous by solution; (f) rock rendered porous by fracturing. (12:25)

Table 2. Typical values of Porosity (30:1 - 3)

Well sorted sand or gravel	25 - 50%
Sand and gravel, mixed	20 - 35%
Glacial till	10 - 20%
Silt	35 - 50%
Clay	33 - 60%

Hydraulic Conductivity

Permeability is the term which refers to the capacity of soil to transmit a fluid and is related to hydraulic conductivity. Hydraulic conductivity refers to the rate at which an aquifer conveys water. Hydraulic conductivity values are usually obtained from testing at a site.

Typical values for various soil types are included in Table 3.

Table 3. Typical Hydraulic Conductivity Values (cm/sec) (30:1-7)

Clay	$10^{-9} - 10^{-6}$
Silt,sandy silts, clayey sands, tills	$10^{-6} - 10^{-4}$
Silty sands, fine sands, Well-sorted sands, Glacial outwash	$10^{-3} - 10^{-1}$
Well-sorted gravel	$10^{-2} - 1$

Factors to Consider for Selection

Factors that affect the natural attenuation process in the saturated zone need to be understood. General site parameters that must be investigated when considering the applicability of natural attenuation include (8:178):

- Soil microbiology: First of all, microorganisms which have the ability to degrade petroleum products must exist in the zone of contamination.
- Soil chemistry: In order to maintain a healthy population of microorganisms, not only must oxygen and nitrogen supplies be sufficient but other soil nutrients must also be in adequate supply. Furthermore, conditions which preclude a healthy environment must not exist, such as toxic salts or heavy metals in the soil.

- Soil physics: The soil must be porous and permeable enough for oxygen transfer to take place. Movement of nutrients, including oxygen and nitrogen, into the area of contamination must proceed, as well as transfer of carbon dioxide away from the contaminated area.
- Soil morphology: Understanding of the subsurface geology is necessary for an effective remediation design.
- Hydrogeology: As much information as possible should be gathered concerning aquifer characteristics: depth to the water table, hydraulic gradient, direction of flow, and initial concentrations of nutrients and contaminants. The smaller the contaminant source, the more likely it is that natural attenuation will be sufficient to degrade the contaminant plume.

Other parameters that help assess whether or not natural attenuation ought to be considered as a remediation option include the following (17:117-118):

- suitability of groundwater for consumption
- potential for exposure, i.e. distance to exposure point
- feasibility of active restoration techniques
- projected future demand for groundwater
- proximity to a surface water discharge area with subsequent dilution to environmentally safe levels
- attainability of acceptable contaminant and risk levels.

Noonan includes sociopolitical considerations as another factor that ought to be considered in the remediation design and argues that:

Because in situ treatment [natural attenuation] is accomplished largely underground, little, if any, evidence of activity may be discernible by the general public. This lack of observable activity may lead to a public perception of no action. The public in general may be more prone to respond positively to corrective actions that manifest significant levels of activity. (26:83)

In order to derive maximum benefit from the natural attenuation process, it would be advantageous to be able to predict which site conditions favor natural attenuation, thereby indicating which sites would be candidates for natural attenuation as the preferred remediation method. In this study, it is proposed to examine the parameters involved in natural attenuation for the purpose of predicting general site conditions which favor the natural attenuation process. Investigation of these parameters and their effect on the natural attenuation process will be accomplished using the BIOPLUME II™ model.

BIOPLUME II™

The purpose of this research is threefold: 1) to investigate, through the use of the BIOPLUME II™ model, the conditions and parameters which favor natural attenuation, 2) to assess the degradation rate for these conditions and parameters, and 3) to theoretically estimate whether this degradation rate causes the contaminant concentrations to fall within established risk and contamination limits before reaching a potential exposure point and becoming a hazard to human health or the environment. If risk and contaminant levels fall within established guidelines, the no-action or natural attenuation alternative may be the appropriate remediation elective.

BIOPLUME II™ is an extremely versatile, two-dimensional computer model which simulates the migration and attenuation of dissolved hydrocarbon plumes. The model includes aerobic and anaerobic biodegradation, sorption, and dispersion of the contaminant plume. The model is also able to simulate reaeration and radioactive decay. Reaeration and the anaerobic biodegradation process are modeled as first order reactions (28:v).

An input data set is presented in Appendix B. This data set is simplified and input data can be varied to consider parameters of particular interest. The output data for the model is much more extensive. An example is provided as Appendix C. The output file includes all the input data, followed by the simulation results. The length of the output is dependent on the input data and can be very lengthy. Specific input parameters are included as Appendix D.

The model calculates changes in the contaminant and oxygen concentrations for a given time period by solving the solute transport equation for the contaminant and oxygen plumes and then superimposing the results. The model assumes an instantaneous reaction between oxygen and hydrocarbon to simulate the biodegradation processes (28:v). This assumption is evident in viewing the output. Even though contaminant effects are evident in a cell, by observing the oxygen reduction taking place, contaminant concentrations are not displayed as an increase or accumulation in a cell until oxygen concentrations are zero.

BIOPLUME IITM includes three sources of oxygen into an aquifer: initial dissolved oxygen in the uncontaminated aquifer, natural recharge of oxygen across a vertical cross-section, and vertical exchange of oxygen from the unsaturated zone (reaeration) (28:v). These three sources can be used to provide oxygen to drive natural biodegradation processes to attenuate a contaminant plume. In the event one desires to investigate "active" bioremediation techniques, injection wells can be specified as oxygen sources into a contaminated aquifer as well(28:v).

The BIOPLUME IITM model has been used effectively at several sites. The model provided an adequate simulation of a plume of contamination from a forty year old creosote

waste lagoon. The plume had undergone significant attenuation over twenty years, migrating only 400 meters. BIOPLUME II™ simulations indicated that the contaminant plume had reached its maximum extent (38:3).

In another study, the model was applied to an alkylbenzene plume emanating from a flare pit of a natural gas facility. Again, the model adequately predicted contaminant concentrations at the site (38:3)

A sensitivity analysis conducted by Hanadi Rifai, author of the model, is provided as Appendix E. The sensitivity analysis relates the parameters in the model to the natural attenuation process. It was concluded that naturally attenuated contaminant mass in the model is most sensitive to hydraulic conductivity, the coefficient of reaeration, and the coefficient of anaerobic decay (28:2-8). In this study, to add further insight to plume behavior, these three parameters were investigated more fully. Chapter three provides a detailed methodology of this investigation.

Summary

Due to various mechanisms, natural attenuation begins almost immediately upon release of a contaminant to the environment. (6:sessions 1-4). In general, physical mechanisms have a lower attenuation potential; however, they can be important in support of physiochemical, chemical, and biological mechanisms. For example, dispersion can increase the effectiveness of adsorption because "spreading" of the contaminant plume exposes the pollutants to a greater volume of soil particles at a reduced concentration. In addition, dispersion increases the potential for biological reactions which rely upon exposure to nutrients, bacteria and/or oxygen. Information about chemical mechanisms, although

important, has not been particularly useful to fate and transport modelers. Biodegradation is currently receiving the most attention as a remediation option, primarily due to the advantages associated with this technology.

Although natural attenuation is an attractive option, it will not be appropriate for every site. One must consider many factors when choosing a remediation strategy. As much information should be gathered as possible in supporting a decision.

Models have been designed to assist with predictions about the fate and transport of contaminants. BIOPLUME II™ is one of those models and it is used in this study to gain a better understanding of the parameters and mechanisms affecting natural attenuation in the saturated zone.

III. Methodology

Introduction

From the review of the numerous mechanisms and parameters associated with the natural attenuation process in the last chapter, it is evident that the development of a model which includes every mechanism and parameter would be a formidable task indeed. In fact, no such model exists.

When using models to predict the fate and transport of a contaminant plume, one must be conscious of the limitations of the model and in light of those limitations, view the output with caution. In this study, the objective is to examine some of the parameters which affect natural attenuation and to formulate some general guidelines which will indicate the feasibility of natural attenuation as a remediation alternative for given conditions.

Research Design

To meet this research objective, the computer model, BIOFLUME II™ will be employed to simulate the fate and transport of a theoretical contaminant plume as it migrates through a theoretical site under various site conditions.

Rifai and others have conducted a sensitivity analysis of the model. This sensitivity analysis has been included as Appendix E for the convenience of the field engineer investigating the effects of these parameters on natural attenuation. From the sensitivity analysis, it was concluded that the biodegraded mass in the model is most sensitive to hydraulic conductivity and the coefficients of reaeration and anaerobic biodegradation. This sensitivity analysis focused primarily on the percentage of mass biodegraded and ignored the distance that the contaminant plume migrates. Depending on the characteristics of a given

site, the distance a contaminant plume is expected to migrate may be more relevant than the amount of contaminant mass biodegraded. The current study consists of two parts. The first part will repeat the sensitivity analysis conducted by Rifai with some minor modifications and focus on the distance which the contaminant plume migrates rather than the amount of contaminant mass biodegraded. Additionally, this study will further examine the three parameters identified as being the most significant to biodegradation by varying all three over a range of values rather than one at a time, as is typically done in a sensitivity analysis. By varying all three parameters, a general relationship can be postulated regarding the effect of these parameters on natural attenuation.

Part I - Sensitivity Analysis

BIOPLUME II™ will be applied to theoretical plumes of JP-4 of constant source strength and duration. The model will be set up to analyze the natural attenuation of the contaminant plume and to project the distance the plume will travel in a specified length of time.

To estimate which parameters have the most significant effect on the distance a contaminant plume travels, a sensitivity analysis will be conducted. Natural attenuation mechanisms included in the model are dispersion, sorption, and biodegradation. Both aerobic and anaerobic biodegradation can be simulated (28: 2-5).

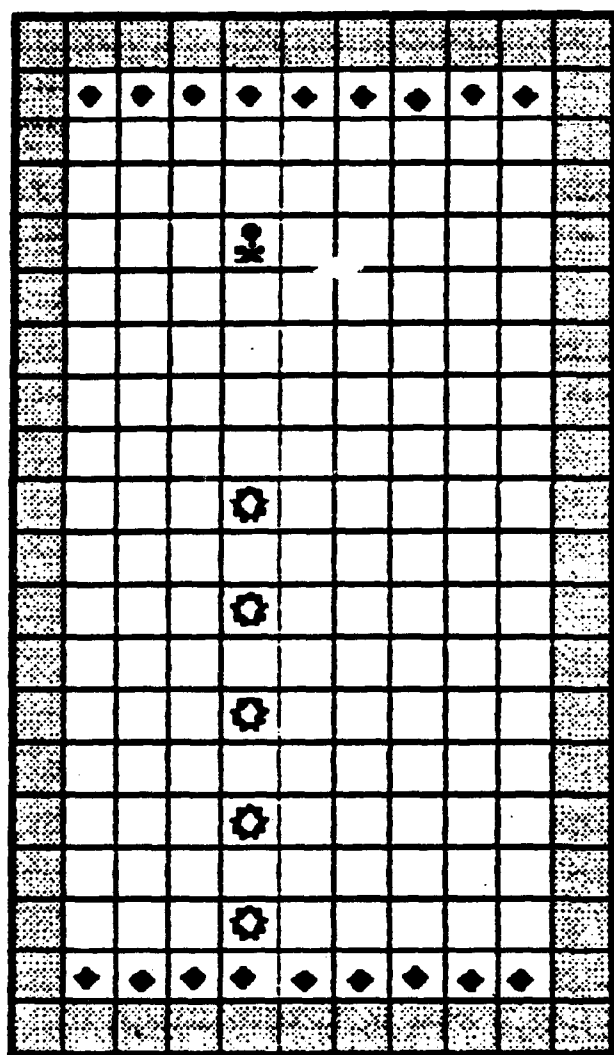
To begin the analysis of the parameters affecting natural attenuation in the saturated zone, a hypothetical site will be simulated. The hypothetical site will be a simple, homogeneous aquifer with constant hydraulic gradient and a single contaminant source. The site is mapped as an eleven-cell by twenty-cell grid. The initial site dimensions will be 500

feet by 1000 feet. A simulated injection well will serve as the contaminant source and five simulated observation wells will be strategically located downgradient from the injection well at regular intervals to track the migration of the contaminant plume through the site. The site and wells are depicted in Figure 6. Considering that for the majority of restoration projects, the contaminant source is removed, the injection well simulation should serve as a worst case scenario and yield conservative guidance.

The model output shows a maximum concentration for the cell in which the source is located. This concentration is a maximum average concentration in the 50 ft by 50 ft cell and not the concentration precisely at the source. The distance is also not precise but related to the cell size, in this case 50 ft. The distance that a plume travels in 50 years is considered to be the incremental distance to the first unaffected grid cell.

Input variables for the BIOPLUME IITM model are listed in Appendix D. Values for the variables of interest are obtained from the literature. Table 4 lists initial site data which is pertinent to this study and was used for the base run.

In order to make comparisons with Rifai's work, the same parameters were chosen to be investigated. These parameters include, porosity, hydraulic conductivity, and longitudinal dispersivity. Because JP-4 is less dense than water and floats on top of the water table, reaeration by oxygen transfer from the vadose zone may be potentially significant to natural attenuation of JP - 4 (38:4). Rifai also found these parameters to be significant contributors to biodegradation. Therefore, a reaeration parameter will be introduced as well as a rate of decay term to simulate anaerobic biodegradation.



Cell Size
50 ft x 50 ft

Grid Size
550 ft x 1000 ft

Explanation

-  - Contaminant Source
-  - Observation Wells
-  - Constant head node
-  - No-flow boundaries

Figure 6. Simulated Site and Observation Wells

Table 4. Input data for initial computer simulation

Simulation time	50 years
Grid Size	11 X 20
Cell Size	50 ft X 50 ft
Porosity	.3
Longitudinal Dispersivity	10 ft
Transverse Dispersivity	3 ft
Txx	.0025 ft²/s
Tyy	.0025 ft²/s
Aquifer Thickness	25 ft
Hydraulic Gradient	4.29E-3 ft/ft
Injection Well at Cell	x = 6, y = 6
Injection Rate	0.0002 cfs
Conc. of Contaminant in injected water	150 mg/l
Conc. of Oxygen in Injected Water	0.0 mg/l
Conc. of Natural Recharge of Oxygen	8.0 mg/l

Porosity

Typical values for porosity were listed in chapter two. Porosity values will be varied from .1 to .6. The variation in the distance a contaminant plume travels over this range of porosities will be shown. Since velocity is inversely proportional to porosity, it is expected that the distance a plume travels in a given time period will be significantly affected.

Hydraulic Conductivity

Some values for hydraulic conductivity were also given in chapter two. There are some model limitations which prevent examining the full range of hydraulic conductivities presented in chapter two; however, a trend should be evident from the examined range from which general guidelines can be formulated. Because there is no direct input parameter in the model for hydraulic conductivity, the transmissivity and aquifer thickness will be varied to vary the hydraulic conductivity from 10^{-3} to 10^{-6} ft/sec. Hydraulic conductivity is related to transmissivity and thickness by the following relationship:

$$K = \frac{T}{b}$$

where

K - hydraulic conductivity (ft/sec)
T - transmissivity (ft²/sec)
b - aquifer thickness (ft)

The distance the contaminant plume travels will be plotted over this range of values. Rifai's analysis showed hydraulic conductivity to have a significant effect on biodegradation and from the above relationship it is, likewise, expected to affect plume transport.

Dispersivity

Values for longitudinal dispersivity will be varied from 1 ft to 10 ft and the relationship to plume travel plotted. Because longitudinal dispersion spreads the contaminant in the direction of groundwater flow, it is expected that longitudinal dispersivity will have an effect on the distance the plume travels in 50 years.

Reaeration

The reaeration coefficient will be varied over the same range which Rifai used, 0.001 per day to 0.005 per day. A plot will present the results. From Rifai's sensitivity analysis, it is expected that the reaeration coefficient will have a significant effect on the distance a contaminant plume travels.

Anaerobic Degradation

Anaerobic degradation will be evaluated by varying the rate of decay from 0.002 per day to .01 per day. According to Rifai, anaerobic degradation can be expected to have a significant effect on the contaminant plume.

Results from the simulations will be compiled and presented in graphical format showing the effect of varying different parameters on maximum concentration and plume travel. The output data from the model should show how the value of various parameters affect the movement of the contaminant plume, contaminant levels along the plume, and the time and distance that it takes the contaminant to degrade to acceptable limits. These relationships will be illustrated by plotting them on a graph which will show how changes in the value of a parameter affect these plume characteristics.

Part II

The site and site conditions to be simulated in the second part of the study were the same as the base conditions for Part I.

The reaeration coefficient was varied over a range from $.001 \text{ day}^{-1}$ to $.005 \text{ day}^{-1}$ and the coefficient of anaerobic decay varied from $.002 \text{ day}^{-1}$ to $.01 \text{ day}^{-1}$.

For the first set of data, the hydraulic conductivity was held constant at 10^{-4} ft/sec as the values for reaeration and anaerobic decay were varied over their respective ranges. This approach produced 25 sets of data input for the model for each value of hydraulic conductivity. This procedure was repeated for hydraulic conductivity values of 10^{-5} ft/sec , 10^{-6} ft/sec , and finally, for 10^{-3} ft/sec for a total of 100 data sets. Computer simulations for hydraulic conductivity of 10^{-3} were rather time consuming and values greater than 10^{-3} ft/sec would have been infeasible to investigate in this study. A regression analysis was performed on this data to generate a mathematical relationship between these parameters.

Summary

The research design and analysis methodology that were used in this research project were designed to examine several of the parameters involved in the natural attenuation of JP-4 in the saturated zone. The effects that the three parameters: hydraulic conductivity, reaeration, and anaerobic biodegradation have on the natural attenuation of JP-4 were further studied to estimate how these three parameters in conjunction with one another affect natural attenuation.

IV. Data Presentation and Discussion

Introduction

The analysis of the results from this research are presented in the order outlined in chapter three. Part one, a sensitivity analysis of the parameters porosity, hydraulic conductivity, longitudinal dispersivity, reaeration, and anaerobic biodegradation will be presented followed by a discussion of part two, the sensitivity and regression analysis of hydraulic conductivity, reaeration, and anaerobic biodegradation varying in concert.

Part I - Sensitivity Analysis

Porosity

In order to investigate the effect porosity has on natural attenuation, the values were varied as described in chapter three while holding all other baseline parameters constant. Porosity was varied from .1 to .6, covering the full range of porosities presented in chapter two. The results are presented in Table 5 and Figure 7. Rifai concluded from her sensitivity analysis that porosity did not have a significant impact on biodegradation; however, these results indicate that porosity does have a significant impact on the distance which a contaminant plume is expected to travel and an unpredictable effect on maximum concentration levels. Combining the results of the two analyses, one may be able to predict that increasing porosity decreases the distance the plume will migrate in a given time period, but porosity does not have a predictable effect on biodegradation.

Table 5. Data for varying porosity

Porosity .1				
Well #	Hydrocarbon time to reach well (years)	Oxygen	Max Conc. mg/liter	Distance Feet
Source	0	0	53	0
1	1.633	1.02	46.2	250
2	2.449	1.429	43.2	300
3	3.061	2.041	40.2	350
4	3.878	2.653	37.9	400
5	4.694	3.469	35.8	450
Porosity .2				
Source	0	0	55	0
1	3.252	2.033	46	250
2	4.878	2.846	42.7	300
3	6.098	4.065	40	350
4	7.724	5.285	37.7	400
5	9.35	6.911	35.7	450
Porosity .3				
Source	0	0	53	0
1	4.878	3.049	46	250
2	7.317	4.268	42.7	300
3	9.146	6.098	40	350
4	11.585	7.927	37.7	400
5	14.024	10.366	35.7	450
Porosity .4				
Source	0	0	56	0
1	6.452	4.032	45.8	250
2	9.677	5.645	42.9	300
3	12.903	8.065	40.5	350
4	15.323	10.484	38.2	400
5	18.548	13.71	35.8	450
Porosity .5				
Source	0	0	61	0
1	8.163	5.102	45.9	250
2	12.245	7.143	43	300
3	15.306	10.204	40.1	350
4	19.388	13.265	37.8	400
5	23.469	17.347	35.7	450
Porosity .6				
Source	0	0	55	0
1	9.756	6.098	45.5	250
2	14.634	8.537	42.7	300
3	18.293	12.195	39.8	350
4	23.171	15.854	37.4	400
5	28.049	23.171	34.6	450

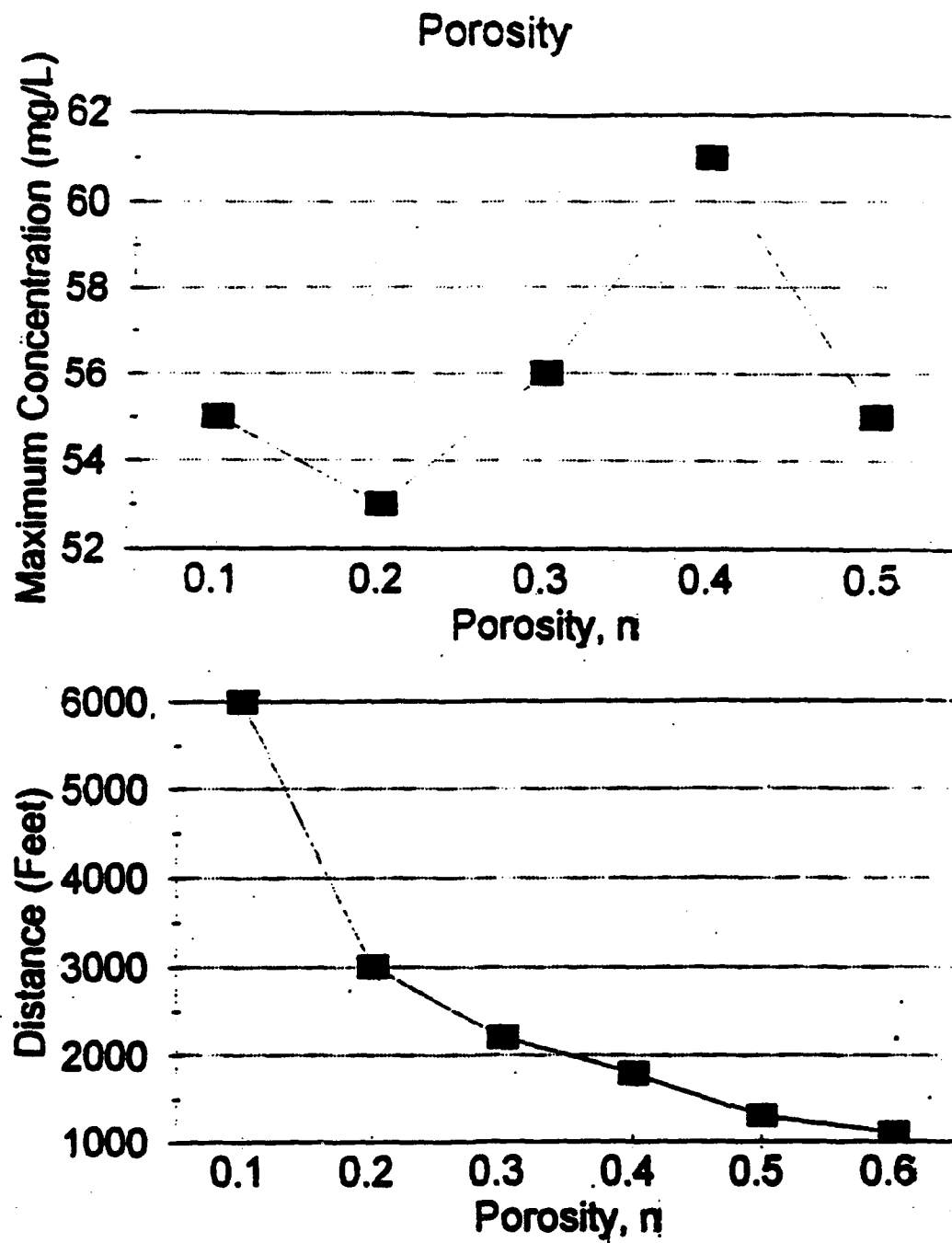


Figure 7. Changes in maximum concentration and distance with changes in porosity

Hydraulic Conductivity

Hydraulic Conductivity was varied from 10^{-6} to 10^{-3} ft/sec. The results are presented in Table 6 and Figure 8 and Figure 9. Hydraulic Conductivity had the most significant effect of any parameter on the behavior of the contaminant plume. Both maximum contaminant concentrations and plume migration distance were significantly affected over the range of hydraulic conductivity values. Because of the significant impact this parameter has on plume behavior, it was chosen as one of the three parameters to be investigated in Part II of this study. The results of the sensitivity analysis show that the larger the value of the hydraulic conductivity at a site, the less favorable conditions are for natural attenuation.

Longitudinal Dispersivity

Longitudinal Dispersivity was varied from 1 ft. to 10 ft. The results are presented in Table 7 and Figure 10. Longitudinal Dispersivity in this range had negligible effect on the distance a contaminant plume is expected to migrate. There was a slight effect on the maximum contaminant concentration. From both the percent mass biodegraded in Rifai's sensitivity analysis and the distance which a contaminant plume is expected to migrate, it can be concluded that longitudinal dispersivity does not have a significant impact on natural attenuation of JP-4 in the saturated zone.

Reaeration

The reaeration coefficient was varied from $.001 \text{ day}^{-1}$ to $.005 \text{ day}^{-1}$. The results are presented in Table 8 and Figure 11. It is evident from the results that reaeration has a significant effect on both the distance which a contaminant plume is expected to migrate and on the maximum contaminant concentration in the plume. Rifai also concluded that

Table 6. Data for varying hydraulic conductivity

Hydraulic Conductivity 10E-06				
Well #	Hydrocarbon	Oxygen	Max Conc	Distance
	time to reach well (years)		mg/liter	feet
Source	0	0	131	0
1	>50	>50	0	250
2				300
3				350
4				400
5				450
Hydraulic Conductivity 10E-05				
Source	0	0	150	0
1	27.273	11.364	90.6	250
2	43.182	25	6.6	300
3	>50	40.909	0	350
4		>50		400
5				450
Hydraulic Conductivity 10E-04				
Source	0	0	53	0
1	4.878	3.049	46	250
2	7.317	4.268	42.7	300
3	9.146	6.098	40	350
4	11.585	7.927	37.7	400
5	14.024	10.366	35.7	450
Hydraulic Conductivity 10E-03				
Source	0	0	9	0
1	31.579	21.053	0.7	5000
2	44.737	31.579	0.2	7000
3	>50	42.105	0	9000
4		50		11000
5		>50		13000

Hydraulic Conductivity

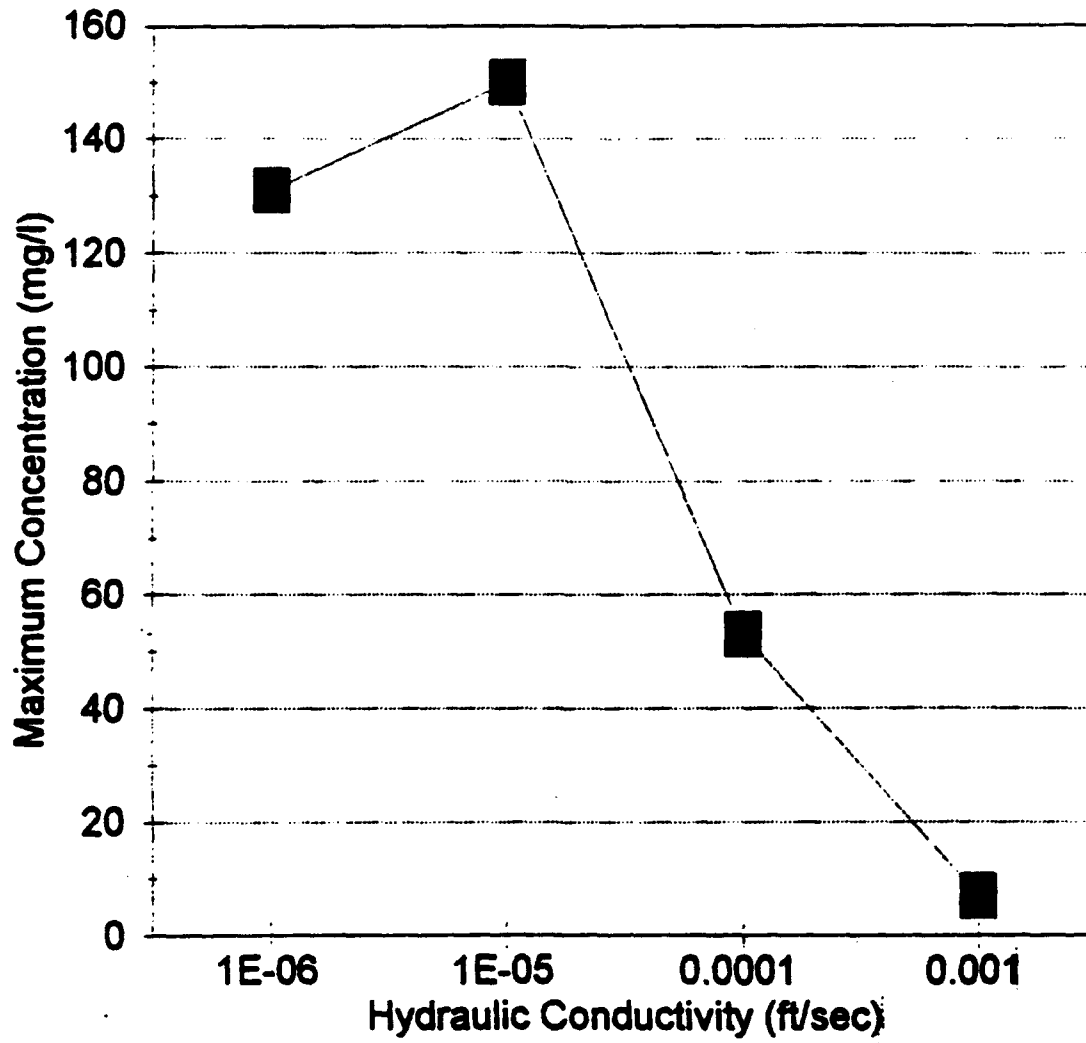


Figure 8. Changes in maximum concentration with changes in hydraulic conductivity

Hydraulic Conductivity

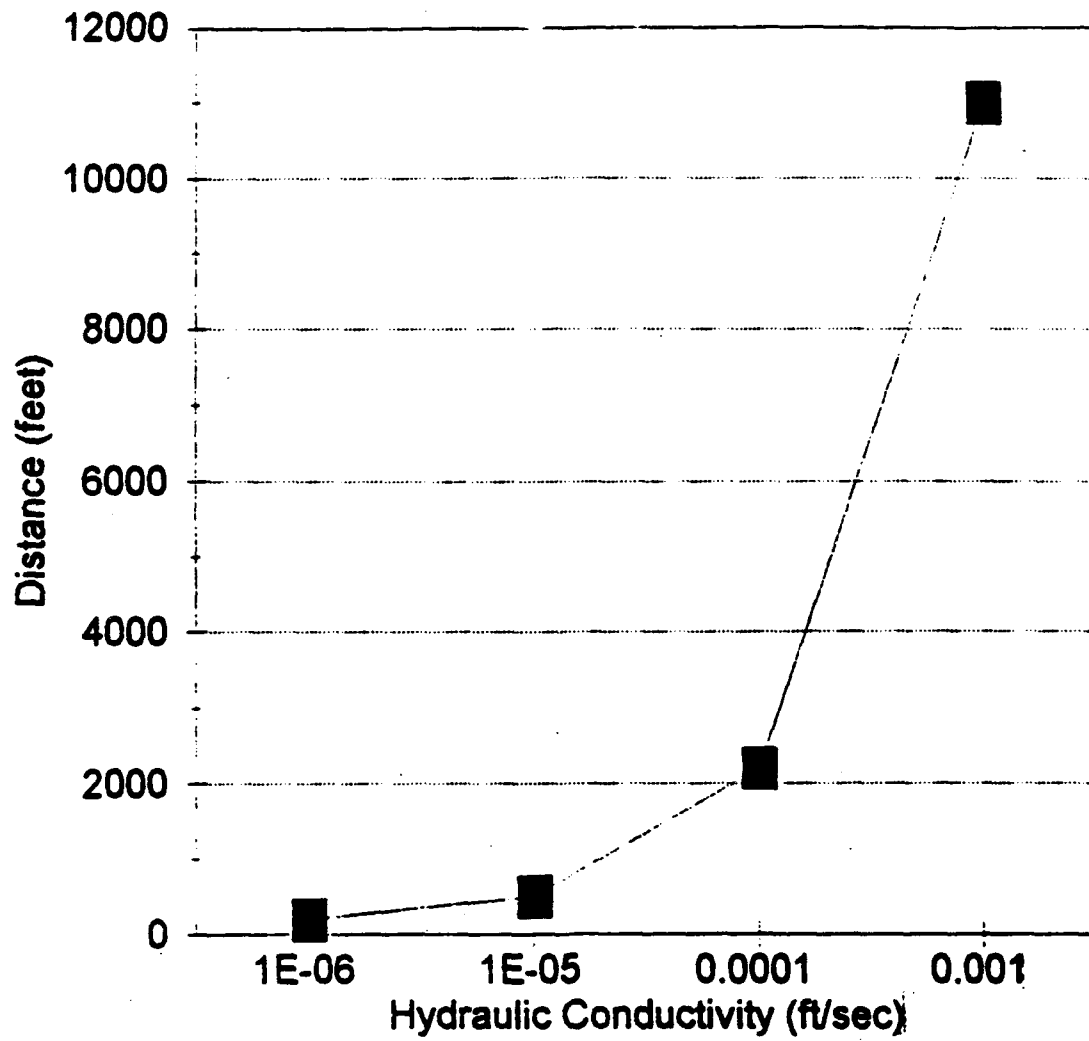


Figure 9. Changes in distance with changes in hydraulic conductivity

Table 7 Data for varying longitudinal dispersivity

Logitudinal Dispersivity 1				
Well #	Hydrocarbon	Oxygen	Max Conc.	Distance
	time to reach well (years)		mg/liter	Feet
Source	0	0	57	0
1	6.093	4.268	56.4	250
2	9.146	6.098	58.7	300
3	10.976	8.537	58.4	350
4	13.415	10.976	57.8	400
5	15.854	13.415	56.7	450
Logitudinal Dispersivity 2				
Source	0	0	56	0
1	6.098	3.659	56.9	250
2	7.927	6.098	56.5	300
3	10.366	7.927	55.2	350
4	12.805	10.366	54.2	400
5	15.854	12.805	53.2	450
Logitudinal Dispersivity 3				
Source	0	0	56	0
1	5.488	3.659	55.2	250
2	7.927	5.488	54.3	300
3	10.366	7.927	52.3	350
4	12.805	9.756	51.3	400
5	15.244	12.195	50	450
Logitudinal Dispersivity 4				
Source	0	0	56	0
1	5.488	3.659	53.6	250
2	7.927	5.488	52.3	300
3	10.366	7.927	49.8	350
4	12.805	9.756	48.6	400
5	15.244	12.195	47.1	450
Logitudinal Dispersivity 5				
Source	0	0	55	0
1	5.488	3.049	52	250
2	7.317	4.878	50.4	300
3	9.756	7.317	47.8	350
4	12.195	9.146	46.2	400
5	14.634	11.585	44.6	450

Table 7 (cont.) Data for varying longitudinal dispersivity

Logitudinal Dispersivity 6				
Source	0	0	55	0
1	4.878	3.049	50.6	250
2	7.317	4.878	48.6	300
3	9.756	6.707	45.9	350
4	12.195	9.146	44	400
5	14.634	10.976	42.6	450
Logitudinal Dispersivity 7				
Source	0	0	54	0
1	4.878	3.049	49.4	250
2	7.317	4.878	46.5	300
3	9.756	6.707	44.3	350
4	12.195	8.537	42.2	400
5	14.024	10.976	40.5	450
Logitudinal Dispersivity 8				
Source	0	0	54	0
1	4.878	3.049	48.2	250
2	7.317	4.878	45.4	300
3	9.146	6.707	42.8	350
4	12.195	8.537	40.6	400
5	14.024	10.366	38.9	450
Logitudinal Dispersivity 9				
Source	0	0	53	0
1	4.878	3.049	47.1	250
2	7.317	4.268	44	300
3	9.146	6.098	41.4	350
4	12.195	8.537	39.1	400
5	14.024	10.366	37.2	450
Logitudinal Dispersivity 10				
Source	0	0	53	0
1	4.878	3.049	46	250
2	7.317	4.268	42.7	300
3	9.146	6.098	40	350
4	11.585	7.927	37.7	400
5	14.024	10.366	35.7	450

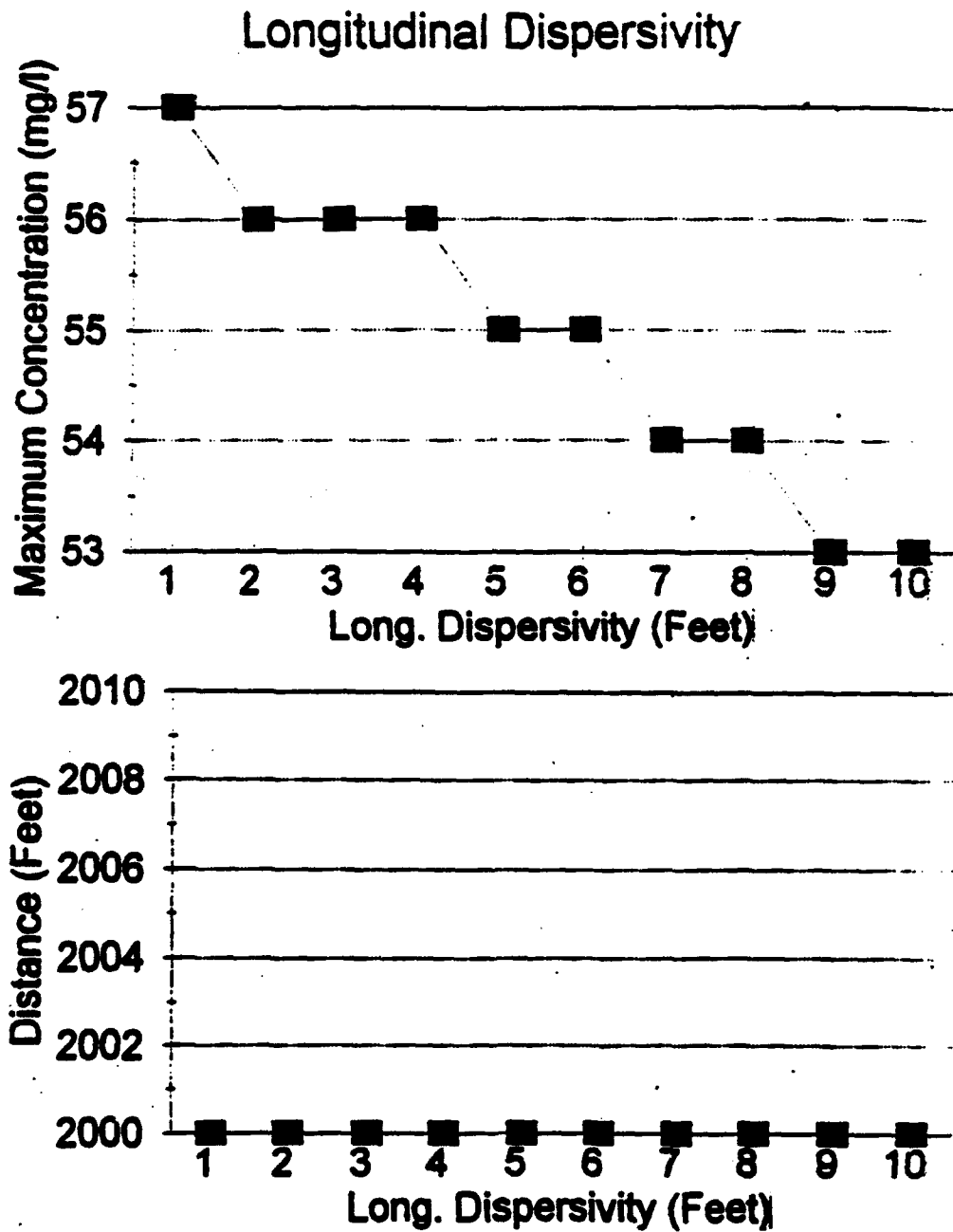


Figure 10. Changes in maximum concentration and distance with changes in longitudinal dispersivity

Table 8. Data for varying reaeration coefficient

Reaeration Coefficient .001				
Well #	Hydrocarbon time to reach well (years)	Oxygen	Max Conc. mg/liter	Distance feet
Source	0	0	43	0
1	5.488	3.049	13	250
2	7.927	4.268	7.6	300
3	11.585	6.707	4.3	350
4	17.073	8.537	2.4	400
5	28.659	10.976	1.3	450
Reaeration Coefficient .002				
Source	0	0	39	0
1	6.098	3.049	4.2	250
2	26.829	4.878	1.5	300
3	>50	6.707	0.3	350
4		9.146	0	400
5		10.976	0	450
Reaeration Coefficient .003				
Source	0	0	35	0
1	26.829	3.049	1.4	250
2	>50	4.878	0.1	300
3		7.317	0	350
4		9.146	0	400
5		11.585	0	450
Reaeration Coefficient .004				
Source	0	0	33	0
1	28.659	3.049	0.4	250
2	>50	4.878	0	300
3		7.317	0	350
4		9.146	0	400
5		11.585	0	450
Reaeration Coefficient .005				
Source	0	0	31	0
1	>50	3.049	0	250
2		4.878	0	300
3		7.317	0	350
4		9.146	0	400
5		11.535	0	450

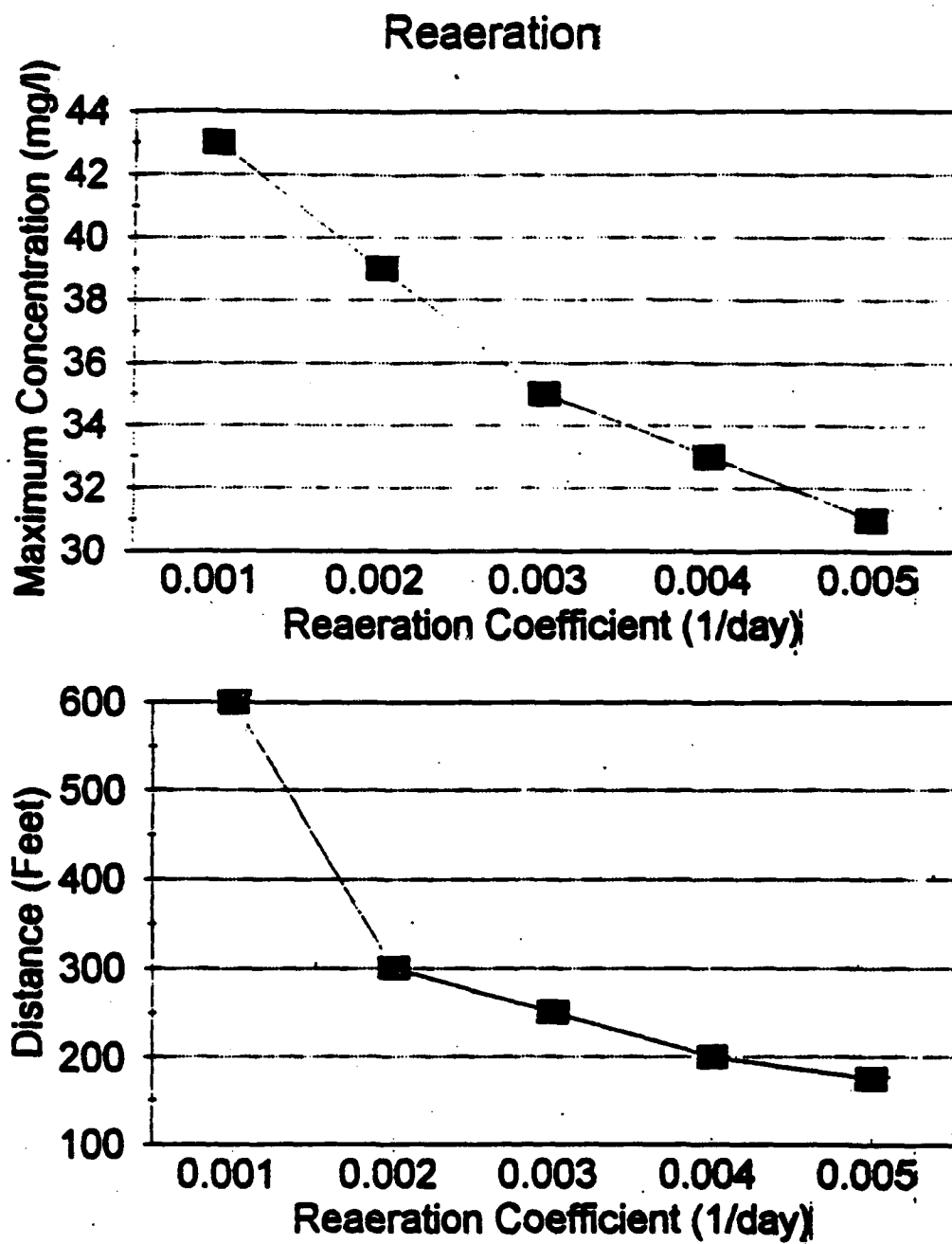


Figure 11. Changes in maximum concentration and distance with changes in reaeration coefficient

reaeration had a significant effect on biodegradation of a contaminant plume. Because reaeration appears to be a significant contributor to the natural attenuation process, it was included as a parameter of interest in Part II of this study. Results from these analyses indicate that increasing reaeration is important to natural attenuation and the higher the coefficient of reaeration the more likely it is that natural attenuation will be a candidate for a remediation of the site.

Anaerobic Biodegradation

Values for the coefficient of anaerobic biodegradation were varied from $.002 \text{ day}^{-1}$ to $.01 \text{ day}^{-1}$. The results are presented in Table 9 and Figure 12. It was anticipated that anaerobic biodegradation would have a similar effect as reaeration because both are handled by the model in a similar manner. This was indeed the case; however, anaerobic biodegradation appears to have a slightly more significant effect than reaeration. This result is probably due to the fact that the contaminant concentration near the source or near the center of the plume increases as the oxygen at the center of the plume is being depleted by the aerobic biodegradation process. Once all oxygen is completely gone and anaerobic microbes become acclimated, anaerobic biodegradation progresses faster than aerobic biodegradation. As was noted in chapter two, however, anaerobic biodegradation is less certain and the anaerobic microbes take time to acclimate. The model does not account for the acclimation period.

Wilson has measured anaerobic biodegradation rates of $.002 \text{ day}^{-1}$ for certain chemicals at one site (37:8). The model indicates that even rates this low may have

Table 9. Data for varying coefficient of anaerobic biodegradation

Anaerobic Coefficient .002				
Well #	Hydrocarbon	Oxygen	Max Conc.	Distance
	time to reach well (years)		mg/liter	Feet
Source	0	0	39	0
1	6.098	3.049	4.2	250
2	26.829	4.858	1.5	300
3	31.707	7.317	0.3	350
4	>50	9.146	0	400
5		10.976	0	450
Anaerobic Coefficient .004				
Source	0	0	33	0
1	28.659	3.049	0.4	250
2	>50	4.878	0	300
3		7.317	0	350
4		9.146	0	400
5		11.585	0	450
Anaerobic Coefficient .006				
Source	0	0	30	0
1	>50	3.049	0	250
2		5.488	0	300
3		7.927	0	350
4		9.756	0	400
5		12.195	0	450
Anaerobic Coefficient .008				
Source	0	0	28	0
1	>50	3.049	0	250
2		5.488	0	300
3		7.927	0	350
4		9.756	0	400
5		12.195	0	450
Anaerobic Coefficient .01				
Source	0	0	27	0
1	>50	3.049	0	250
2		5.488	0	300
3		7.927	0	350
4		9.756	0	400
5		12.195	0	450

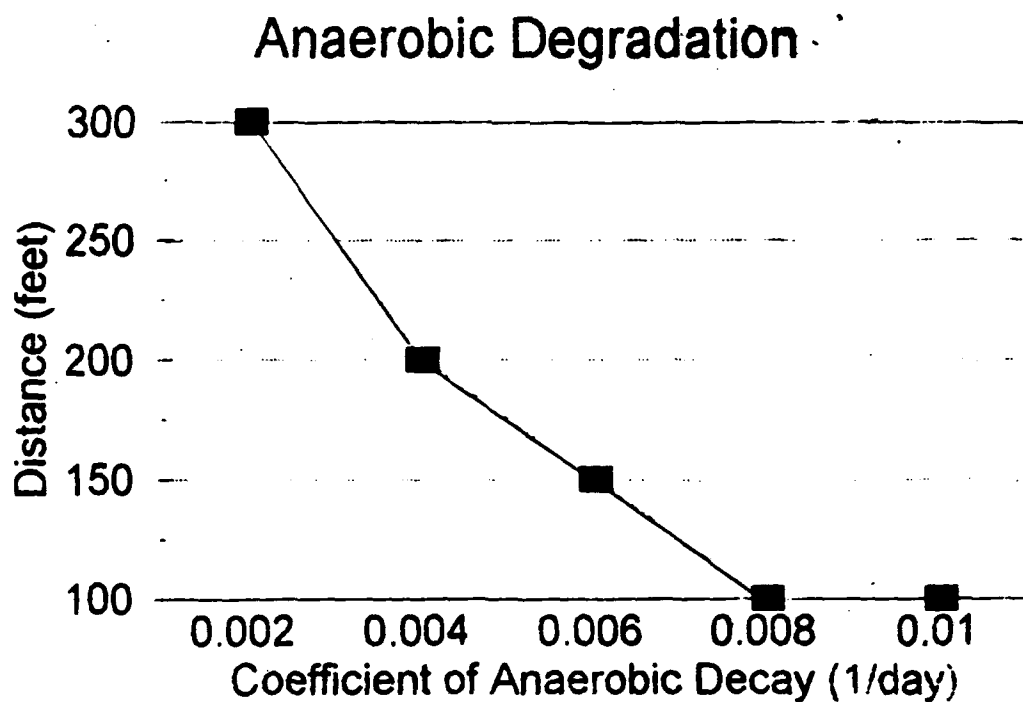
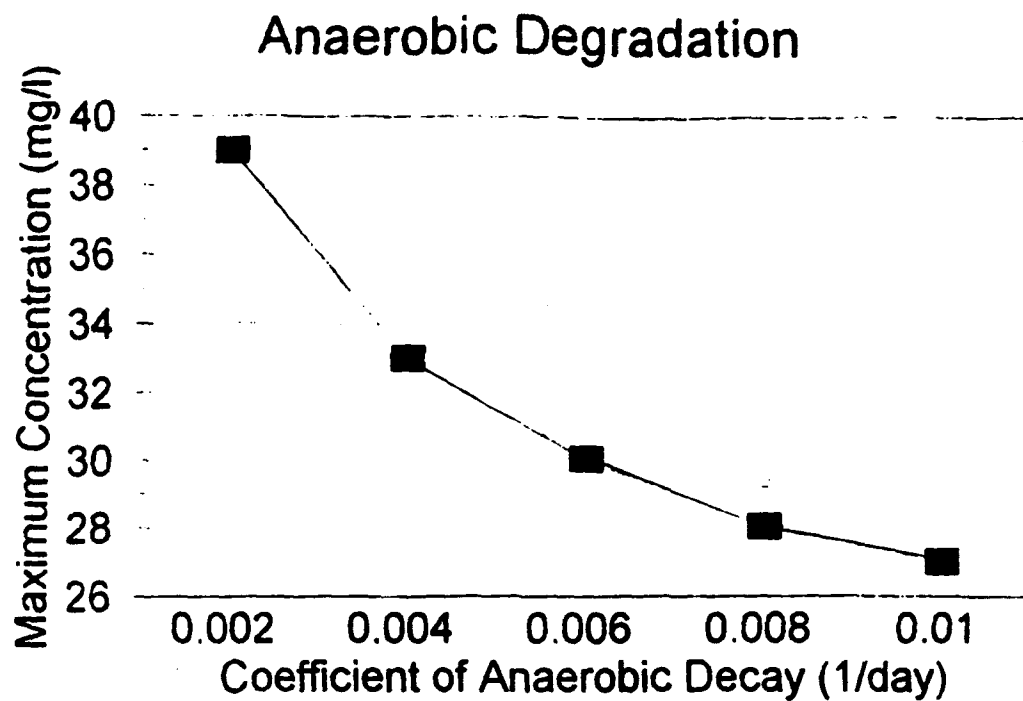


Figure 12. Changes in maximum concentration and distance with changes in coefficient of anaerobic biodegradation

significant impact on natural attenuation. If anaerobic degradation can be verified at a site, it can be concluded that it has a significant effect on natural attenuation.

Part II

The three parameters chosen for investigation were hydraulic conductivity, coefficient of reaeration, and anaerobic degradation. These three parameters were chosen because they were identified in both Rifai's sensitivity analysis and the Part I sensitivity analysis as having a significant impact on contaminant plume behavior.

The Part II study was conducted to derive a general relationship between these parameters as they relate to natural attenuation. The results from 100 computer simulations are shown in tables 10 - 13. The tables show the value for each parameter, the distance which a contaminant plume is expected to migrate in 50 years and the maximum concentration at the source for the various combinations of parameter values. As can be seen, hydraulic conductivity was the dominant parameter. Neither distance nor maximum contaminant concentrations were significantly affected by variations in the coefficient of reaeration and anaerobic decay for a given hydraulic conductivity. For a hydraulic conductivity value of 10^{-3} ft/sec, expected migration distance of the contaminant plume begins to be affected when the other two parameters are varied.

Table 10: Computer Simulations for Hydraulic Conductivity of 10^{-6} ft/sec

RC	ADC	MAX CONC	DISTANCE
.001	.002	3	150 - 200
.001	.004	3	150 - 200
.001	.006	3	150 - 200
.001	.008	3	150 - 200
.001	.010	3	250
.002	.002	3	150
.002	.004	3	150
.002	.006	3	150
.002	.008	3	150
.002	.010	3	150
.003	.002	3	150
.003	.004	3	150
.003	.006	3	150
.003	.008	3	150
.003	.010	3	150
.004	.002	3	150
.004	.004	3	150
.004	.006	3	150
.004	.008	3	150
.004	.010	3	150
.005	.002	3	150
.005	.004	3	150
.005	.006	3	150
.005	.008	3	150
.005	.010	3	150

Table 11: Computer Simulations for Hydraulic Conductivity of 10^{-5} ft/sec

RC	ADC	MAX CONC	DISTANCE
.001	.002	20	250
.001	.004	19	250
.001	.006	19	250
.001	.008	19	250
.001	.010	19	250
.002	.002	19	250
.002	.004	19	250
.002	.006	19	250
.002	.008	19	250
.002	.010	19	250
.003	.002	19	250
.003	.004	19	250
.003	.006	19	250
.003	.008	19	250
.003	.010	19	250
.004	.002	19	250
.004	.004	19	250
.004	.006	19	250
.004	.008	19	250
.004	.010	19	250
.005	.002	19	250
.005	.004	19	250
.005	.006	19	250
.005	.008	19	250
.005	.010	19	250

Table 12. Computer Simulations for Hydraulic Conductivity of 10^{-4} ft/sec

RC	ADC	MAX CONC	DISTANCE
.001	.002	35	1800
.001	.004	31	2000
.001	.006	29	2000
.001	.008	27	2000
.001	.010	26	2000
.002	.002	33	2000
.002	.004	30	2000
.002	.006	28	2000
.002	.008	27	2000
.002	.010	26	2000
.003	.002	31	2000
.003	.004	29	2000
.003	.006	27	2000
.003	.008	26	2000
.003	.010	25	2000
.004	.002	30	2000
.004	.004	28	2000
.004	.006	27	2000
.004	.008	26	2000
.004	.010	25	2000
.005	.002	29	2000
.005	.004	27	2000
.005	.006	26	2000
.005	.008	25	2000
.005	.010	25	2000

Table 13: Computer Simulations for Hydraulic Conductivity of 10^{-3} ft/sec

RC	ADC	MAX CONC	DISTANCE
.001	.002	5	3500
.001	.004	5	3000
.001	.006	4	3000
.001	.008	4	2500
.001	.010	4	2500
.002	.002	5	3500
.002	.004	5	3000
.002	.006	4	2500
.002	.008	4	2500
.002	.010	4	2500
.003	.002	5	3000
.003	.004	5	3000
.003	.006	4	2500
.003	.008	4	2500
.003	.010	4	2500
.004	.002	5	3000
.004	.004	5	2500
.004	.006	4	2500
.004	.008	4	2500
.004	.010	4	2500
.005	.002	5	3000
.005	.004	5	2500
.005	.006	4	2500
.005	.008	4	2500
.005	.010	4	2500

Regression

To derive the relationship between these parameters, as they relate to the natural attenuation process of JP-4 in the saturated zone, a regression analysis was performed on the data from these computer simulations. The regression analysis suggested the following mathematical relationships:

$$S = 880.2644 + 2133161.421(HC) - 21750 (RC) - 20750 (ADC)$$

$$C = 18.6688 - 10994.81377 (HC) + 210 (RC) - 232.5 (ADC)$$

where

- S - Distance, in feet, which the plume is expected to travel in 50 years
- C - Maximum average concentration, in mg/liter, in the cell in which the injection well is located
- HC - Hydraulic Conductivity (ft/sec)
- RC - Reaeration Coefficient (day⁻¹)
- ADC - Anaerobic Decay Coefficient (day⁻¹)

It is evident from the parameter coefficients in these equations how significant hydraulic conductivity is to plume behavior. Statistical results indicate that the distance equation is more useful than the concentration equation. The R² value for the distance equation was .6448 and the R² value for the concentration equation was .1981. The R² measures the goodness of fit of a regression model. It measures the proportion of variance of the regression analysis.

The field engineer may be able to use these relationships to gain a precursory idea whether or not natural attenuation should be considered as a remediation option. If the distance to an exposure point is known, the distance equation can be used to estimate how far

the plume is expected to travel in 50 years. If the calculated distance is much less than the distance to the exposure point, natural attenuation may suffice and more costly remediation technologies may not need to be implemented. The concentration equation can be used by calculating the concentration at the source. If the calculated concentration is much less than regulatory limits, further remediation may not be necessary.

Some General Observations

The BIOPLUME IITM model exhibited some unusual characteristics. These characteristics may have been due to simplifications made in this study or may be inherent to the model. The model seemed to generate a "pulsing" contaminant plume when a reaeration coefficient or coefficient of anaerobic decay are introduced.

An article by David L. Freyburg in a 1988 issue of Groundwater magazine suggests that calibration of a model does not necessarily lead to accurate predictions. Also, a model is only as good as the data you put into it. In light of these cautions, it would be unwise to extend the results of this study alone to a site and decide to implement natural attenuation based on these findings. Hopefully, these results have provided some general guidelines which can be followed in choosing a remediation alternative.

V. Conclusions and Recommendations

Introduction

In reviewing the literature and previous studies of natural attenuation mechanisms, it was evident that the study of natural attenuation is new and not yet well understood. There is extensive ongoing research to gain a better understanding of the mechanisms and the parameters involved in the natural attenuation process. As evidenced in this study, the number of mechanisms and parameters are numerous indeed. Coupled with the number of mechanisms and parameters are the differing site conditions and numerous chemicals of concern.

Natural Attenuation of JP-4 in the Saturated Zone

It is well recognized that certain chemical contaminants, including JP-4, are naturally attenuated under certain conditions. Many models have been developed to simulate the fate and transport of these chemicals in different media. Unfortunately, no model includes every parameter and condition and is, therefore, unable to predict exactly what will happen to a certain chemical under certain conditions. The BIOPLUME II™ model was developed to predict the fate and transport of hydrocarbons in the saturated zone. Results from this study indicate that JP-4 is naturally attenuated in the saturated zone and certain conditions are favorable to the process. It was found that decreasing hydraulic conductivity, increasing reaeration rate and increasing anaerobic biodegradation all favor natural attenuation. A general mathematical relationship was suggested which should give the field engineer a precursory idea whether natural attenuation will be effective in reducing contaminant

concentration and plume travel at the site. At a site where these mechanisms can be verified, it may be sufficient to rely on natural attenuation to restore a site.

Although results from the model simulations indicate that natural attenuation is enhanced by large values of hydraulic conductivity, reaeration, and anaerobic biodegradation rates, it would be erroneous to state that under these circumstances, natural attenuation should be assumed to be applicable to reduce risk at a site. There are too many assumptions built into the model, too many simplifications made, and too many parameters excluded to conclude that natural attenuation should be implemented at a site even though these three parameters indicate a favorable attenuation environment. All the factors discussed in chapter two must be considered before natural attenuation is implemented.

In many cases, natural attenuation may be sufficient as a remediation option and where it is sufficient it ought to be implemented. Natural attenuation can be an effective and cost efficient method for site restoration.

Recommendations for Further Research

The model used in this study includes numerous parameters that were not investigated during this study. Further investigation of the model and associated parameters may prove useful. The code for the model is available and it may be interesting to improve the model by adding other parameters not presently included.

Data is currently being gathered at three Air Force sites which would provide real data for the model. An investigation of the capabilities of the model could be examined using this data.

In light of the current budget situation, an investigation of the cost savings associated with natural attenuation may be useful for justifying use of this alternative.

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Appendix A
Glossary of Terms

Appendix A: Glossary of Terms

This glossary was taken from Mobility and Degradation of Organic Contaminants in Subsurface Environments by Warren J. Lyman and others.

Anaerobe: An organism that does not require air or free oxygen to maintain its life process.

Abiotic: Referring to the absence of living organisms.

Advection: The process of transfer of fluids (vapors or liquids) through a geologic formation in response to a pressure gradient which may be caused by changes in barometric pressure, water table levels, wind fluctuations, or rainfall percolation. Advection can result from a thermal gradient caused by a heat source. See Darcy's law.

Aliphatic: Of or pertaining to a broad category of carbon compounds distinguished only by a straight, or branched, open chain arrangement of the constituent carbon atoms. The carbon-carbon bonds may be saturated or unsaturated.

Anisotropy: The dependence of property upon direction of measurement (e.g., hydraulic conductivity, porosity, compressibility, dispersion, etc.).

Aromatic: Of or pertaining to organic compounds that resemble benzene in chemical behavior.

Bentonite: A colloidal clay, largely made up of the mineral sodium montmorillonite, a hydrated aluminum silicate.

Brownian Movement: Random movement of molecules or colloids suspended in a fluid.

Biodegradation: A process by which microbial organisms transform or alter through enzymatic action the structure of chemicals introduced into the environment.

Biomass: The amount of living matter in a given area or volume.

Biota: A term that encompasses the spectrum of living things within a given area.

Biotic: Of or pertaining to life and living organisms. Induced by the actions of living organisms.

Caliche: A layer of calcium and magnesium carbonate deposited in a near-surface soil horizon by evaporating soil water or groundwater. It may occur as a soft thin soil horizon, as a hard thick bed just below the land surface, or as a surface layer exposed by erosion.

Capillarity: The pressure difference across the interface of two immiscible liquids or between a liquid and a solid. In a porous medium, capillarity is zero in the saturated zone and less than zero in the vadose zone. See surface tension, saturated zone, vadose zone.

Capillary Fringe: The zone of a porous medium above the water table within which the porous medium is saturated but is at less than atmospheric pressure. The capillary fringe is considered to be part of the vadose zone, but not of the unsaturated zone.

Catalyst: A substance that alters the rate of a chemical reaction and may be recovered, essentially unaltered, in form and amount at the end of the reaction.

Chemisorption: A process in which weak chemical bonds are formed between gas or liquid molecules and a solid surface.

Clay: A mineralogical term describing a family of aluminosilicate minerals formed by the decomposition of primary minerals (e.g., mica and feldspars) and re-composed into clay minerals. A textural term referring to particles < 2 micrometers in diameter.

Coalescence: The bonding of welded materials into one body, or the uniting by growth in one body as particles, gas or liquid.

Colloid: Particles having dimensions of 10-10,000 angstroms (1-1000 nanometers) and which are dispersed in a different phase, such as a fluid or liquid.

Complex: A combination of two or more atoms into a molecular species, usually charged, and existing in water or some other fluid.

Compressibility: The change in volume of a porous medium in response to an applied stress which is counterbalanced by the incompressibility of the saturating fluid and the granular skeleton of the porous medium which it saturates. Compressibility has units of inverse force (Pa⁻¹).

Constituents: An essential part or component of a system or group: examples are an ingredient of a chemical system, or a component of an alloy.

Containment: The prevention of the spreading of oil or other hazardous materials by the placing of booms or physical barriers and the use of absorbents, gelling, or herding agents or other materials to restrain, entrap, and collect a spill.

Corrective Action: The removal of chemicals and/or contaminated soils, objects and groundwater, from a site, or other clean-up activities designed to restore the local environment to acceptable conditions. Corrective actions may include, for example, vacuum extraction of the vadose zone, soil washing, and the extraction and treatment of contaminated groundwater.

Cytoplasm: The protoplasm of an animal or plant cell external to the nucleus.

Darcy's Law: An empirical relationship between hydraulic gradient and the viscous flow of water in the saturated zone of a porous medium under conditions of laminar flow. The flux of vapors through the voids of the vadose zone can be related to pressure gradient through the air permeability by Darcy's law. See hydraulic conductivity, air permeability, hydraulic gradient, pressure gradient, laminar flow, vadose zone, saturated zone.

Dehydrogenation: Removal of hydrogen from a compound.

Density: The amount of mass of a substance per unit volume of the substance (g/cm^3).

Desorption: The process of removing a sorbed substance by the reverse of adsorption or absorption.

Diffusion: The process whereby the molecules of a compound in a single phase equilibrate to a zero concentration gradient by random molecular motion. The flux of molecules is from regions of high concentration to low concentration and is governed by Fick's Second Law. See Fick's Second Law, effective diffusion coefficient.

Dispersion: The process by which a substance or chemical spreads and dilutes in flowing groundwater or soil gas. On a microscale, dispersion is due to mixing within individual pores, mixing between pore channels, and mixing due to molecular diffusion. At larger scales, geologic heterogeneity and anisotropy cause dispersion. Dispersion has units of squared length per time (cm^2/sec).

Dissociation: Separation of a molecule into two or more fragments (atoms, ions, radicals) by collision with a second body or by the absorption of electromagnetic radiation.

Dissolution: Dissolving of a material in a liquid solvent (e.g., water).

Dynamic Viscosity: The measure of internal friction of a fluid that resists shear within the fluid; the constant of proportionality between a shear stress applied to liquid and the rate of angular deformation within the liquid, having units of mass per length per time (gm/cm/sec).

Effective Diffusion Coefficient: The constant of proportionality in Fick's Second Law which is dependent on tortuosity, porosity, and moisture content and properties of the diffusing compound, having units of squared length per time (cm^2/sec). See tortuosity, porosity, moisture content.

Emulsification: The process of dispersing one liquid in a second immiscible liquid.

Entrainment: A process in which solid particles or liquid droplets are, by force of friction with a passing fluid (e.g., air or water), lifted from a resting place and carried along with the flowing fluid.

Fick's Second Law: An equation relating the change of concentration with time due to diffusion to the change in concentration gradient with distance from the source of concentration. See diffusion, effective diffusion coefficient.

Field Capacity: The percentage of water remaining in the soil 2 or 3 days after gravity drainage has ceased from saturated conditions.

Fluid Conductivity: The constant of proportionality in Darcy's law relating the rate of flow of a fluid through a cross-section of porous medium in response to a hydraulic gradient. Fluid conductivity is a function of the intrinsic permeability of a porous medium and the kinematic viscosity of the fluid which flows through it. Fluid conductivity has units of length per time (cm/sec).

Flux: The rate of movement of mass through a unit cross-sectional area per unit time in response to a concentration gradient or some advective force, having units of mass per area per time ($\text{g}/\text{cm}^2 \cdot \text{sec}$).

Freundlich Isotherm: An expression relating the equilibrium between the sorbed chemical concentration and its aqueous phase concentration through a power law.

Fugacity: A function used as an analog of the partial pressure in applying thermodynamics to real systems; at a constant temperature, it is proportional to the exponential of the ratio of the chemical potential of constituent of a system divided by the product of the gas constant and the temperature, and it approaches the partial pressure as the total pressure of the gas approaches zero.

Fulvic Acid: A term of varied usage but usually referring to the mixture of organic substances remaining in solution upon acidification of a dilute alkali extract from the soil. Thus, fulvic acids are soluble under all pH conditions.

Funicular Zone: A narrow band above the groundwater table bounded above by the capillary rise in the slimmest continuous pores, and bounded below by the capillary rise in the widest pores.

Half-life: The time required for half of a substance to decay or alter by a process, (e.g., radioactive decay, biodegradation, volatilization, photolysis, hydrolysis, oxidation, etc.).

Henry's Law: The relationship between the partial pressure of a compound and the equilibrium concentration in the liquid through a constant of proportionality known as Henry's law constant. See partial pressure.

Heterogeneity: The dependence of property upon location of measurement (e.g., hydraulic conductivity, porosity, compressibility, dispersion, etc.). Heterogeneity may be due to grain size trends, stratigraphic contacts, faults, and vertical bedding.

Homogeneity: The independence of property with location of measurement (e.g., hydraulic conductivity, porosity, compressibility, dispersion, etc.).

Humic acid: That fraction of humic substances that is not soluble in water under acid conditions (below pH 2), but becomes soluble at greater pH.

Humic substances: A general category of naturally occurring, biogenic heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight, and refractory. Humic substances include humin, humic acids and fulvic acids.

Humin: That fraction of humic substances that is not soluble in water at any pH value.

Hydraulic Conductivity: The constant of proportionality in Darcy's law relating the rate of flow of water through a cross-section of porous medium in response to a hydraulic gradient. Also known as the coefficient of permeability, hydraulic conductivity is a function of the intrinsic permeability of a porous medium and the kinematic viscosity of the water which flows through it. Hydraulic conductivity has units of length per time (cm/sec).

Hydraulic Gradient: The change in piezometric head between two points divided by the horizontal distance between the two points, having dimensions of length per length (cm/cm). See piezometric head.

Hydraulic Head: A measure of mechanical energy per unit weight density of water as the sum of elevation head and pressure head, having units of length (cm).

Hydrocarbon: One of a very large group of chemical compounds composed only of carbon and hydrogen; the largest source of hydrocarbons is from petroleum crude oil.

Hydrolysis: Decomposition or alteration of a chemical substance by reaction with water.

Hydrophobic: Lacking an affinity for, repelling, or failure to absorb or dissolve in, water.

Hysteresis: The dependence of the state of a system on direction of the process leading to it; a non-unique response of a system to stress, responding differently when the stress is released. Compressibility, moisture content, soil adsorption and unsaturated hydraulic conductivity exhibit hysteretic behavior.

Illite: A group of 2:1, non-expanding, hydrous potassium-magnesium aluminosilicate clay minerals of intermediate properties between kaolinite and montmorillonite.

Immersion: Placement into or within a fluid, usually water.

Infiltration: The downward movement of water through a soil from rainfall or from the application of artificial recharge in response to gravity and capillarity.

Intrinsic Permeability: A measure of the ease with which a porous medium transmits a fluid which is independent of the properties of the fluid and which has units of squared length (cm²).

Isotropy: The independence of a property with direction of measurement (e.g., hydraulic conductivity, porosity, compressibility, dispersion, etc.).

Kaolinite: A 1:1, non-expanding, hydrous aluminosilicate clay mineral formed by the alteration of micas and feldspars.

Kinematic Viscosity: The ratio of the dynamic viscosity of a fluid to its density, having units of squared length per time (cm²/sec).

Locus (pl., Loci): In this report, the term locus is used to refer to one of 13 generic contaminated environments in the subsoil region. Each locus is defined by considering: (1) its position relative to the groundwater table (above, on, below); (2) the phase of the contaminant (liquid, vapor, aqueous solution, sorbed to soil); and (3) the nature of the local natural matter (unconsolidated sediments, fractured rock, flowing water).

Macropore: A large pore in a porous medium which may be formed by physical phenomena or biological activity, and through which water, or other fluids, flows solely under the influence of gravity, unaffected by capillarity.

Meniscus: The curved surface of a liquid between solid boundaries (e.g., capillary tube, mineral grains) which is caused by the surface tension of the liquid. The geometry of the meniscus is affected by the surface tension of the liquid, the difference in density between the liquid and overlying air, the distance between the solid boundaries, and the hydrophobic nature of the liquid.

Mica: A family of platy, igneous and metamorphic, aluminosilicate minerals which weather and form clays. Micas separate readily into thin sheets or flakes.

Microbe: A microorganism, especially a bacterium.

Microorganisms: Microscopic organisms including bacteria, protozoans, yeast, fungi, viruses and algae.

Mobilization: The process or processes by which a liquid contaminant in a locus is made more mobile in the locus or more transferable between loci.

Moisture Content: The amount of water lost from the soil upon drying to a constant weight, expressed as the weight per unit weight of dry soil or as the volume of water per unit bulk volume of the soil. For a fully saturated medium, moisture content equals the porosity; in the vadose zone, moisture content ranges between zero and the porosity value for the medium. See porosity, vadose zone, saturated zone.

Mole Fraction: The ratio of the number of moles of a substance in a mixture or solution to the total number of moles of all the components in the mixture or solution.

Monovalent: A radical or atom whose valency is 1.

Montmorillonite: A 2:1, expanding, hydrous magnesium aluminosilicate clay mineral exhibiting pronounced swelling-shrinkage behavior and high plasticity and cohesion.

Oxidation: A chemical reaction that increases the oxygen content of a compound, or raises the oxidation state of an element.

Oxidation Potential: The difference in potential between an atom or ion and the state in which an electron has been removed to an infinite distance from this atom or ion.

Partial Pressure: The portion of total vapor pressure in a system due to one or more constituents in the vapor mixture.

Percolation, Soil Water: The downward movement of water through soil. Especially, the downward flow of water in saturated or nearly saturated soil at hydraulic gradients of the order of 1.0 or less.

Phreatic Level: The groundwater level that would be seen in an observation well projecting down into an aquifer.

Polymerization: The bonding of two or more monomers to produce a polymer.

Porosity: The volume fraction of a rock or unconsolidated sediment not occupied by solid material but usually occupied by water and/or air. Porosity is a dimensionless quantity.

Redox: A chemical reaction in which an atom or molecule losses/gains electrons to/from another atom or molecule. Also called oxidation-reduction. Oxidation is the loss of electrons; reduction is the gain in electrons.

Reduction: A chemical reaction in which an atom of molecule gains electrons. Sometimes results by reaction of the substance with hydrogen.

Refractory: A nonspecific characteristic of some chemicals implying resistance to biodegradation or other degradation or treatment processes.

Residence Time: The average time that water remains in a porous medium or a particle remains in a reservoir. Residence time is calculated as the ratio of reservoir volume to total water inflow rate having units of time (sec).

Residual Saturation: The amount of water or oil remaining in the voids of a porous medium and held in an immobile state by capillarity and dead-end pores.

Salinity: The quantity of anions and cations in water, usually between 33 and 37 parts per thousand in sea water.

Sinter: A chemical sedimentary rock deposited by precipitation from mineral waters, especially siliceous sinter and calcareous sinter.

Slurry: A thick mixture of liquid, especially water, and any of several finely divided substances, such as cement or clay particles.

Solubility: The maximum amount of mass of a compound that will dissolve into a unit volume of solvent, usually water, having units of mass per volume (gm/cm³).

Sorption: A general term used to encompass the process of absorption, adsorption, ion exchange, and chemisorption.

Specific Gravity: The ratio of the weight of a given volume of the material at 4°C (or some stated temperature) to the weight of an equal volume of distilled water. Materials with specific gravity of less than 1 will float on water; materials with specific gravity over 1 will sink in water.

Surface Tension: A measure of the interfacial tension due to molecular attraction between two fluids in contact or between a liquid in contact with a solid, having units of mass per squared time (dyne/cm).

Surfactant: Also Surface Active Agent. A chemical material which provides a "linking action" between two materials, such as oil and water, which normally resist mixing or readily joining in solution. Surfactants provide the emulsification forces which allow oil and water to mix and remain in either oil-in-water or water-in-oil solutions.

Tortuosity: The ratio of path length through a porous medium to the straight-line flow path which describes the geometry of the porous medium. Tortuosity is a dimensionless parameter which ranges in value from 1 to 2.

Transpiration: The release of water withdrawn from the soil by plants during photosynthesis and other life processes.

Unsaturated Zone: The portion of a porous medium, usually above the water table in an unconfined aquifer, within which the moisture content is less than saturation and the capillary pressure is less than atmospheric pressure. The unsaturated zone does not include the capillary fringe.

Vadose Zone: The portion of a porous medium above the water table within which the capillary pressure is less than atmospheric and the moisture content is usually less than saturation. The vadose zone includes the capillary fringe.

Vapor Pressure: The equilibrium pressure exerted on the atmosphere by a liquid or solid at a given temperature. Also a measure of a substance's propensity to evaporate or give off flammable vapors. The higher the vapor pressure, the more volatile the substance.

Vermiculite: A 2:1, hydrous ferro-magnesium aluminosilicate clay mineral similar in structure and property to montmorillonite.

Vitrification: Formation of a glassy or noncrystalline material.

Volatilization: The process of transfer of a chemical from the water or liquid phase to the air phase. Solubility, molecular weight, and vapor pressure of the liquid and the nature of the air-liquid/water interface affect the rate of volatilization. See solubility, vapor pressure.

Water Table: The water surface in an unconfined aquifer at which the fluid pressure in the voids is at atmospheric pressure.

Wilting Point: The point at which a plant wilts, no longer able to withdraw water from a soil or sediment to support transpiration processes and retain turgor pressure.

Appendix B
Sample Input Data

Appendix B: Sample Input Data

Sample Input Data - NATURAL BIODEGRADATION

[illegible][illegible]

1	1.0	0.0	8.0	0.0	0					
1		1.0								
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	100.	100.	100.	100.	100.	100.	100.	100.	100.	0.
0.										
0.										
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0.										
0.										
0.										
0.										
0.										
0.	97.	97.	97.	97.	97.	97.	97.	97.	97.	0.
0	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0		0.0								
0		8.0								

- Card 1
- Card 2
- Card 3
- Card 4
- Data Set 1
- Data Set 2
- Data Set 3
- Data Set 4
- Data Set 5
- Start of Data Set 6

- End of Data Set 6
- Data Set 7
- Start of Data Set 8

- End of Data Set 8
- Data Set 9
- Data Set 10

Appendix C
Sample Output Data

Appendix C: Sample Output Data

```
1          BIOPLUME II
1CONTAMINANT TRANSPORT UNDER THE INFLUENCE OF OXYGEN LIMITED BIODEGRADATION
0 Bioplume II - Sample Data
0          INPUT DATA
0          GRID DESCRIPTORS
          NX (NUMBER OF COLUMNS)          = 11
          NY (NUMBER OF ROWS)              = 20
          XDEL (X-DISTANCE IN FEET)         = 50.0
          YDEL (Y-DISTANCE IN FEET)         = 50.0
```

TIME PARAMETERS

NTIM (MAX. NO. OF TIME STEPS) = 1
 NPMP (NO. OF PUMPING PERIODS) = 1
 PINT (PUMPING PERIOD IN YEARS) = 6.000
 TIMX (TIME INCREMENT MULTIPLIER) = .00
 TINIT (INITIAL TIME STEP IN SEC.) = 0.

0 HYDROLOGIC AND CHEMICAL PARAMETERS

S (STORAGE COEFFICIENT) = .000000
 POROS (EFFECTIVE POROSITY) = .300
 BETA (LONGITUDINAL DISPERSIVITY) = 10.0
 DLTRAT (RATIO OF TRANSVERSE TO
 LONGITUDINAL DISPERSIVITY) = .10
 ANFCTR (RATIO OF T- YY TO T-XX) = 1.000000

0 EXECUTION PARAMETERS

NITP (NO. OF ITERATION PARAMETERS) = 7
 TOL (CONVERGENCE CRITERIA - ADIP) = .0010
 ITMAX (MAX. NO. OF ITERATIONS - ADIP) = 100
 CELDIS (MAX. CELL DISTANCE PER MOVE
 OF PARTICLES - M.O.C.) = .500
 NPMAX (MAX. NO. OF PARTICLES) = 2000
 NPDPND (NO. PARTICLES PER NODE) = 9

1
 0

PROGRAM OPTIONS

NPNT (TIME STEP INTERVAL FOR
 COMPLETE PRINTOUT) = 1
 NPNTMV (MOVE INTERVAL FOR CHEM.
 CONCENTRATION PRINTOUT) = 0
 NPNTVL (PRINT OPTION-VELOCITY
 0=NO; 1=FIRST TIME STEP;
 2=ALL TIME STEPS) = 0
 NPNTD (PRINT OPTION-DISP.COEF.
 0=NO; 1=FIRST TIME STEP;
 2=ALL TIME STEPS) = 0
 NUMOBS (NO. OF OBSERVATION WELLS
 FOR HYDROGRAPH PRINTOUT) = 1

NREC (NO. OF PUMPING WELLS) = 1
 NCODES (FOR NODE IDENT.) = 1
 NPNCHV (PUNCH VELOCITY) = 0
 NPDELC (PRINT OPT.-CONC. CHANGE) = 0

0 REACTION TERMS

DK (DISTRIBUTION COEFFICIENT) = .00000E+00
 RHOB (BULK DENSITY OF SOLIDS) = .00000E+00
 RF (RETARDATION FACTOR) = .10000E+01
 THALF (HALF LIFE OF DECAY, IN SEC) = .00000E+00
 DECAY (DECAY CONSTANT=LN 2/THALF) = .00000E+00

0 DECAY TERMS

DEC1 (ANAEROBIC DECAY COEFF.) = .00000E+00
 DEC2 (REAERATION DECAY COEFF.) = .00000E+00

1 STEADY-STATE FLOW

TIME INTERVAL (IN SEC) FOR SOLUTE-TRANSPORT SIMULATION = .18935E+09

0 LOCATION OF OBSERVATION WELLS

NO.	X	Y	
1		6	10

0 LOCATION OF PUMPING WELLS

X	Y	RATE(IN CFS)	CONC.	CONC(O2)	
6		6	-.20E-03	100.00	.00

0 AREA OF ONE CELL = 2500.

0

TRANSMISSIVITY MAP (FT*FT/SEC)

[illegible]

1AQUIFER THICKNESS (FT)

[illegible]

[illegible]

1DIFFUSE RECHARGE AND DISCHARGE (FT/SEC)

[illegible]

1PERMEABILTY MAP (FT/SEC)

0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04			
1.00E-04	1.00E-04	1.00E-04	0.00E+00						
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									

0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
0.00E+00									
0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
0.00E+00									

0 NO. OF FINITE-DIFFERENCE CELLS IN AQUIFER = 162

AREA OF AQUIFER IN MODEL = .40500E+06 SQ. FT.

NZCRIT (MAX. NO. OF CELLS THAT CAN BE VOID OF
PARTICLES; IF EXCEEDED, PARTICLES ARE REGENERATED) = 3

1NODE IDENTIFICATION MAP

0	0	0	0	0	0	0	0	0	0	0	0
0	1	1	1	1	1	1	1	1	1	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	
0	0	0	0	0	0	0	0	0	0	0	

```

0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 1 1 1 1 1 1 1 1 1 0
0 0 0 0 0 0 0 0 0 0 0

```

0 NO. OF NODE IDENT. CODES SPECIFIED = 1

0 THE FOLLOWING ASSIGNMENTS HAVE BEEN MADE:

	CODE NO.	LEAKANCE	SOURCE CONC.	O2 CONC	RECHARGE
0	1	.100E+01	.00	8.00	

1 VERTICAL PERMEABILITY/THICKNESS (FT/(FT*SEC))

```

0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
0.00E+00
0.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00 1.00E+00
0.00E+00
0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
0.00E+00
0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
0.00E+00
0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
0.00E+00
0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00 0.00E+00
0.00E+00

```


0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
0.	97.	97.	97.	97.	97.	97.	97.	97.	97.	0.
0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.

1HEAD DISTRIBUTION - ROW

NUMBER OF TIME STEPS = 0

TIME(SECONDS) = .00000

TIME(DAYS) = .00000E+00

TIME(YEARS) = .00000E+00

0	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000
.00000000	0							
0	100.0000000	100.0000000	100.0000000	100.0000000	100.0000000	100.0000000	100.0000000	100.0000000
100.0000000	100.0000000	0						
0								
0								
0								

```

0 97.00000000 97.00000000 97.00000000 97.00000000 97.00000000 97.00000000 97.00000000 97.00000000
97.00000000 0
0 .00000000 .00000000 .00000000 .00000000 .00000000 .00000000 .00000000 .00000000 .00000000
0

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.428249

1.00000

.000000

.000000

.000000

.000000

.000000

.000000

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.000000

.000000

.000000

1CONCENTRATION OF CONTAMINANT

NUMBER OF TIME STEPS = 0

TIME(SECONDS) = .00000

CHEM.TIME(SECONDS) = .00000E+00

CHEM.TIME(DAYS) = .00000E+00

TIME(YEARS) = .00000E+00

CHEM.TIME(YEARS) = .00000E+00

NO. MOVES COMPLETED = 0

0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0

1CONCENTRATION OF OXYGEN

NUMBER OF TIME STEPS = 0

TIME(SECONDS) = .00000

CHEM.TIME(SECONDS) = .00000E+00

CHEM.TIME(DAYS) = .00000E+00

TIME(YEARS) = .00000E+00

CHEM.TIME(YEARS) = .00000E+00

NO. MOVES COMPLETED = 0

0 0 0 0 0 0 0 0 0 0 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
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0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
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0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 8 8 8 8 8 8 8 8 8 0
0 0 0 0 0 0 0 0 0 0 0

N = 1

NUMBER OF ITERATIONS = 20

HEAD DISTRIBUTION - ROW

NUMBER OF TIME STEPS = 1

TIME(SECONDS) = .18935E+09

TIME(DAYS) = .21915E+04

TIME(YEARS) = .60000E+01

0 .0000000 .0000000 .0000000 .0000000 .0000000 .0000000 .0000000 .0000000 .0000000
0

```

0 99.9999998 99.9999998 99.9999998 99.9999998 99.9999998 99.9999998 99.9999998
99.9999998 0
0 99.8291477 99.8294635 99.8302416 99.8310992 99.8315824 99.8310992 99.8302416
99.8294635 99.8291477 0
0 99.6586734 99.6595657 99.6612187 99.6633789 99.6649445 99.6633789 99.6612187
99.6595657 99.6586734 0
0 99.4866865 99.4880365 99.4909366 99.4955451 99.5007236 99.4955451 99.4909366
99.4880365 99.4866865 0
0 99.3131983 99.3147908 99.3187861 99.3270257 99.3467482 99.3270257 99.3187861
99.3147908 99.3131983 0
0 99.1386046 99.1399849 99.1429669 99.1476276 99.1528277 99.1476276 99.1429669
99.1399849 99.1386046 0
0 98.9622862 98.9632029 98.9650297 98.9673115 98.9689244 98.9673115 98.9650297
98.9632029 98.9622862 0
0 98.7848457 98.7853475 98.7863989 98.7874966 98.7880871 98.7874966 98.7863989
98.7853475 98.7848457 0
0 98.6071305 98.6074165 98.6079959 98.6085203 98.6087643 98.6085203 98.6079959
98.6074165 98.6071305 0
0 98.4289299 98.4290704 98.4293942 98.4296452 98.4297534 98.4296452 98.4293942
98.4290704 98.4289299 0
0 98.2503905 98.2504197 98.2506138 98.2507353 98.2507850 98.2507353 98.2506138
98.2504197 98.2503905 0
0 98.0720432 98.0720689 98.0721733 98.0722224 98.0722427 98.0722724 98.0721733
98.0720689 98.0720432 0
0 97.8934704 97.8934850 97.8932556 97.8935769 97.8935868 97.8935769 97.8935556
97.8934850 97.8934704 0
0 97.7145462 97.7144821 97.7145573 97.7145736 97.7145774 97.7145736 97.7145573
97.7144821 97.7145462 0
0 97.5361558 97.5361572 97.5361729 97.5361670 97.5361656 97.5361670 97.5361729
97.5361572 97.5361558 0
0 97.3576164 97.3576574 97.3576539 97.3576438 97.357642 97.3576438 97.3576539
97.3576574 97.3576164 0
0 97.1784342 97.1783588 97.1784118 97.1784250 97.1784260 97.1784250 97.1784118
97.1783588 97.1784342 0
0 97.0000002 97.0000002 97.0000002 97.0000002 97.0000002 97.0000002 97.0000002
97.0000002 97.0000002 0
0 .0000000 .0000000 .0000000 .0000000 .0000000 .0000000 .0000000
.0000000 .0000000 .0000000 0

```

1HEAD DISTRIBUTION - ROW

```

NUMBER OF TIME STEPS = 1
TIME(SECONDS) = .18935E+09
TIME(DAYS) = .21915E+04
TIME(YEARS) = .60000E+01

```

```

0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 100 100 100 100 100 100 100 100 100 0
0 0 100 100 100 100 100 100 100 100 100 0
0 0 100 100 100 100 100 100 100 100 100 0
0 0 99 99 99 99 100 99 99 99 99 0

```

```

0 0 99 99 99 99 99 99 99 99 0
0 0 99 99 99 99 99 99 99 99 0
0 0 99 99 99 99 99 99 99 99 0
0 0 99 99 99 99 99 99 99 99 0
0 0 99 99 99 99 99 99 99 99 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 98 98 98 98 98 98 98 98 0
0 0 97 97 97 97 97 97 97 97 0
0 0 97 97 97 97 97 97 97 97 0
0 0 97 97 97 97 97 97 97 97 0
0 0 0 0 0 0 0 0 0 0 0

```

1DRAWDOWN

```

0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 -99 -99 -99 -99 -99 -99 -99 -99 0
0 -99 -99 -99 -99 -99 -99 -99 -99 0
0 -98 -98 -98 -98 -99 -98 -98 -98 0
0 -98 -98 -98 -98 -98 -98 -98 -98 0
0 -98 -98 -98 -98 -98 -98 -98 -98 0
0 -98 -98 -98 -98 -98 -98 -98 -98 0
0 -98 -98 -98 -98 -98 -98 -98 -98 0
0 -98 -98 -98 -98 -98 -98 -98 -98 0
0 -97 -97 -97 -97 -97 -97 -97 -97 0
0 -97 -97 -97 -97 -97 -97 -97 -97 0
0 -97 -97 -97 -97 -97 -97 -97 -97 0
0 -97 -97 -97 -97 -97 -97 -97 -97 0
0 -97 -97 -97 -97 -97 -97 -97 -97 0
0 -97 -97 -97 -97 -97 -97 -97 -97 0
0 -96 -96 -96 -96 -96 -96 -96 -96 0
0 -96 -96 -96 -96 -96 -96 -96 -96 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0

```

```

0 CUMULATIVE MASS BALANCE - (IN FT**3)
  RECHARGE AND INJECTION   = -.37869E+05
  PUMPAGE AND E-T WITHDRAWAL = .00000E+00
  CUMULATIVE NET PUMPAGE   = -.37869E+05
  WATER RELEASE FROM STORAGE = .00000E+00
  LEAKAGE INTO AQUIFER     = .72354E+06
  LEAKAGE OUT OF AQUIFER   = -.76007E+06
  CUMULATIVE NET LEAKAGE   = -.36531E+05

```

```

0 MASS BALANCE RESIDUAL   = 1338.6
  ERROR (AS PERCENT)     = .17596

```

0 RATE MASS BALANCE - (IN C.F.S.)
 LEAKAGE INTO AQUIFER = .38213E-02
 LEAKAGE OUT OF AQUIFER = -.40142E-02
 NET LEAKAGE (QNET) = -.19293E-03
 RECHARGE AND INJECTION = -.20000E-03
 PUMPAGE AND E-T WITHDRAWAL = .00000E+00
 NET WITHDRAWAL (TPUM) = -.20000E-03

STABILITY CRITERIA - M.O.C.

FLUID VELOCITIES

VMAX = 9.32E-08 VMAY = 1.26E-06
 VMXBD= 1.31E-07 VMYBD= 1.29E-06
 TMV (MAX. INJ.) = .43898E+08
 TIMV (CELDIS) = .19338E+08
 0 TIMV = 1.93E+07 NTIMV = 9 NMOV = 10
 TIM (N) = .18935E+09
 TIMEVELO = .18935E+08
 TIMEDISP = .87852E+08
 0 TIMV = 1.89E+07 NTIMD = 2 NMOV = 10

THE LIMITING STABILITY CRITERION IS CELDIS

0 NO. OF TIME STEPS REQUIRED TO COMPLETE THIS TIME STEP = 20

0 NP = 1709 IMOV = 1
 TIM(N) = .18935E+09 TIMV = .18935E+08 SUMTCH = .18935E+08
 0 NP1 = 1709 IMOV(O2) = 1
 TIM(N) = .18935E+09 TIMV = .18935E+08 SUMTCH = .18935E+08
 0 NP = 1715 IMOV = 2
 TIM(N) = .18935E+09 TIMV = .18935E+08 SUMTCH = .37869E+08
 0 NP1 = 1715 IMOV(O2) = 2
 TIM(N) = .18935E+09 TIMV = .18935E+08 SUMTCH = .37869E+08

```

0 NP      = 1715      IMOV = 3
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .56804E+08
0 NP1     = 1715      IMOV(02) = 3
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .56804E+08
0 NP      = 1724      IMOV = 4
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .75738E+08
0 NP1     = 1724      IMOV(02) = 4
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .75738E+08
0 NP      = 1740      IMOV = 5
  TZM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .94673E+08
0 NP1     = 1740      IMOV(02) = 5
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .94673E+08
0 NP      = 1748      IMOV = 6
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .11361E+09
0 NP1     = 1748      IMOV(02) = 6
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .11361E+09
0 NP      = 1757      IMOV = 7
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .13254E+09
0 NP1     = 1757      IMOV(02) = 7
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .13254E+09
0 NP      = 1757      IMOV = 8
  TIM(N)   = .18395E+09  TIMV = .18935E+08  SUMTCH = .15148E+09
0 NP1     = 1757      IMOV(02) = 8
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .15148E+09
0 NP      = 1760      IMOV = 9
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .17041E+09
0 NP1     = 1760      IMOV(02) = 9
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .17041E+09
0 NP      = 1764      IMOV = 10
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .18935E+09
0 NP1     = 1764      IMOV(02) = 10
  TIM(N)   = .18935E+09  TIMV = .18935E+08  SUMTCH = .18935E+09

```

1CONCENTRATION OF CONTAMINANT

NUMBER OF TIME STEPS = 1

DELTA T = .18935E+09

TIME(SECONDS) = .18935E+09

CHEM.TIME(SECONDS) = .18935E+09
CHEM.TIME(DAYS) = .21918E+04
TIME(YEARS) = .60000E+01

CHEM.TIME(YEARS) = .60000E+01

NO. MOVES COMPLETED = 10

0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	0	0	0	0
0	0	0	0	0	0	0	30	0	0	0	0
0	0	0	0	0	0	0	35	0	0	0	0
0	0	0	0	0	0	0	30	0	0	0	0
0	0	0	0	0	0	0	26	0	0	0	0
0	0	0	0	0	0	0	18	0	0	0	0
0	0	0	0	0	0	0	9	0	0	0	0
0	0	0	0	0	0	0	1	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0

CHEMICAL MASS BALANCE

MASS IN BOUNDARIES	= .00000E+00
MASS OUT BOUNDARIES	= -.82523E-03
MASS PUMPED IN	= .37869E+07
MASS PUMPED OUT	= .00000E+00

MASS LOST W. BIODEG. = .78974E+06
MASS LOST BY RADIO. DCY= .00000E+00
MASS LOST BY ANAER. DCY= .00000E+00
MASS LOST BY REAER. DCY= .00000E+00
MASS ADSORBED ON SOLIDS= .00000E+00

INITIAL MASS ADSORBED = .00000E+00
INFLOW MINUS OUTFLOW = .37869E+07
INITIAL MASS DISSOLVED = .00000E+00
PRESENT MASS DISSOLVED = .32136E+07
CHANGE MASS DISSOLVED = .40033E+07
CHANGE TOTL.MASS STORED= .40033E+07

COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION:

MASS BALANCE RESIDUAL = -.21638E+06
ERROR (AS PERCENT) = -.57140E+01

1CONCENTRATION OF OXYGEN

NUMBER OF TIME STEPS = 1

DELTA T = .18935E+09
TIME (SECONDS) = .18935E+09
CHEM. TIME (SECONDS)= .18935E+09
CHEM. TIME (DAYS)= .21915E+04
TIME (YEARS) = .60000E+01
CHEM. TIME (YEARS)= .60000E+01

NO. MOVES COMPLETED = 10

0	0	0	0	0	0	0	0	0	0	0	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	7	8	8	8	8	8	0
0	8	8	8	8	0	8	8	8	8	8	0
0	8	8	8	7	0	7	8	8	8	8	0
0	8	8	8	2	0	2	8	8	8	8	0
0	8	8	8	0	0	0	8	8	8	8	0
0	8	8	8	0	0	0	8	8	8	8	0
0	8	8	8	1	0	1	8	8	8	8	0
0	8	8	8	5	0	5	8	8	8	8	0
0	8	8	8	7	0	7	8	8	8	8	0
0	8	8	8	8	6	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	8	8	8	8	8	8	8	8	8	8	0
0	0	0	0	0	0	0	0	0	0	0	0

CHEMICAL MASS BALANCE FOR OXYGEN

MASS IN BOUNDARIES = .57883E+07
MASS OUT BOUNDARIES = -.60806E+07
MASS PUMPED IN = .00000E+00
MASS PUMPED OUT = .00000E+00
MASS LOST W. BIODEG. = .23692E+07
INFLOW MINUS OUTFLOW = -.20225E+06
INITIAL MASS DESOLVED = .24300E+08
PRESENT MASS DESOLVED = .21722E+08
CHANGE MASS DISSOLVED = -.20918E+06
CHANGE TOTL.MASS STORED= -.20918E+06

COMPARE RESIDUAL WITH NET FLUX AND MASS ACCUMULATION FOR OXYGEN:

MASS BALANCE RESIDUAL = -.83069E+05
ERROR (AS PERCENT) = -.14351E+01

COMPARE INITIAL MASS STORED WITH CHANGE IN MASS STORED FOR OXYGEN:

ERROR (AS PERCENT) = .33778E+00

0 TIME VERSUS HEAD AND CONCENTRATION AT SELECTED
OBSERVATION POINTS

PUMPING PERIOD NO. 1

0 STEADY-STATE SOLUTION

OBS.WELL NO.	X	Y	N	HEAD (FT)	CONC (mg/l)	TIME (Yrs)
1	6	10				
		0	98.6	.0		.000
		1	98.6	.0		.600
		2	98.6	.0		1.200
		3	98.6	.0		1.800
		4	98.6	.0		2.400
		5	98.6	.0		3.000
		6	98.6	.0		3.600
		7	98.6	2.6		4.200
		8	98.6	9.7		4.800
		9	98.6	13.6		5.400
		10	98.6	17.5		6.000

1 Bioplume II - Sample Data

0 TIME VERSUS HEAD AND CONCENTRATION(O2) AT SELECTED
OBSERVATION POINTS

PUMPING PERIOD NO. 1

STEADY-STATE SOLUTION FOR OXYGEN

OBS.WELL NO.	X	Y	N	HEAD (FT)	CONC (mg/l)	TIME (Yrs)
--------------	---	---	---	-----------	-------------	------------

1

6

10

	0	.0	8.0			.000
--	---	----	-----	--	--	------

1	98.6	8.0			.600
---	------	-----	--	--	------

2	98.6	8.0			1.200
---	------	-----	--	--	-------

3	98.6	8.0			1.800
---	------	-----	--	--	-------

4	98.6	7.7			2.400
---	------	-----	--	--	-------

5	98.6	5.6			3.000
---	------	-----	--	--	-------

6	98.6	.5		3.600
---	------	----	--	-------

7	98.6	.0		4.200
---	------	----	--	-------

8	98.6	.0		4.800
---	------	----	--	-------

9	98.6	.0		5.400
---	------	----	--	-------

10	98.6	.0		6.000
----	------	----	--	-------

Appendix D
Data Input Formats

Appendix D: Data Input Formats

Card	Column	Format	Variable	Definition
1	1-80	10A8	TITLE	Description of problem
2	1-4	I4	NTIM	Maximum number of time steps in a pumping period (1..100)*.
	5-8	I4	NPMP	Number of pumping periods. If NPMP > 1, then data set 11 must be completed.

9-12	I4	NX	Number of nodes in the x direction (3..20).
13-16	I4	NY	Number of nodes in the y direction (3..30).
17-20	I4	NPMAX	Maximum number of particles (1..8100).
21-24	I4	NPNT	Time step interval for printing hydraulic and chemical output data (1...).
25-28	I4	NITP	Number of iteration parameters (usually 4..7).
29-32	I4	NUMOBS	Number of observation points to be specified in a following data set (0..5).
33-36	I4	ITMAX	Maximum allowable number of iterations in ADIP (usually 100..200).
37-40	I4	NREC	Number of pumping or injection wells to be specified in a following data set (0..50).

* The possible ranges which a value may take are indicated in parentheses. The form (X..Y) indicates that X is a lower bound and Y is an upper bound. The form (X...) indicates that X is a lower bound and there is no upper bound.

Card	Column	Format	Variable	Definition
2	41-44	I4	NPTPND	Initial number of particles per node (4,5,8,9).
	45-48	I4	NCODES	Number of node identification codes to be specified in a following data set (1..9).
	49-52	I4	NPNTMV	Particle movement interval (IMOV) for printing chemical

				output data (0 to print only at end of time steps).
53-56	I4	NPNTVL		Option for printing computed velocities (0=do not print; 1=print for first time step; 2=print for all time steps).
57-60	I4	NPNTD		Option for printing computed dispersion equation coefficients (0=do not print; 1=print for first time step; 2=print for all time steps).
61-64	I4	NPDELC		Option for printing computed changes in concentration (0=do not print; 1 =print).
65-68	I4	NPNCHV		Option to punch velocity data (0=do not punch; 1 =punch the node velocities on unit 7).
69-72	I4	NREACT		Option for retardation and decay (0=retardation factor is equal to 1 and no decay; 1=retardation factor >1 and/or decay).

Card	Column	Format	Variable	Definition
3	1-5	G5.0	PINT	Pumping period in years (0.01..99.99).
	6-10	G6.0	TOL	Convergence criteria in ADIP (usually < 0.01).
	11-15	G5.0	POROS	Effective porosity (0.01..1).

16-20	G5.0	BETA	Characteristic length (longitudinal dispersivity) in feet (0.01..99.99).
21-25	G5.0	S	Storage coefficient (set S=0 for steady flow problems).
26-30	G5.0	TIMX	Time increment multiplier for transient flow problems (0.01..99.99). TIMX is disregarded if S=0.
31-35	G5.0	TINIT	Size of initial time step in seconds (0...). TINIT is disregarded if S=0.
36-40	G5.0	XDEL	Width of finite difference cell in the x direction in feet (0.1..999.9).
41-45	G5.0	YDEL	Width of finite difference cell in the y direction in feet (0.1..999.9).
46-50	G5.0	DLTRAT	Ratio of transverse to longitudinal dispersivity (0.001..1).
51-55	G5.0	CELDIS	Maximum cell distance per particle move (0.001..1).
56-60	G5.0	ANFCTR	Ratio of Tyy to Txx (0.001..9.99).

Card	Column	Format	Variable	Definition
4		Free Format (separated by spaces or commas)	DK	Distribution coefficient (L^3 / M).
			RHOB	Bulk density of the solid (M/L^3)
			THALF	Half-life of the solute (seconds)
			DEC1	Anaerobic decay coefficient

(day⁻¹)

DEC2

Reacration coefficient (day⁻¹)

Data Set	Number of Lines	Format	Variable	Definition
1	NUMOBS	2I2	IXOBS, IYOBS	Coordinates of observation points. This data set is not used if NUMOBS=0.
2	NREC	2I2,3G8.2	IX, IY	Coordinates of pumping (+) or injection (-) wells for contaminant or oxygenated water
			REC	Pumping/injection rate in cfs
			CNRECH	Concentration of injected contaminated water
			CNRECO	Concentration of injected oxygenated water

Data Set	Number of Lines	Format	Variable	Definition
3	1 or NY	I1	INPUT	Parameter card for transmissivity (0=constant transmissivity is defined by FCTR; 1=transmissivity is read from following array).

G10.0	FCTR	Constant transmissivity in ft /s OR factor to multiply transmissivity array.
20G4. 1	VPRM	Array for temporary storage of transmissivity data in ft ² /s. For an anisotropic array, enter the values of Txx and the values for Tyy will be computed by multiplying by ANFCTR.

4	1 or NY	I1	INPUT	Parameter card for thickness (0=constant thickness is defined by FCTR; 1=thickness is read from following array).
		G10.0	FCTR	Constant thickness in feet, OR factor to multiply thickness array.
		20G3.0	THCK	Array of saturated thickness in feet.

Data Set	Number of Lines	Format	Variable	Definition
5	1 or NY	I1	INPUT	Parameter card for recharge (0=constant recharge is defined by FCTR; 1=recharge is read from following array)
		G10.0	FCTR	Constant diffuse recharge (-) or discharge (+) in ft/s OR

		20G4.1	RECH	factor to multiply recharge array Array of diffuse recharge (-) or discharge (+) in ft/s.
6	1 or NY	I1	INPUT	Parameter card for node identification (0=all nodes identified by FCTR; 1=node identifications in following array)
		G10.0	FCTR	Node identification OR factor to multiply node identification array
		20I1	NODEID	Node identification matrix (used to define constant-head nodes or other boundary conditions and stresses).

Data Set	Number of Lines	Format	Variable	Definition
7	NCODES	I2	ICODE	Instructions for using the NODEID array. When NODE ID= ICODE, then the following factors are set. Otherwise, the values remain set as they were previously.
		4G 10.2	FCTR1	Leakance

		FCTR2	Concentration of contaminated water
		FCTR4	Concentration of oxygenated water
		FCTR3	Diffuse recharge (-) or discharge (+)
I2		OVERRD	If OVERRD=0, then the value of RECH is not changed. If OVERRD is nonzero, then the value of RECH is set to FCTR3

8	1 or NY	11	INPUT	Parameter card for water table (0=constant water table defined by FCTR; 1=water table is read from following array)
		G10.0	FCTR	Initial water table, potentiometric elevation, or constant head in stream or source bed in feet OR factor to multiply water table array.
		20G4.0	WT	Array of initial water table, potentiometric elevation, or constant head in stream or source bed in feet.

Data Set	Number of Lines	Format	Variable	Definition
9	1 or NY	I1	INPUT	Parameter card for initial contaminant concentration (0=constant concentration defined by FCTR; 1=contaminant concentration is read from following array)

		G10.0	FCTR	Initial contaminant concentration in aquifer OR factor to multiply contaminant concentration array
		20G4.0	CONC	Array of initial contaminant concentration in aquifer.
10	1 or NY	I1	INPUT	Parameter card for initial oxygen concentration (0=constant concentration defined by FCTR; 1=oxygen concentration is read from following array)
		G10.0	FCTR	Initial oxygen concentration in aquifer OR factor to multiply oxygen concentration array
		20G4.0	CONC 1	Array of initial oxygen concentration in aquifer.

Data Set	Number of Lines	Format	Variable	Definition
11	1	I1	ICHK	Parameter to check whether any revisions are desired (1=revision is desired, more data to follow; 0=no revision desired, end of data set). This data set allows 13 timing, printing, and pumping

			variables to be revised for each pumping period. Data set 11 can only be used if NPMP > 1. The sequence of cards in this data set must be repeated NPMP-1 times (for each pumping period after the first).
1	1014, 3G5.0	NTIM NPNT, NITP, ITMAX, NREC, NPNTMV, NPNTVL, NPNTD, NPDELC, NPNCHV, P I N T, T I M X, T I N I T	Previously defined variables for cards 2 and 3 which will be revised for the next pumping period. This card is used only if ICHK=1.
NREC	212, 3G8.2	IX, IY, REC, CNRECH, CNRECO	Previously defined variables for data set 2 which will be revised for the next pumping period. This card is used only if ICHK=1 and NREC > 0

Appendix E
BIOPLUME II™ Sensitivity Analysis

Appendix E: BIOPLUME II™ Sensitivity Analysis

2.3 Sensitivity Analysis

In order to define which parameters have the most effect on biodegradation in BIOPLUME II™, the following detailed sensitivity analysis was performed. The parameters that were investigated included: hydraulic conductivity, dispersivity (longitudinal and transverse), porosity, reaeration, and retardation.

A hypothetical contaminant plume was generated using a single continuous hydrocarbon source. The above mentioned parameters were then varied individually to determine their effect on biodegradation. The results from the sensitivity analyses indicate that biodegradation in the model is most sensitive to hydraulic conductivity, the coefficient of reaeration, and the coefficient of anaerobic decay. The following input data was utilized in the base run:

Simulation time	10 years
Grid size	20 x 30
Cell size	50 ft x 50 ft
Porosity	0.3
Longitudinal Dispersivity	10 ft
Transverse Dispersivity	3 ft
Txx	.0025 ft /s
Tyy	.0025 ft /s
Aquifer thickness	25 ft
Hydraulic Gradient	4.29E-3 ft/ft
Injection well at cell	X=10,Y=10
Injection rate	0.0002 cfs
Conc. of contaminant in injected water	150 mg/l
Conc. of oxygen in injected water	0.0 mg/l
Initial Conc. of oxygen	8.0 mg/l
Conc. of natural recharge of oxygen	8.0 mg/l

A detailed discussion of the sensitivity analyses is included in the following sections.

2.3.1 Variation of Concentrations with Hydraulic Conductivity

The hydraulic conductivity (K) was varied from 10^{-4} ft/sec to 10^{-7} ft/sec. Figure 2.3 is a plot of the contaminant and oxygen concentrations along the centerline of the plume (cross section A - A, Figure 2.2) for three values of hydraulic conductivity. It can be seen that the hydraulic conductivity has a significant effect on biodegradation. The maximum contaminant concentration varied from 29.6 mg/l ($K = 10^{-4}$ ft/sec) to 130 mg/l ($K = 10^{-7}$ ft/sec). The change in biodegraded mass with hydraulic conductivity is illustrated in Figure 2.4.

2.3.2 Variation of Concentrations with Retardation

The effect of retardation on biodegradation was studied by using a retardation factor, R , greater than 1. Figure 2.5 presents the variation in contaminant and oxygen concentrations along the centerline of the plume (section A - A, Figure 2.2) for three values of R . It can be seen that the mass of hydrocarbon remaining at the end of the simulation period decreases with increasing values of R . The percent of mass biodegraded relative to the total dissolved mass, however, decreases for increasing values of R (Figure 2.4b).

Table 2.1 lists the percent of mass biodegraded relative to the total dissolved mass and the percent of mass biodegraded relative to the total stored mass. Table 2.1 also lists the percent of mass adsorbed relative to the total stored mass for the three values of R . Table 2.1 indicates that the percent of biodegraded mass decreases with increasing values of retardation (columns A and B).

Table 2.1 - Percent Biodegraded Mass as a Function of the Retardation Factor (R)

R	A	B	C
1	30.25	30.25	0.00
2	27.73	13.86	50.00
3	25.74	8.58	66.67

$A = BM/TDM$

$B = BM/TSM$

$C = AM/TSM$

$BM =$ Biodegraded Mass

$AM =$ Adsorbed Mass

$TDM =$ Dissolved Mass + Biodegraded Mass

$TSM =$ Dissolved Mass + Biodegraded Mass
+ Adsorbed Mass

2.3.3 Variation of Concentrations with Dispersivity

The variation of contaminant concentrations with dispersivity was examined by looking at the longitudinal and transverse dispersivities independently.

2.3.3.1 Longitudinal Dispersivity

The longitudinal dispersivity was varied from 10 ft to 1 ft. Figure 2.6 presents the variation in contaminant and oxygen concentrations along the centerline of the contaminant plume (section A - A, Figure 2.2) for three values of longitudinal dispersivity. It can be seen that the longitudinal dispersivity also has a slight effect on biodegradation. The maximum contaminant concentrations varied from 29.6 mg/l (10 ft) to 41.7 mg/l (1 ft). The change in biodegraded mass with longitudinal dispersivity is illustrated in Figure 2.7.

2.3.3.2 Transverse Dispersivity

The transverse dispersivity was varied from 1 ft to 5 ft. Figure 2.8 shows the variation of contaminant and oxygen concentrations with transverse dispersivity along a transverse cross section through the centerline of the plume (cross section B - B, Figure 2.2). The transverse dispersivity does not seem to have an appreciable effect on biodegradation. The areal extent of the plume is not very sensitive to the transverse dispersivity, however, the maximum concentrations exhibit a wide range of variation. The maximum contaminant concentrations varied from 26.5 mg/l (5 ft) to 35.5 mg/l (1 ft). The change in biodegraded mass with transverse dispersivity is illustrated in Figure 2.7

2.3.4 Variation of Concentrations with Porosity

The porosity was varied from 0.25 to 0.7. Figure 2.9 shows the variation of contaminant and oxygen concentrations with porosity along the centerline of the plume (section A - A, Figure 2.2). It is evident that porosity does not have a significant effect on biodegradation. The maximum contaminant concentrations varied from 29.0 mg/l ($n = 0.25$) to 35.0 mg/l ($n = 0.5$). The change in biodegraded mass with porosity is illustrated in Figure 2.4b.

2.3.5 Variation of Concentrations with Reaeration Coefficient

The reaeration coefficient, k , was varied from 0.0 day to 0.005 day . Figure 2.10 presents the variation of contaminant and oxygen concentrations with k along the centerline of the plume (cross section A - A, Figure 2.2). It is evident that the coefficient of reaeration has a significant effect on biodegradation. The areal extent of the contaminant plume as well as the maximum concentrations exhibit a wide range of variation with k . The maximum concentrations varied from 29.6 mg/l ($k = 0.0$ day) to 17.6 mg/l ($k = 0.005$ day). The change in biodegraded mass with k is presented in Figure 2.4a.

2.4 Model Output

Typical output from BIOPLUME II includes an oxygen and hydrocarbon distribution matrix at selected points in time. These matrices can be plotted as contour plots (Figure 4.1) or surface plots using the SURFER graphics package (Golden Software, 1987). The graphics option in the BIOPLUME II preprocessor will transform the oxygen and hydrocarbon matrices to the required format for direct use in SURFER.

It can be seen from Figure 4.1 that whenever hydrocarbon is present in relatively high concentrations, then oxygen is absent. The oxygen plume forms an envelope for the hydrocarbon plume with oxygen concentrations gradually increasing to initial background levels as one moves away from the contaminant plume. The model output also includes a mass balance computation for oxygen and hydrocarbon at the selected points in time. The dissolved mass present in the system for each is computed, as well as the biodegraded mass. The hydrocarbon mass balance computation details the

biodegraded mass due to the different processes available in the model (aerobic, anaerobic, reaeration and radioactive decay). It is noted at this point that a detailed analysis of mass balance errors computed in BIOPLUME I I is being performed for a variety of conditions and geometries. The results of the analysis will be included in future updates to the manual.

2.5 Summary

BIOPLUME II simulates hydrocarbon transport under the influence of oxygen limited biodegradation. A dual particle mover concept is used to compute an oxygen plume and a hydrocarbon plume. An instantaneous reaction between the solute (hydrocarbon) and the substrate (oxygen) is assumed and the method of superposition is utilized to represent the reaction between the two. An independent mass balance is performed for oxygen and hydrocarbon and is adjusted to account for the mass loss due to biodegradation.

The model can be used to simulate naturally occurring biodegradation processes and to simulate in-situ restoration processes. Injection wells can be used as oxygen sources in the model. Three other sources of oxygen are included in BIOPLUME I I: (1) dissolved oxygen in the aquifer; (2) natural recharge, and; (3) oxygen exchange from the unsaturated zone.

The biodegraded mass in the model is most sensitive to hydraulic conductivity, the coefficient of reaeration, and the coefficient of anaerobic decay. The model has been applied to two sites: a wood creosoting process waste site in Conroe, Texas (Borden et al., 1986) and a jet fuel spill site in Traverse City, Michigan. The model application to the Traverse City site is presently being submitted for publication. The model provided a good match to field conditions at both sites. BIOPLUME II is presently being used to design an in-situ bioreclamation field experiment at the Traverse City field site. Results from the experiment will also be published in the literature.

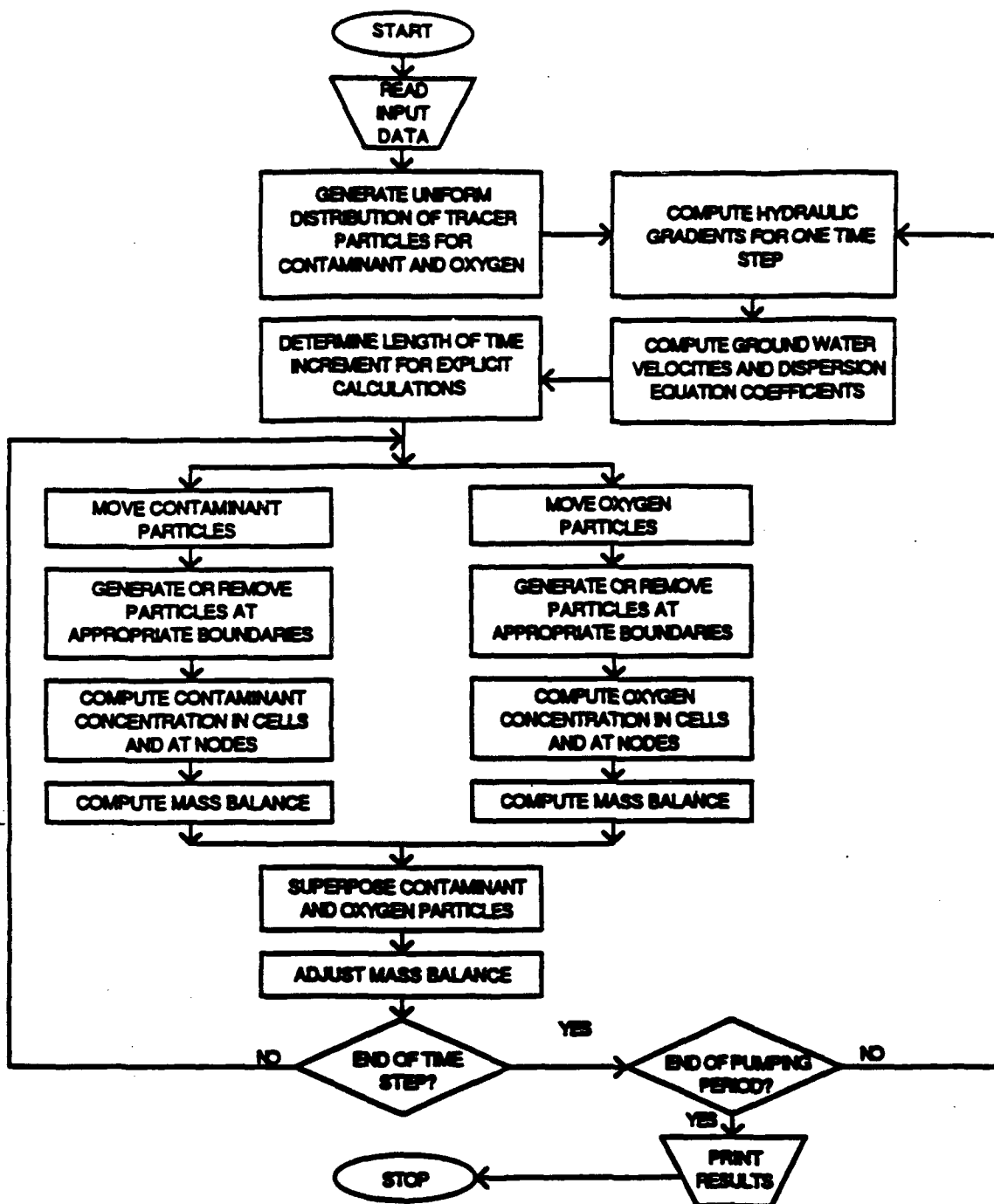
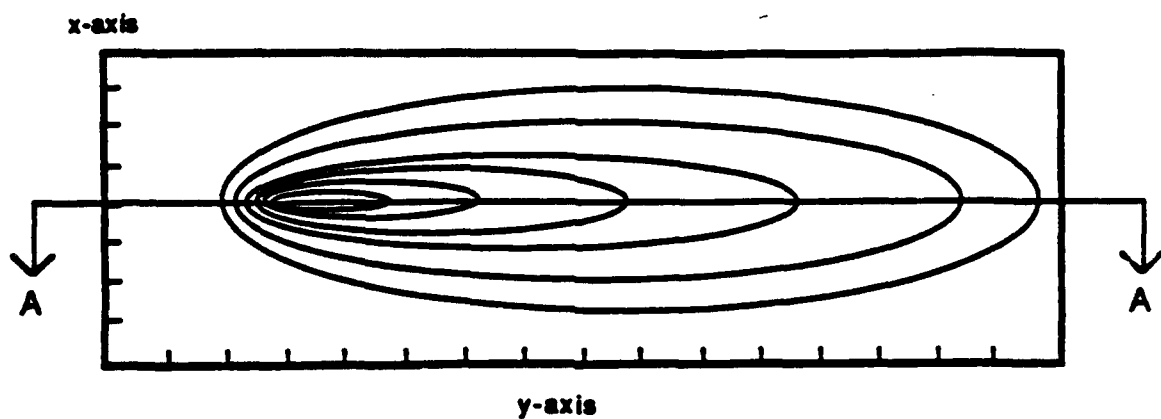
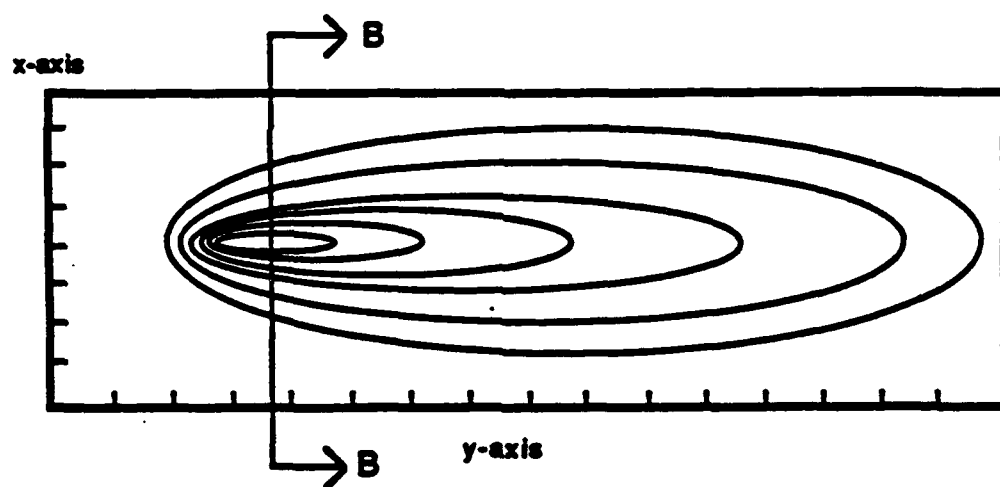


FIGURE 2.1 - Simplified Flowchart of BIOPLUME II



Section A-A is the Centerline of the Plume



Section B-B is the Transverse Section of the Plume

FIGURE 2.2 - Schematic of the Centerline and Transverse Section of a Plume

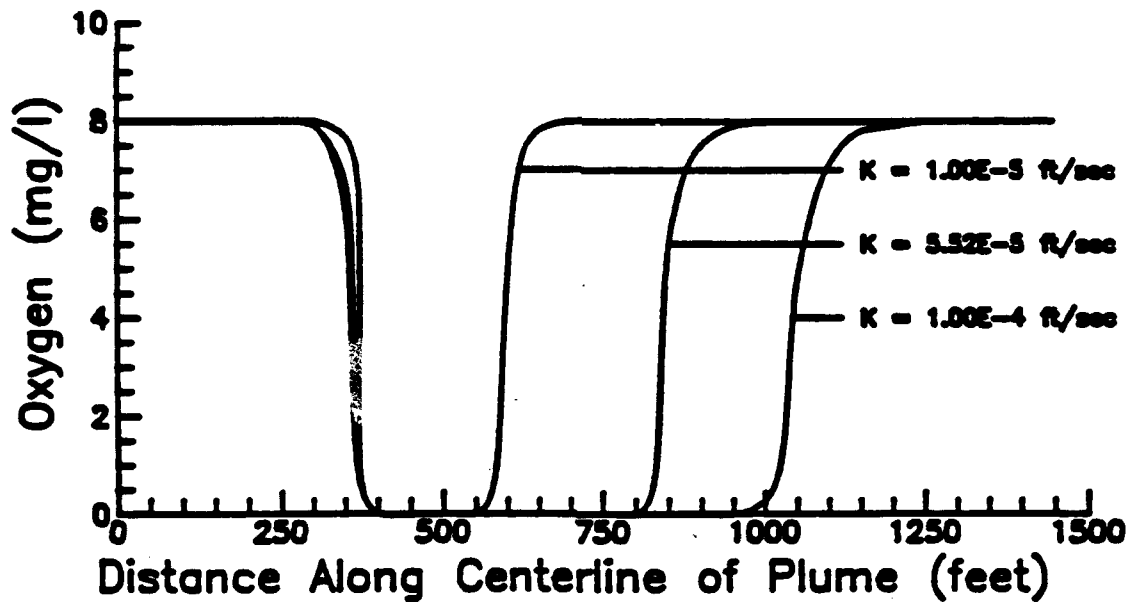
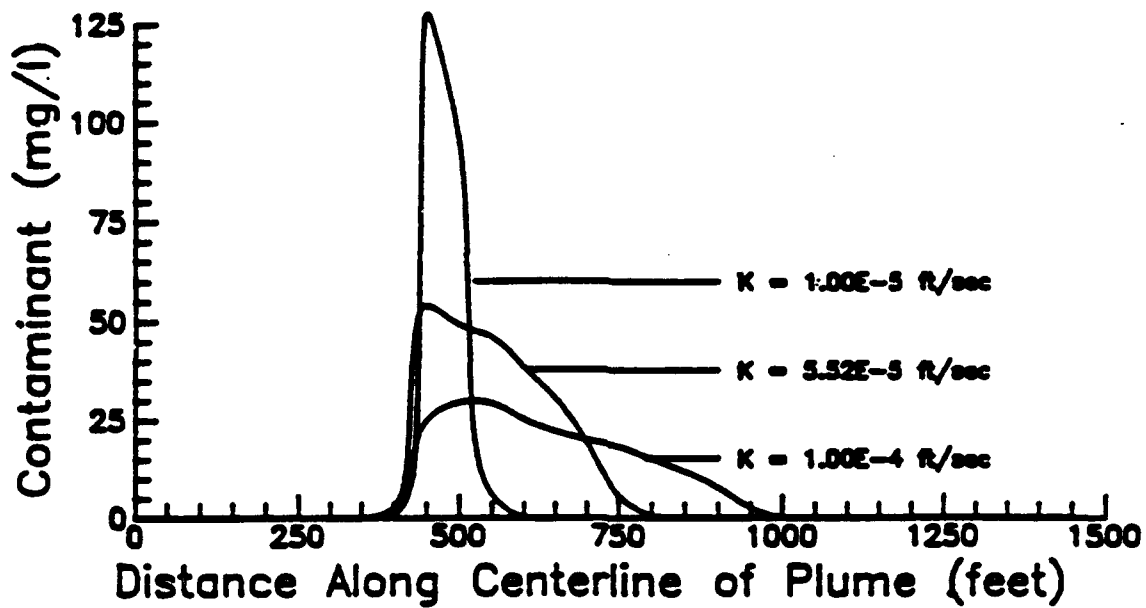


Figure 2.3 — Concentration Distributions for Various Values of Hydraulic Conductivity

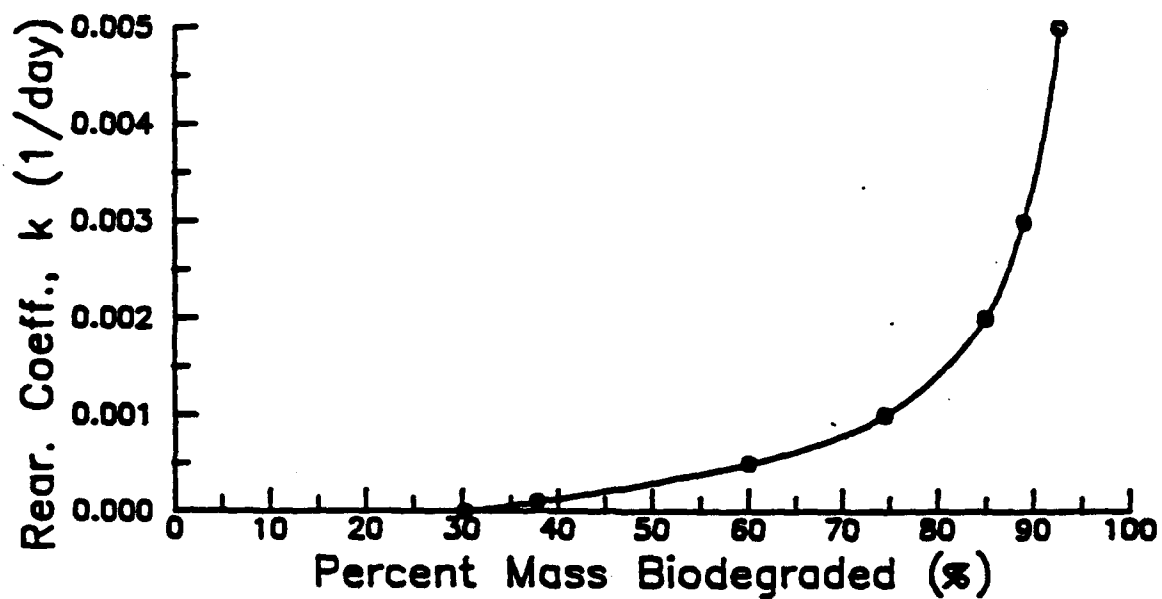
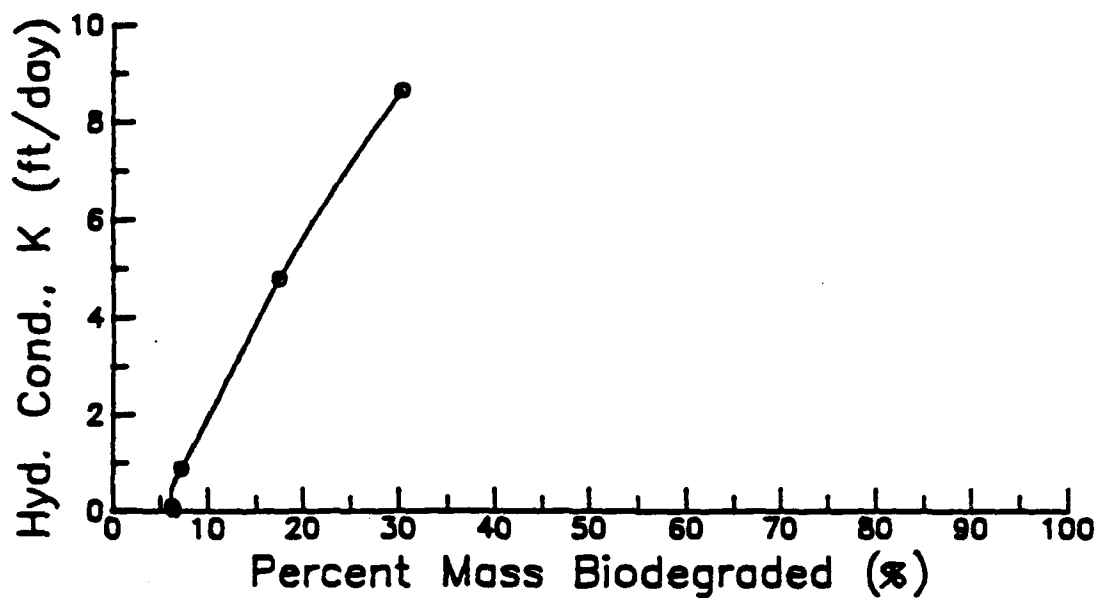


Figure 2.4a — Variation of Biodegraded Mass with Various Parameters

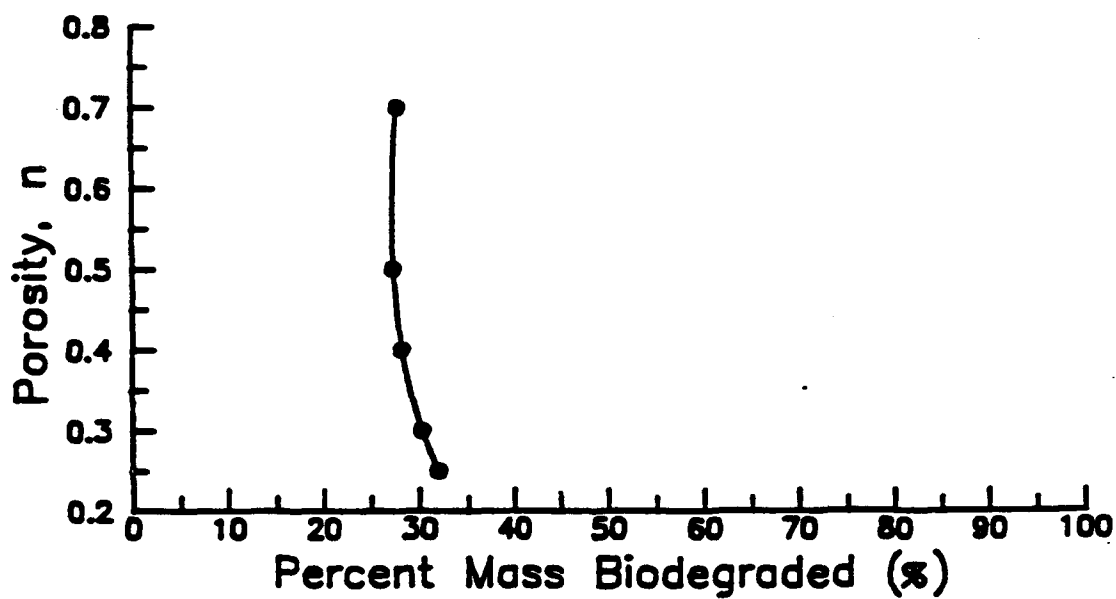
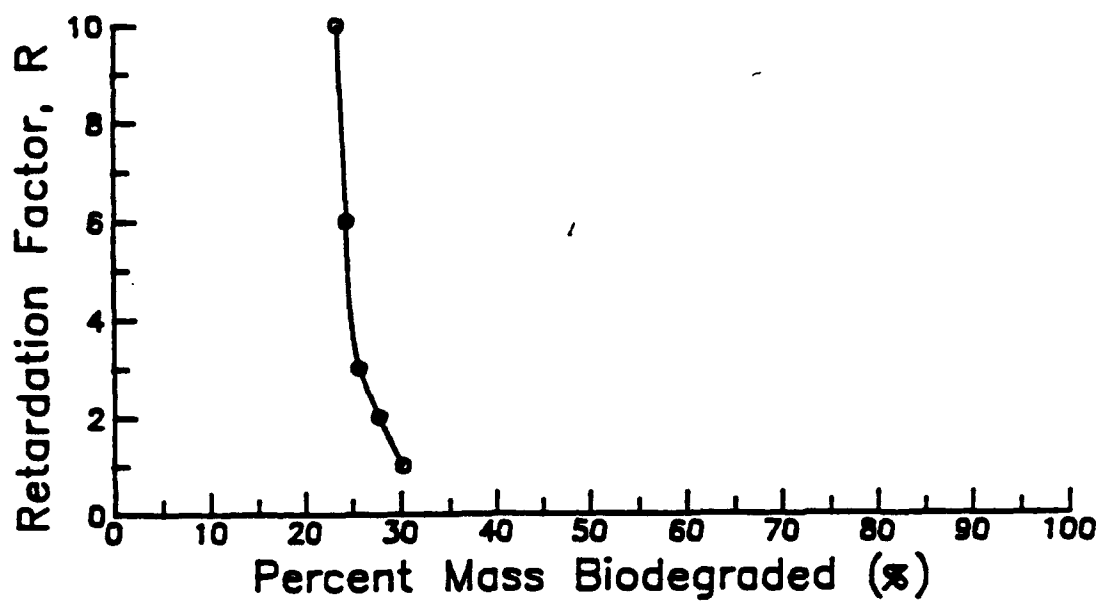


Figure 2.4b — Variation of Biodegraded Mass with Various Parameters

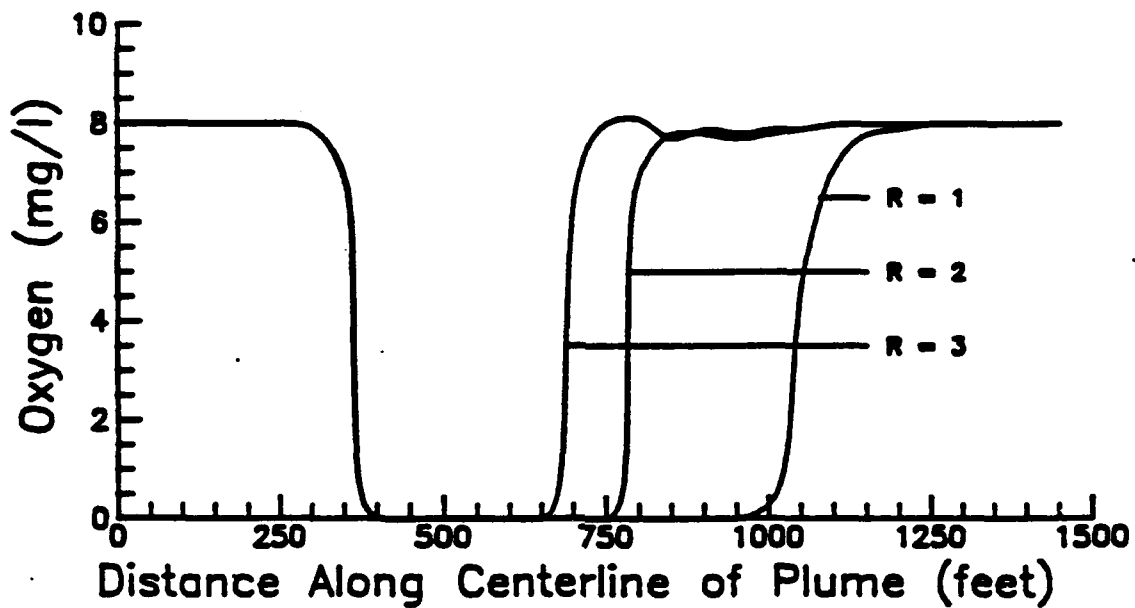
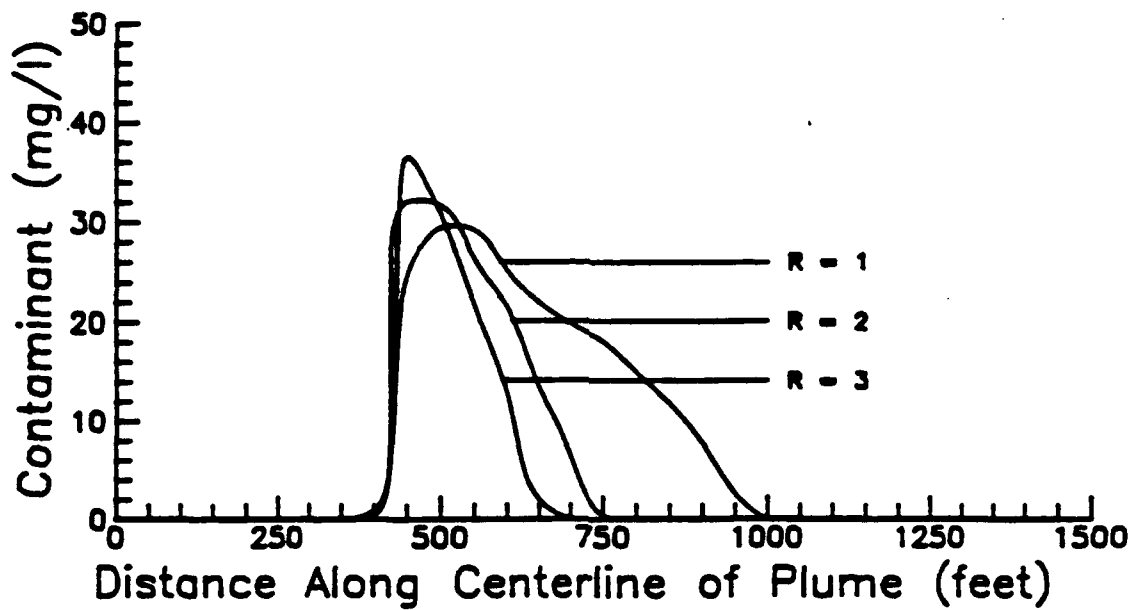


Figure 2.5 — Concentration Distributions for Various Values of Retardation

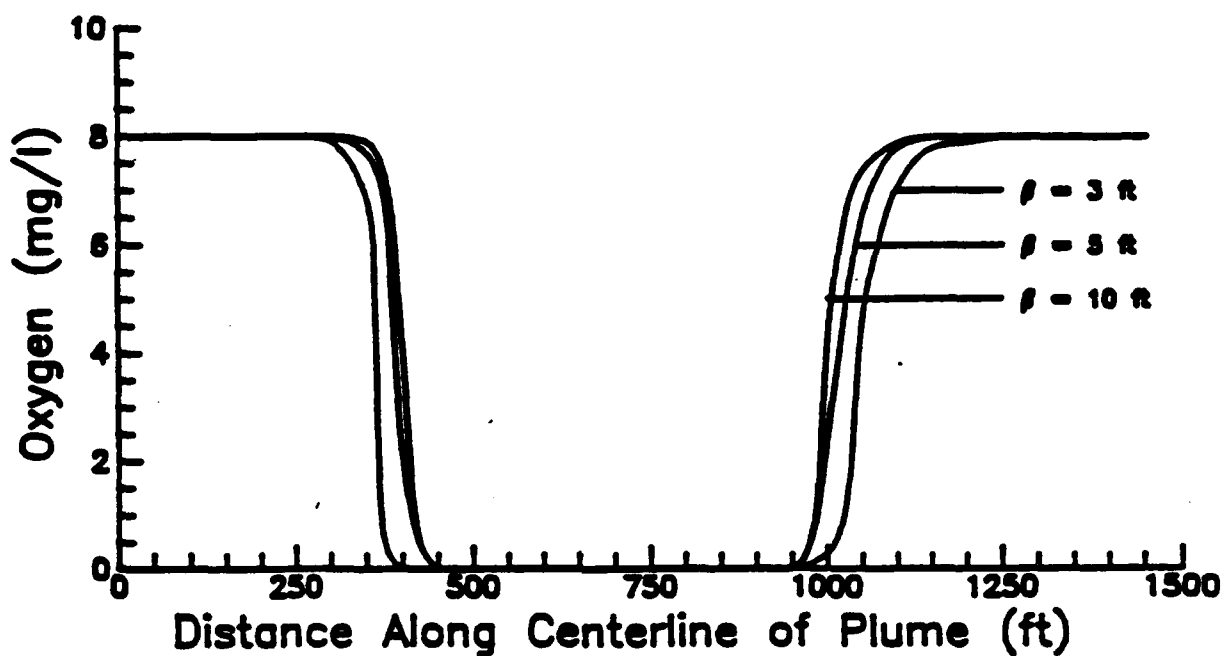
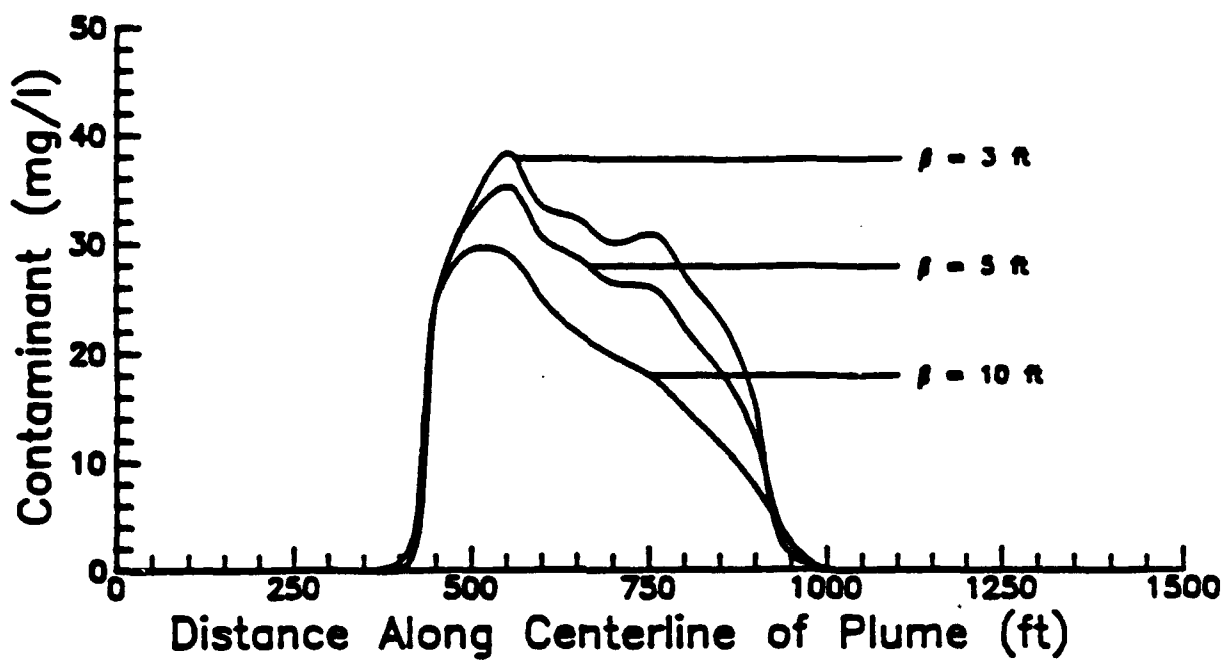


Figure 2.6 — Concentration Distributions for Various Values of Longitudinal Dispersivity

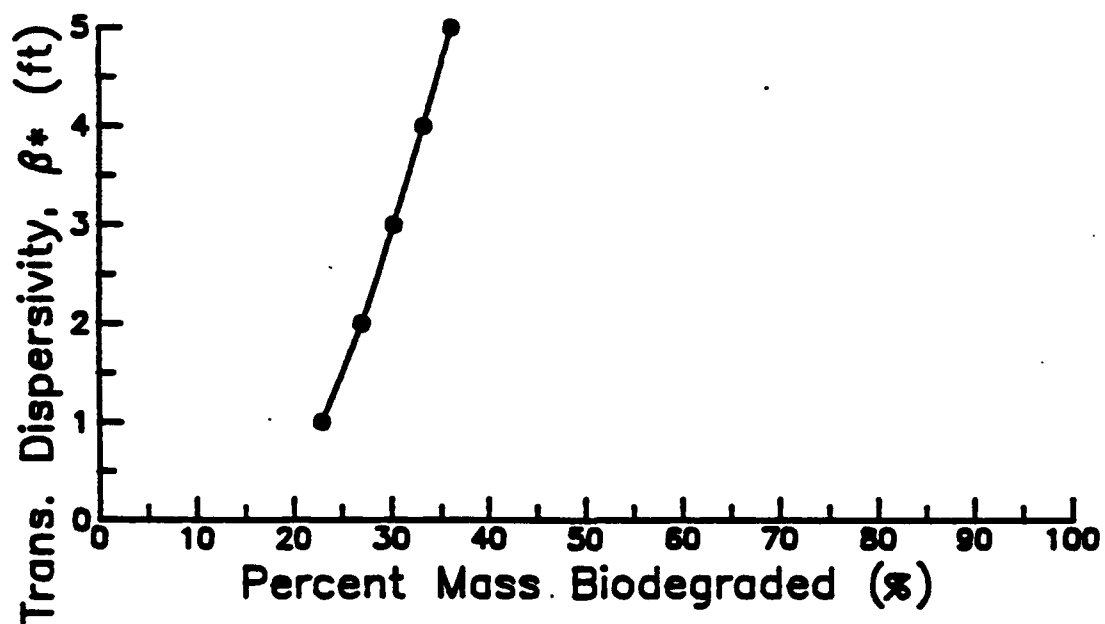
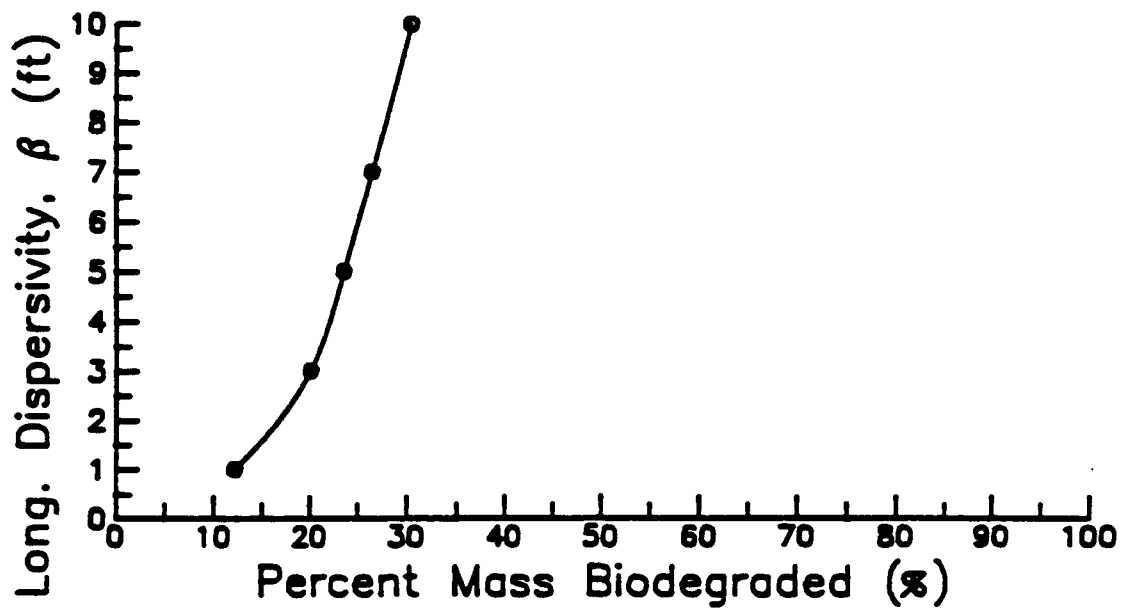


Figure 2.7 — Variation of Biodegraded Mass with Dispersivity

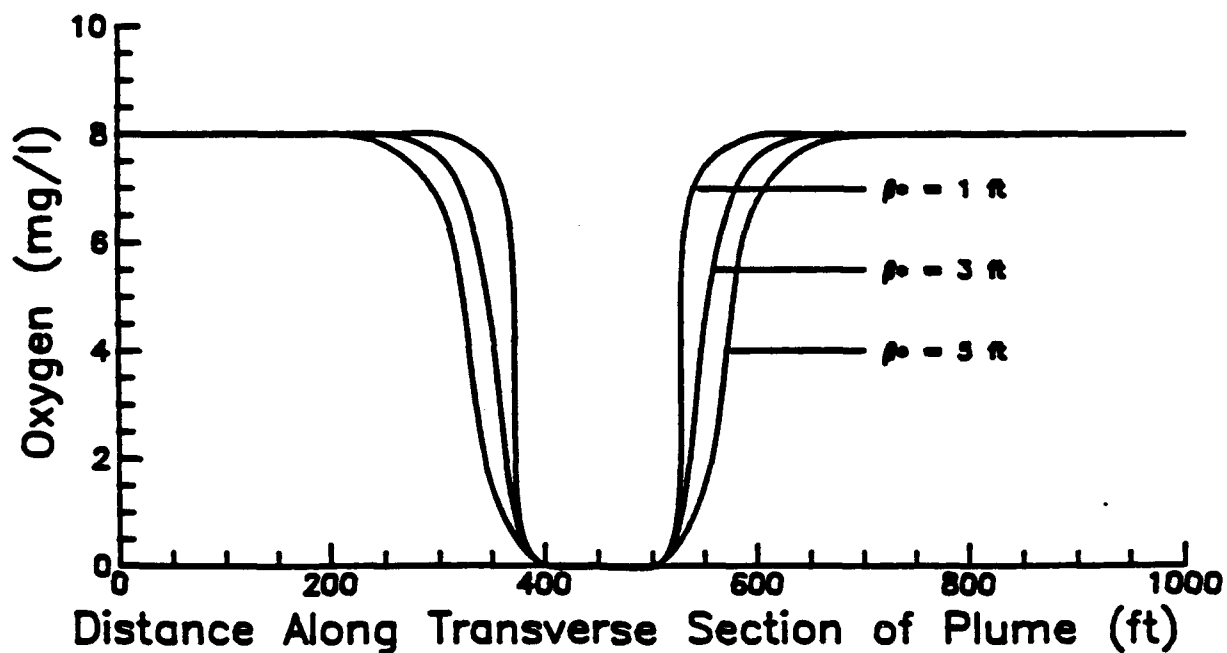
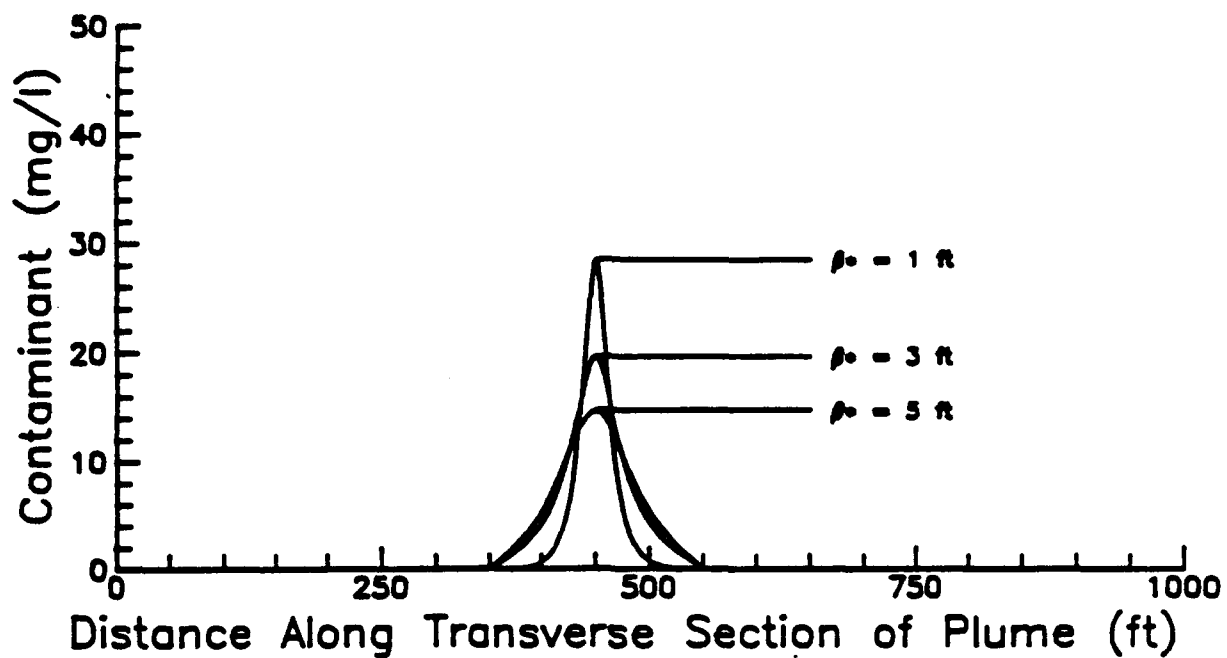


Figure 2.8 — Concentration Distributions for Various Values of Transverse Dispersivity

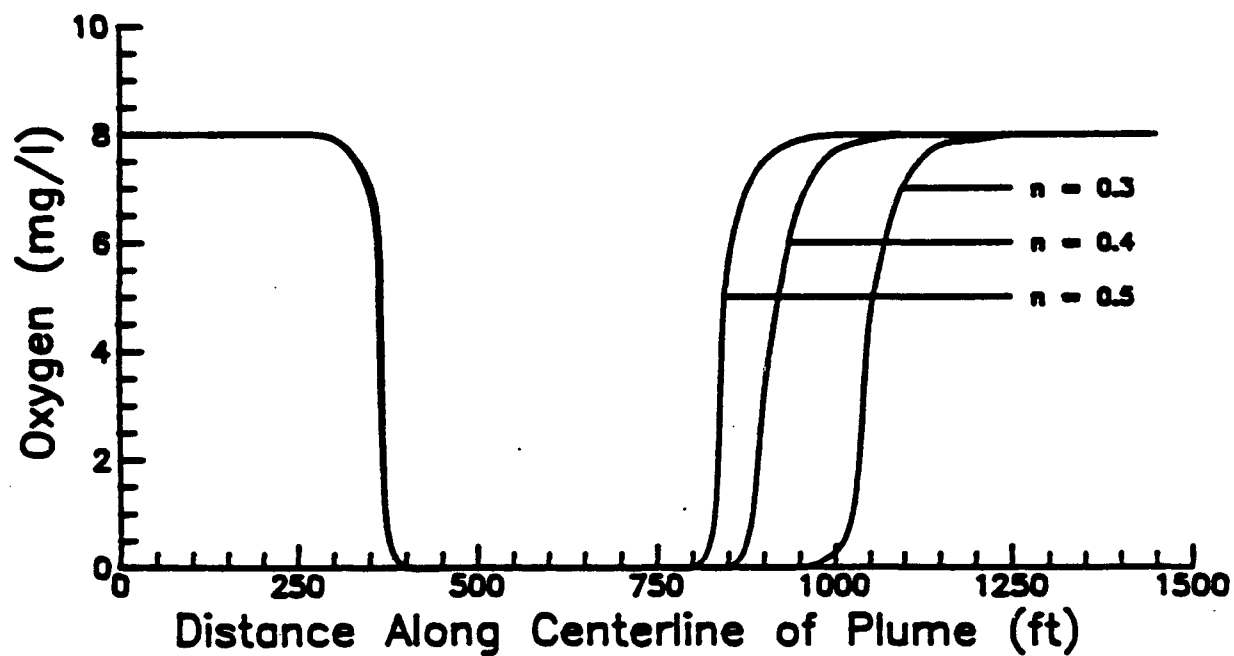
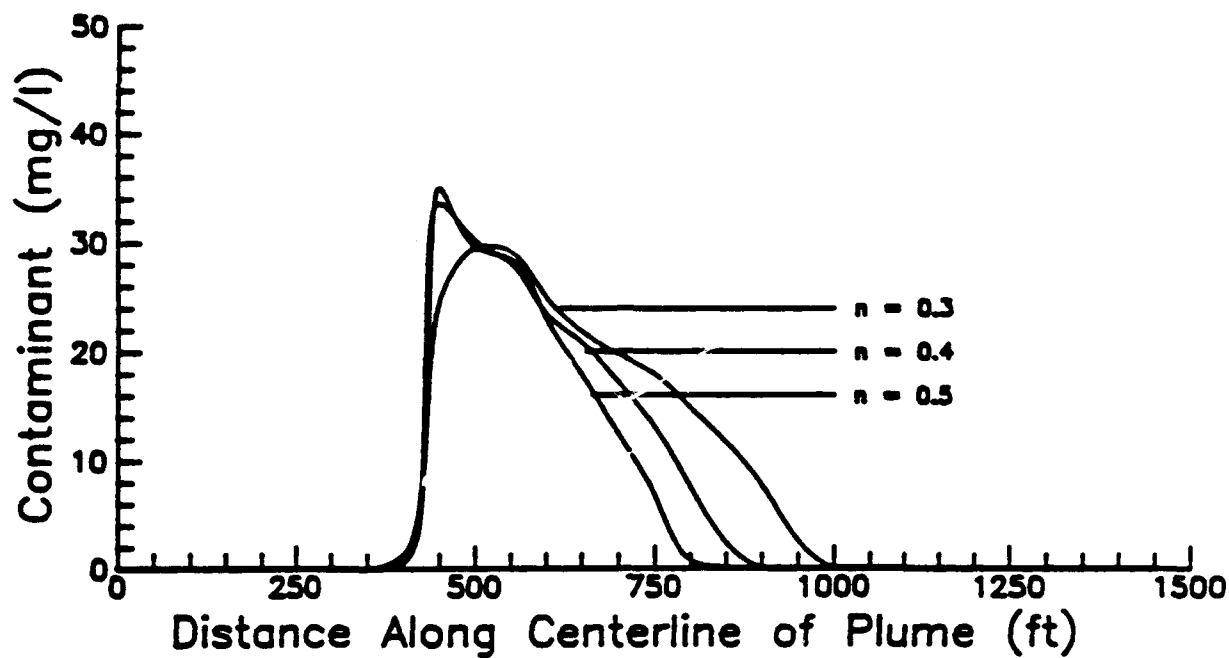


Figure 2.9 – Concentration Distributions for Various Values of Porosity

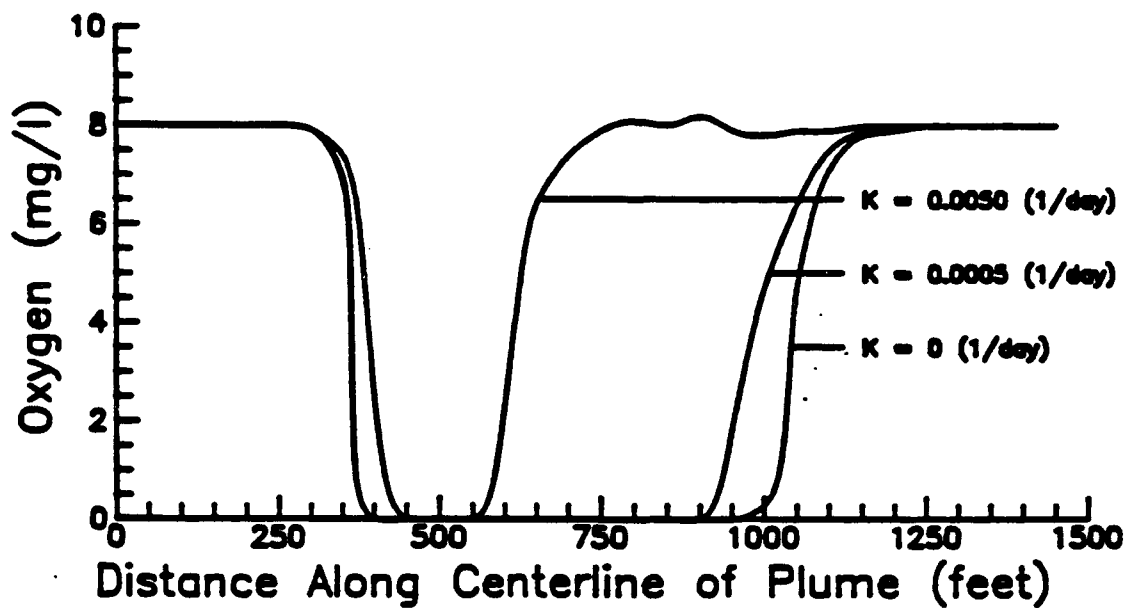
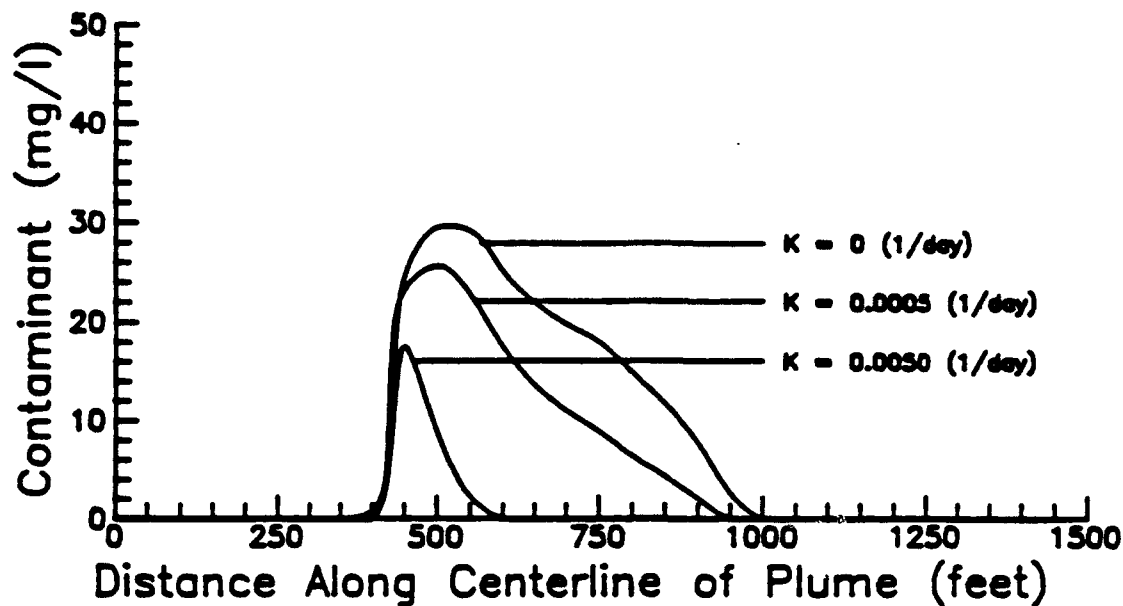


Figure 2.10 – Concentration Distributions for Various Values of the Reaeration Coefficient

Vita

Captain William H. Potts was born on 2 March 1957 in Nampa, Idaho. He graduated from Brown High School, Sturgis, South Dakota and attended Bartlesville Wesleyan College, Bartlesville, Oklahoma, where he earned a Bachelor of Arts degree in Theology in 1980. After spending a year as an assistant minister, he enlisted in the United States Air Force in August of 1981, serving three years as a security specialist at McChord Air Force Base, Washington before being selected for the Airman Education and Commissioning Program. After earning a Bachelor of Science degree in Mechanical Engineering from Texas Tech University, Lubbock, Texas, in 1987, he attended Officer Training School and was commissioned a Second Lieutenant.

Captain Potts served as a mechanical design engineer at March AFB, California and Lajes Field, Azores, Portugal before entering the School of Engineering, Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio in 1992.

Captain Potts is married to the former Kathy Stehman of Greeley, Colorado. They have five children: Micole, John, Aubrey, Ruthanne, and Shannon.

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13. ABSTRACT (Maximum 200 words) This study investigated the natural attenuation mechanisms and some of the parameters affecting those mechanisms in the saturated zone. A literature search revealed numerous studies of various attenuation mechanisms and the associated parameters. Much of the literature emphasized biodegradation as the most promising attenuation mechanism. BIOPLUME II TM , a fate and transport model, was used to simulate the fate and transport of contaminant plume. The effects of the model parameters were investigated by observing the distance a contaminant plume was expected to migrate over a fifty year period. The model simulations indicated that parameters which exhibited significant influence on natural attenuation include hydraulic conductivity, reaeration, and coefficient of anaerobic biodegradation. These three parameters were investigated further to observe how they affected natural attenuation in concert. Results from the model simulations indicated that the lower the value of hydraulic conductivity and the higher the value of aerobic and anaerobic coefficients, the more favorable are conditions for natural attenuation. A regression analysis was performed on the data to generate a mathematical relationship between site parameters and natural attenuation.				
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