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INFLUENCE OF ADSORPTION AND OXYGEN LIMITED BIODEGRADATION ON THE TRANSPORT AND FATE OF A CREOSOTE PLUME: FIELD METHODS AND SIMULATION TECHNIQUES

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by

ROBERT C. BORDEN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

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Abstract

Field monitoring at the United Creosoting Company (UCC) site in Conroe, TX has shown that the shallow aquifer has become contaminated by leakage from two unlined ponds. A plume of hydrocarbon contaminated ground water is present and is contained within a larger plume of elevated chloride concentrations. This difference in size could be due to two processes: adsorption and biodegradation. A series of field tests and computer simulations was performed to identify which processes were limiting the transport of the hydrocarbon. A seven day injection-production test was performed in the shallow semi-confined aquifer at the site and clearly demonstrated that adsorption was not significant in retarding the movement of naphthalene. Loss of naphthalene and paradichlorobenzene during the test suggested that biotransformation of the hydrocarbon could be significant. Previous laboratory studies [Lee and Ward, 1984] had shown the potential for rapid biotransformation of the hydrocarbon when oxygen was added but very minimal transformation in the absence of oxygen. In the shallow aquifer at the UCC site, oxygen is present at low concentrations and could potentially result in limited biotransformation of the hydrocarbon plume. In order to study this phenomenon, a series of numerical models was developed to simulate the transport of oxygen and
hydrocarbon in ground water and resulting biodegradation. Numerical simulations generated with these models suggested that in most ground water environments, microbial kinetics will be rapid relative to mass transport and biodegradation will be limited by the rate of mixing between oxygen and hydrocarbon. The numerical models were then tested by comparing numerical simulations to field data collected at the UCC site and the results of a series of single well push-pull tests designed to measure in situ biotransformation. Finally, the calibrated model was used to compare various alternatives for restoration of the UCC site.
Acknowledgements

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1.0 Description of the Problem

The production of organic chemicals has risen tremendously in the last fifty years. With this rise has come a major threat to the purity of our nations ground waters. In our early history when the major disposal problem was human waste, storage of this waste in unlined pits or burial in the ground was an acceptable disposal method.

Unfortunately, these practices were carried over to the disposal of organic chemicals. These chemicals are often toxic at very low concentrations and degrade very slowly or not at all. This has resulted in a vast number of ground water contamination problems throughout the United States.

An abandoned creosoting site in Conroe, Texas provides a typical example of ground water contamination problems. The site was operated by United Creosoting Company, Inc. from 1946 to 1972 as a wood preserving facility. The primary preservatives used were creosote derived from coal tar and pentachlorophenol dissolved in diesel fuel. The wood preserving process involved first drying the wood under high temperature and pressure followed by application of the preservatives under pressure. This process generates a great deal of waste water which was disposed of in a series of unlined ponds on the property. The majority of the ground water contaminants appear to originate from these
ponds. Following closure, the property was subdivided and sold for use by a bottling company, a small construction company, and further subdivided for a housing development. Several houses were constructed directly over or immediately adjoining the filled in disposal lagoons. A plume of contaminated ground water is currently moving to the southwest under the housing subdivision. The major organic contaminants in the plume are the polycyclic aromatics found in creosote and pentachlorophenol.

The purpose of this research is to develop methods for describing the transport and decay of organic chemicals in ground water with particular emphasis on the contaminants and field conditions present at the United Creosoting site. Two general processes will be considered: adsorption and biodegradation. It is hoped that methods developed at this site will be applicable to a large category of problems including the transport of aromatic and aliphatic hydrocarbons in ground water away from concentrated waste sources.
2.0 Processes Controlling the Transport and Fate of Ground Water Contaminants

Many instances of ground water pollution originate from definable sources. The contaminant plume which emanates from such a source will have a distinct direction, velocity, and spatial distribution. If methods can be developed for predicting the spatial and temporal distribution of the contaminants, then different alternatives for minimizing health risks, environmental damages and costs can be evaluated. The major processes known to significantly affect the transport of common organic contaminants can be grouped into three categories: physical, chemical and biological processes.

Physical processes include advection and dispersion. Advection is the transport of a contaminant by the bulk ground water flow. Dispersion is the spreading of a contaminant front due to molecular diffusion and small scale variations in fluid velocity throughout the aquifer.

The major chemical processes of interest are adsorption, hydrolysis and oxidation-reduction reactions. Adsorption is "the process in which matter is extracted from the solution phase and concentrated on the surface of the solid material" [Weber, 1972].
In most classical waste treatment studies, biological processes are considered to be those processes in which microorganisms use the contaminant of interest as either a carbon source or as an electron acceptor for growth. In this research, biological processes will also be considered to include microbially mediated reactions in which the contaminant may or may not be used for growth.

Most previous attempts at quantifying the transport of contaminants in ground water have relied on a solution of the classical advection-dispersion equation. The general form of this equation is

\[
\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C - vC) + \sum R_i \tag{2-1}
\]

where

- \( C \) = contaminant concentration
- \( t \) = time
- \( v \) = velocity vector
- \( D \) = dispersion tensor
- \( R_i \) = chemical and biological reaction terms

Solutions to this equation have been obtained using a variety of analytical and numerical methods. Thorough reviews of these methods may be found in Anderson [1984] Bear [1979] and Javandel et al. [1984]. The remainder of this chapter will focus on the physical basis of each process and mathematical functions used to describe the process.
2.1 Dispersion

Dispersion, the spreading of a contaminant front as it moves in the ground water is an area of particular controversy at this time. The dispersion process can be most easily described as consisting of three components: 1) molecular diffusion resulting from brownian motion of individual molecules; 2) hydrodynamic dispersion resulting from variations in interstitial pore velocities; and 3) macrodispersion resulting from small scale structural variations in hydraulic conductivity and consequently in velocity. These components combine to form a resultant dispersivity tensor which can frequently be reduced to three main components: longitudinal dispersivity \( (a_l) \) transverse dispersivity \( (a_t) \), and vertical dispersivity \( (a_v) \). Dispersion coefficients \( (D) \) used in the advection dispersion equation are found by

\[
D = a_v^m
\]

where

\[
v \text{ is the resultant velocity scalar}
\]

\[
m \text{ is assumed equal to 1.0}
\]

The physics and mathematics necessary to describe molecular diffusion and hydrodynamic dispersion are well established. Bear [1979] and Fried [1975] provide comprehensive experimental and theoretical reviews of these
processes. The effects of hydrodynamic dispersion and molecular diffusion are not usually significant in the longitudinal spreading of a contaminant front. Laboratory measurements of hydrodynamic dispersivity commonly yield values of 0.01 to 1.0 cm. Theoretical derivations [Bear and Bachmat, 1965] based on interstitial pore velocities agree closely with these values. If a typical value of longitudinal hydrodynamic dispersivity ($a = 0.1$ cm) is used, the width of the breakthrough front can be shown to be only 0.9 m after a travel distance of 100 m.

The significance of the third component, macrodispersion, is the subject of much current debate. The remainder of this section will be devoted to: 1) developing a conceptual framework for the macrodispersion process; 2) examining some of the recent theoretical approaches; and 3) relating these approaches to the available geologic data.

2.1.1 Conceptual Framework

While laboratory measurements of hydrodynamic dispersivity indicate that negligible dispersion should occur, measurements of actual contaminant plumes indicate that substantial spreading of the breakthrough front does occur. Zones of gradually decreasing contaminant concentration have been observed to cover large areas. The width of these zones are often equal to the average distance
traveled. The most popular explanation for this occurrence is that the contaminants are moving rapidly through higher permeability layers resulting in a fingering of the contaminant front. Fully penetrating wells intersecting this front will sample both contaminated and uncontaminated layers resulting in a smoothing of the apparent breakthrough front.

Numerous investigators have studied this problem using various stochastic descriptions of the aquifer permeability. One of the earliest was Mercado [1967] who proposed that an aquifer could be modeled as consisting of \( N \) layers of permeability \( K(i) \) and uniform thickness. Since a contaminant will travel at a velocity directly proportional to \( K \), the fraction of layers contaminated would be:

\[
\frac{\Sigma(K>K_x)}{\Sigma K} = \frac{\text{# layers contaminated}}{\text{total # layers}} = \frac{C}{C(0)} \tag{2-3}
\]

where \( K_x \) is the permeability which would result in an average translation \( X \). If \( K \) is assumed to be normally distributed, then:

\[
\frac{C}{C(0)} = \int_{K_x}^{\infty} \left[ \frac{1}{\sqrt{2\pi}} \exp \left[ -\frac{(K_x - \bar{K})^2}{2\sigma^2} \right] \right] dk \tag{2-4}
\]

where \( \bar{K} \) is the mean permeability.

Substituting the complementary error function
\[
\frac{C}{C(0)} = 0.5 \text{erfc} \left[ \frac{K_x - \bar{K}}{2\sigma} \right]
\]  
(2-5)

where \(\sigma\) is the standard deviation of \(K\).

If equation 2-5 is equated with the 1-D advection dispersion equation of Ogata and Banks [1961],

\[
\left[ \frac{K_x - \bar{K}}{2\sigma} \right] = \left[ \frac{X - V \cdot t}{2\sqrt{D}t} \right]
\]  
(2-6)

and consequently

\[
\lambda_x = \frac{\sigma^2}{K}
\]  
(2-7)

where \(\lambda_x\) is the effective longitudinal macrodispersivity. This indicates that \(\lambda_x\) increases linearly with \(X\).

2.1.2 Theoretical Studies of Macrodispersion

Numerous researchers have investigated the effects of variations in permeability on macrodispersion. In an early study Gelhar et al. [1979] analyzed the effects of dispersion in one dimension for a stratified aquifer. Gelhar et al. concluded that the shape of the breakthrough curve for a pulse input was sensitive to the third and fourth derivatives while no significant errors would be
introduced by eliminating these derivatives for a step input. For the specified boundary conditions:

\[ A_1 \rightarrow A_0 = X \left[ \frac{\sigma}{K} \right]^2 \quad \text{as} \quad X \rightarrow 0 \]

and

\[ A_1 \rightarrow A_\infty = \frac{1}{3} \left[ \frac{L_x}{K^2} \right] \left[ \frac{L_x}{a_t} \right] \quad \text{as} \quad X \rightarrow \infty \]

where \( a_t \) is the hydrodynamic transverse dispersivity and \( L_x \) is the correlation length in the \( x \) direction.

Analyses of the variation of \( \lambda_\ell \) with distance indicated that \( A_\infty \) will increase almost linearly with distance for \( X < \lambda_\ell \) and then converge to within 5% of \( A_\infty \) after 100 \( A_\infty \). To illustrate these results, assume \( \sigma/K = 0.3, a_t = 0.1 \) cm and \( L_x = 2 \) m. Under these conditions \( \lambda_\ell \) will increase linearly for the first 400 m then stabilize at \( \lambda_\ell = 400 \) m after a travel distance of 40 km. If \( a_t \) was 1.0 cm, \( \lambda_\ell \) would stabilize at 40 m after a travel distance of 4 km. Other researchers have also shown the sensitivity of macroscopic \( \lambda_\ell \) to \( a_t \) [Matheron and De Marsily, 1980; Guven, 1983]. Larger values of \( a_t \) buffer the macrodispersion process and cause \( \lambda_\ell \) to converge more quickly.

In the most comprehensive study to date, Gelhar and Axeness [1983] modeled three dimensional flow in a
stratified aquifer and found that when flow is predominantly parallel to the stratification:

1) $A_w = 0.001$ to 0.0001 $A_x$

2) $A_t = 0.007$ to 0.04 $A_x$

3) $A_x$ will stabilize at $X > 10$ to 100 $A_w$

4) vertical and horizontal variations in concentration will be very large near the contaminant source.

5) the behavior of the dispersion process is strongly dependent on the variation in permeability, $\sigma/K$ and the scale of the heterogeneity, $L_x$, $L_y$, and $L_z$.

2.1.3 Geologic Structure

Very little data exists on the small scale spatial variability of aquifer parameters. In a comprehensive survey, Freeze [1975] found that permeability was most commonly log normally distributed with $\sigma/K$ ranging form 0.2 to 2.0 log units. Bakr [1976] analyzed oilfield borehole data and found permeability to be normally distributed with a periodic component vertically.

The most detailed analysis of spatial variations in flow parameters to date was performed by Smith [1981]. Several hundred samples of Quandra Sand were tested for porosity, permeability, compressibility and grain size distribution. The permeability of this uniform sand was shown to be normally distributed. Spectral analysis indicated a distinct
cyclic vertical layering. Horizontal variations in permeability were fit adequately by a simple first order covariance model.

2.2 Chemical Processes

The major abiotic chemical processes which affect the transport of organic contaminants in ground water are adsorption and hydrolysis.

Adsorption is a surface process in which a compound "sticks" to the solid aquifer material. In the case of neutral, nonpolar hydrophobic organics, this stickyness is due to the much higher affinity of the compound for other organics attached to the soil than for the strongly polar water phase. In the case of polar hydrophylic molecules, some attraction may be due to dipole:dipole forces. The attraction due to this mechanism is typically much weaker than for hydrophobic compounds.

Naturally occurring organic material in aquifers is commonly present as a humic-kerogen film over the clay particles. This organic material may originate from organics deposited with the original sediments or from infiltrating rain water. Organic material is most effectively preserved in tight clays where diffusion of oxygen is limited and the redox potential is low.
Hydrolysis reactions can have a major impact on the mobility of organic compounds in aquifers. These reactions are typically pH dependent and catalyzed by metal ions. The pH of most solutions will approach equilibrium shortly after entering an aquifer. In this case, hydrolysis reactions can be modeled as a simple first order decay process.

When attempting to develop models for simulating the adsorption of contaminants in ground water, many early investigators assumed that at low concentrations contaminants move independently of other solutes, the reaction kinetics are fast relative to ground water flow and the natural reactants are uniformly distributed throughout the aquifer. These assumptions allow the reactions to be analyzed using the equilibrium isotherm approach. Under this approach the variation in adsorbed contaminant concentration is described by an adsorption isotherm:

\[ C = f(C) \]  
(2-9)

where \( C \) = concentration of the contaminant in solution and \( \bar{C} \) is the concentration in the nonmobile solid phase. This relationship can be incorporated into the advection dispersion equation by recognizing that

\[ \frac{\partial C}{\partial t} = - \frac{\partial \bar{C}}{\partial t} \]  
(2-10)

and
\[
\frac{\partial \bar{C}}{\partial t} = - \frac{df(\bar{C})}{dC} \frac{\partial C}{\partial t}
\]
(2-11)

Inserting equation 2-11 into the advection dispersion equation
\[
\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C - vC) - \frac{d}{dC} f(\bar{C}) \frac{\partial C}{\partial t} + \Sigma R_i
\]
(2-12)
and rearranging
\[
\frac{df(\bar{C})}{dC} \frac{\partial C}{\partial t} + \frac{d}{dC} f(\bar{C}) \frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C - vC) + \Sigma R_i
\]
(2-13)

If \( \bar{C} \) is a linear function of \( C \) then \( (1 + df(\bar{C})/dC) \) can be replaced by a constant retardation factor (\( R \)). Examination of equation 2-13 reveals that in this special case the adsorbed contaminant will move with an effective velocity, \( v' \) where \( v' = v/R \) and an effective dispersion coefficient \( D' = D/R = a_v v' \). A common method of calculating \( R \) is by the relation [Freeze and Cherry, 1979]
\[
R = 1 + n \cdot K_d/\rho
\]
(2-14)
where \( n \) is the aquifer porosity, \( \rho \) the bulk density, and \( K_d \) the partition coefficient in g contaminant adsorbed/g aquifer.

The use of a retardation factor depends on the following assumptions:

1) Adsorption can be described by a linear relationship between solute and solid phase concentration.
2) The reaction kinetics are fast relative to ground water flow.

3) Natural reactants attached to the aquifer can be assumed uniformly distributed in space.

4) Contaminant transport is independent of other liquid phase organics.

In the following sections, the validity of these assumptions with respect to the transport of trace organics will be considered.

2.2.1 Linear Adsorption

The isotherms most commonly used in ground water studies are the Langmuir, BET and Freundlich. Weber[1972] provides a good description of the theoretical development of these relationships and methods for estimating coefficients in the laboratory.

The Langmuir, BET and many other isotherms reduce to a linear form at low concentrations. This is equivalent to the Freundlich when the exponent n equals 1.0. When this occurs, the change in sorbed concentration with solution concentration can be represented by a partition coefficient (K_d) where:

\[ K_d = \frac{\text{grams solute sorbed per gram sorbent}}{\text{grams solute in solution per gram solvent}} \]
Various researchers have considered the question of when is the $K_d$ approach appropriate. The consensus appears to be that for "hydophobic compounds, if the aqueous phase pollutant concentration is below $1.0 \times 10^{-5}$ molar and less than one half the water solubility, sorption isotherms to natural sediments are linear" [Karickhoff, 1984]. For nonhydophobic compounds, isotherms are also commonly linear at low concentrations.

2.2.2 Reaction Kinetics

Most early investigators assumed that reaction kinetics in an aquifer would be fast relative to the rates of groundwater movement. More recent studies have questioned this assumption. In an early paper, Van Genuchten et al. [1974a] showed that adsorption was much more effective in retarding pesticide movement through soil columns when the pore water velocity was 14.2 cm/d or less. When velocities were greater than this, the column effluent concentration distribution was skewed to the right for an instantaneous pulse input. This behavior has previously been attributed to slow reaction kinetics.

Van Genuchten's results have been confirmed by James and Rubin [1979] using laboratory columns and Pickens et al. [1981] in field tests. James and Rubin correlated the reaction kinetics with the time required for a compound to
move by molecular diffusion into a pore approximately equal to the mean grain size. When studying the transport of reactive (Sr) and nonreactive (I) tracers, Pickens et al. observed much greater spreading of the reactive contaminant than the non-reactive.

Karickhoff [1980] studied the sorption dynamics of river sediments using a specially designed mixing chamber which allowed very rapid and complete contact between the sediment and the bulk solution. Using this procedure, diffusion into soil pores should not limit the reaction kinetics but a strong kinetic effect was still observed. Karickhoff describes the reaction using a two box model which includes a labile phase where adsorption is complete within a few hours and a nonlabile phase where days to weeks are required to reach equilibrium.

2.2.3 Spatial Distribution of Reactants

Natural organic material in aquifers commonly occurs as a film on the surface of clay particles. Because of this association of organics with the clays and the low permeability of clay layers, much of the adsorption capacity of an aquifer may be unavailable or may be only slowly available.
Many researchers have suggested that the presence of clay layers or soil clods may explain the low apparent adsorption observed in some aquifers, but little field or laboratory data is available. Gillham et al. [1984] have proposed a model which may allow the analysis of aquifers in which adsorption is limited by diffusion into clay zones. This model was originally developed to describe the apparent scale dependent dispersion observed during field tests at the Borden landfill. The model assumes that all flow occurs in sand layers and contaminants move in and out of clay layers by molecular diffusion. Simulations with the model show an apparent dispersivity which is dependent on distance traveled and rate of flow.

2.2.4 Transport Dependent on other Contaminants

In the previous sections, transport of organic contaminants was considered to be dependent only on the aquifer material, the contaminant concentration and the aquifer hydraulics. This is probably a reasonable assumption when the concentration of all contaminants is low, but may not be realistic when a number of contaminants or naturally occurring organics are present in the liquid phase.

When there are a number of contaminants present, there may be competition for the available adsorption sites. This
competition can be described using the ratios of the products of the concentrations in the solution phase and the partition coefficient for each compound. This procedure is described in detail by Weber [1972] for Langmuir isotherms.

A second and possibly more important impact of other liquid phase organics is the partitioning of highly hydrophobic compounds between liquid phase organics and solid soil organics. These liquid phase organics may originate as naturally occurring soil humics, as oil globules or micelles. If highly hydrophobic pollutants such as DDT and dioxins adsorb to the liquid phase organics, these pollutants may move through the aquifer with the liquid phase organics and be only weakly retarded by the solid phase organics. West [1984] provides a detailed discussion of the mechanisms of natural humic assisted movement. Tandford [1980] discusses theories relating to micell formation and solubilization.

2.3 Biological Processes

The significance of biological processes on the fate and transport of organic contaminants in the subsurface will depend on several factors:

1) the type and number of organisms present in the subsurface;
2) the ability of these organisms to degrade and/or transform the organic contaminants;

3) the presence of required nutrients; and

4) the kinetics of the degradation process.

2.3.1 Microbial origin and survival

Microorganisms of primary interest in the subsurface may be divided into two categories: 1) foreign organisms which enter from the surface with the contaminant; and 2) indigenous microorganisms already present in the aquifer. Foreign organisms entering aquifers with a contaminant may already be adapted to the contaminant. This would be most likely if the contaminant source was a treatment lagoon or other area receiving a continual input of the contaminant. These organisms, while adapted to the contaminant, may not be capable of survival in the subsurface. Filtration and adsorption by the aquifer material may reduce the rate of microorganism transport, but organism mortality may play a much larger role in limiting the significance of foreign organisms [Corapcioglu and Haridas, 1984]. When the foreign organisms are capable of surviving and reproducing, they may be able to travel large distances [McNabb and Dunlap, 1975].

Early studies of soil microbiology indicated a very rapid drop in microbial population below the soil zone [Alexander,
1977]. This lead many microbiologists to conclude that life below the first few meters of soil was either very limited or nonexistant. More recent studies have shown that quite active, diverse microbial populations do exist in the subsurface, often at great depth. The organisms present appear to be predominantly bacteria [Hirsh and Rades-Rohkohl, 1983] but some eukaryotes have been identified [Ghiorse and Balkwill, 1983]. The indigenous organisms appear to be well adapted to low nutrient, oligotrophic conditions. Many of the organisms identified grow very poorly or not at all under high nutrient conditions yet thrive at low levels of organic carbon [Ghiorse and Balkwill, 1985]. Their morphology is often characterized by the presence of fimbriae and holdfasts allowing attachment to surfaces and possibly more efficient scavaging of nutrients [Hirsh and Rades-Rohkohl, 1983]. Biochemical analyses have indicated the presence of storage granules allowing survival during extended starvation periods [White et al., 1982].

Population densities in the subsurface are typically less than observed in surface soil and aquatic environments, but are still significant. Ghiorse and Balkwill [1983, 1985] observed population densities of approximately $10^6$ cells per gram aquifer material at sites in Louisiana and Oklahoma using epifluorescent microscopy. Other workers have found
comparable cell densities in ground water samples \([10^6\text{ cells/ml - Marxsen, 1981}].\)

2.3.2 Organics Degradation

The rate and extent of biodegradation in ground water may be controlled by environmental conditions, the compound structure and solubility characteristics, the adaptation period, the organization of the microbial community and the specific organisms involved.

Compound structure and solubility characteristics can result in a significant limitation to growth. A number of specific structural properties have been identified which prevent enzymes from acting on the compound. These properties include the presence of amine, methoxy, sulfonate, and nitro groups; chlorine substitutions in the meta position in benzene rings; and the presence of ether linkages and branched carbon chains [Kobayashi and Rittmann, 1982]. Many larger compounds also appear resistant to enzymatic attack. Transfer of the organic pollutants into the cell is also significant in limiting biodegradation. Highly water soluble compounds (log octanol:water partition coefficient less than 1.5) may be limited by their ability to diffuse through the lipid-like cell membrane while extremely insoluble compounds (log partition coefficient greater than 3.5) may be adsorbed by the outer cell wall before they can
enter the region of active enzymatic degradation [Strier and Gallup, 1982].

Degradation may also be limited by the lack of organisms adapted to a compound. In these situations, the rate of adaptation may be the major control, not the rate of degradation. This was demonstrated by Shamat and Maier [1980] who studied the kinetics of chlorinated organics degradation. They showed that maximum specific growth rates for adapted populations were in the range of those observed for domestic waste (0.6 to 2.3/d) but long adaptation periods were sometimes required (10 to 100 d). A large seed population was observed to reduce this lag but could not eliminate it.

Community structure is another major factor in limiting biodegradation. Complete mineralization of a compound to carbon dioxide and water by a single organism does not always occur. Most commonly several organisms are involved in a synergistic relationship. This can result in a complex situation where inhibition of one step results in a build up of waste products and toxicity to the entire process. A significant proportion of biodegradation may also result from cometabolism, a process in which the compound is transformed but the organism does not receive any benefit through carbon and nutrient assimilation or energy gain. The substrate
being cometabolized is probably acted upon by an enzyme with some other function, but the end products of this process cannot be further degraded by the organism. Cometabolism is important since: 1) the products may be more toxic than the parent compound; 2) The products may be more recalcitrant than the parent compound; or 3) the product may provide a substrate for other organisms.

Microbial studies have confirmed that organisms adapted to lower nutrient conditions (oligotrophic bacteria) are frequently more effective in degrading organic pollutants [Poindexter, 1982]. Other organisms which also have been shown to be effective in degrading organic pollutants include the actinomycetes, fungi, phototrophs, and anaerobic bacteria.

Information on biodegradation of xenobiotics by ground water microflora is limited but some studies have been performed, particularly on the degradation of petroleum products, aromatics hydrocarbons, and chorinated solvents and pesticides. Litchfield and Clark [1973] analyzed ground water samples from a variety of aquifers in the United States contaminated by petroleum products. They found hydrocarbon utilizing organisms in all aquifers up to 10^6 cells/ml. Mckee et al. [1972] identified large numbers of gasoline utilizing organisms (5.0x10^4 cells/ml) in a
contaminated aquifer in southern California. Organisms identified included *Pseudomonas* sp. and *Arthrobacter* sp. In a series of papers, workers at Suntech have shown the presence of gasoline utilizing organisms in petroleum contaminated soil and aquifers and concluded that biodegradation of the gasoline was limited by inadequate levels of oxygen, nitrogen, phosphorus and other trace minerals [Jamison et al., 1975; Raymond et al., 1975].

The degradation of naphthalene and other polycyclic aromatics has been studied in a number of systems. Naumova [1960] identified naphthalene utilizing organisms in ground waters near oil and gas bearing formations. Lee and Ward [1984] demonstrated that naphthalene was rapidly transformed in aerobic ground waters but transformation was greatly reduced under anoxic conditions. This result agreed with previous work by Erlich et al. [1982] who found no evidence of anaerobic degradation of naphthalene in an aquifer contaminated by wood creosoting wastes.

Studies of many chlorinated solvents and pesticides have demonstrated that while many are degradable to some extent, degradation rates are often quite low under aerobic conditions. Wilson et al. [1983] studied the aerobic degradation of several solvents including chloroform, trichloroethylene and tetrachloroethylene and found only very
limited degradation. However under methanogenic conditions, Bouwer et al. [1981] found rapid degradation of trichloroethane and tetrachloroethane. Erlich et al. [1982] and Rees and King [1980] have reported evidence of anaerobic degradation of phenols in aquifers.

2.3.3 Growth Limitations and Kinetics

Heterotrophic organisms require organic carbon, suitable electron acceptors and inorganic nutrients for growth. In the subsurface, the organic carbon may originate with the original deposits or may enter with infiltrating rain water. This carbon is available to the microorganisms only very slowly because of the low concentrations present and its recalcitrant nature. The optimum electron acceptor for many organisms, oxygen, is usually present only near the water table and decreases with depth. Other electron acceptors including nitrate, sulfate and carbon dioxide will then be used by subsurface organisms. The primary inorganic nutrients, nitrogen and phosphorus, are commonly found in aquifers but may not be available to the organisms due to strong binding to the surface of clay particles. Under the conditions typical of many shallow aquifers, heterotrophic organisms will be primarily limited by the type and quantity of organic carbon although lack of suitable electron acceptors may also limit growth.
Over the past forty years, numerous methods have been applied to predict the growth and decay of microorganisms in surface waters. The most popular model was originally proposed by Monod [1942] and has since been used in the analysis of sewage treatment plants, streams, lakes and estuaries. Monod's model takes the following form:

\[
\frac{dX}{dt} = \frac{\mu X}{K+C} - bX \tag{2-15}
\]

where
- \( X \) = microbial concentration (mg/l)
- \( \mu \) = maximum specific growth rate (1/day)
- \( C \) = limiting nutrient (mg/l)
- \( b \) = microbial decay rate (1/day)
- \( K \) = substrate half saturation constant (mg/l)

Growth is assumed to be a hyperbolic function of some limiting nutrient. Microbial decay is assumed to be a constant independent of other environmental conditions. This model predicts that as nutrient concentrations drop, the net growth rate will approach zero and eventually become negative. For a population to survive, the long term growth rate must be greater than or equal to zero; consequently, the limiting nutrient concentration may not fall below some minimum (\( C_{\text{min}} \)) where:

\[
C_{\text{min}} = \frac{Kb}{\mu - b} \tag{2-16}
\]
Monod's model was developed and tested on organisms adapted to high nutrient conditions. Recent studies in aquifers and in the open ocean suggest that there may exist a class of microorganisms that do not follow this classic model. These organisms are commonly referred to as oligotrophs and have been shown to survive for long periods with little or no food. Oligotrophs also appear to be inhibited by high concentrations of food. Ishida and Kadota [1981] isolated organisms which grew well in 5 mg/l trypticase and unamended lake water but were inhibited by higher doses of organic carbon. Law and Button [1977] studied a marine coryneform bacterium which showed the ability to enter a resting stage under starvation conditions. At medium to high nutrient conditions, these organisms lost organic constituents and urea to solution, but at lower nutrient conditions leakage stopped and cell yield stabilized.

Concentration of organics at solid surfaces may also aid some organisms when organic carbon is low. Kefferd et al. [1982] identified two different mechanisms by which bacteria could scavenge organics from solid surfaces. Subba-Rao and Alexander [1982] found that the presence of clay particles increased mineralization of benzylamine at moderate concentrations (20 mg/l) but reduced mineralization at low concentrations (20 to 200 ug/l) presumably due to irreversible adsorption.
2.4 Summary

Much research has already been performed on the individual effects of dispersion, adsorption and biodegradation on the transport and fate of organic contaminants in ground water under highly controlled conditions. In this research, the emphasis is on identifying the relative importance of these processes at an actual hazardous waste site and on the synergistic and antagonistic effects of these processes.
3.0 Objectives

Workers at Rice University began studying the United Creosoting Company, Inc. (UCC) site in 1982. Early efforts were aimed at characterizing the extent of ground water contamination, the local hydrology and geology, and the major chemical and microbiological processes affecting the contaminant plume. Monitoring of the contaminant plume showed that several of the organic contaminants were mobile and moving with the ground water [Bedient et al., 1984]. Laboratory work demonstrated the presence of an adapted microbial population capable of degrading many of the polycyclic aromatics present in creosote. Degradation of these aromatics was shown to be rapid in the presence of molecular oxygen but to be greatly inhibited without external oxygen addition [Lee and Ward, 1984].

These past studies have demonstrated the potential significance of adsorption and biodegradation on the transport of creosote wastes in ground water. The objective of this research was to determine the actual significance of these processes in the field and to develop modeling techniques for accessing and predicting their impacts. The specific objectives involved include:

1) Use a three well injection production system to study the major processes affecting the transport and fate of
contaminants at the UCC field site and to evaluate the suitability of this type of test for use at other hazardous waste sites. Processes of greatest interest are adsorption and biodegradation.

2) Develop a simple, two dimensional model to simulate the fate and transport of organic contaminants undergoing oxygen limited biodegradation. The model should include the effects of advection, dispersion, adsorption, atmospheric reaeration, and microbially mediated degradation.

3) Test the transport model against field data from the UCC site and data collected during a series of push-pull tests designed to measure enhanced in situ biodegradation.

4) Examine management strategies for minimizing the risks associated with ground water contamination at the United Creosoting Company, Inc. Superfund site.
4.0 Field Site Description

All field work performed as part of this research was performed at the United Creosoting Company, Inc. site in Conroe, Texas. This site has been under study by the National Center for Ground Water Research (NCGWR) at Rice University and the R.S. Kerr Environmental Research Laboratory (RSKERL) of the U.S. Environmental Protection Agency since 1982. Research at the site has been aimed at characterizing the major physical, chemical and biological processes affecting the transport and fate of organic contaminants in ground water. In this section, a brief history of the site is provided along with a summary of past work relating to the subsurface geology, hydrology, chemistry, and microbiology. Much of the data on the site history, geology and hydrology is taken from the Final Site Investigation by Roy F. Weston [1985] and is summarized here for information purposes.

4.1 Site History

The UCC site was operated by the United Creosoting Company, Inc. from 1946 to 1972 as a wood preserving facility. In the summer of 1972 the facility was closed and the major equipment removed. Between 1972 and 1977 the land was subdivide and sold off for use by the Conroe Construction Company, Clarke Distributing Company and for
development of the Tanglewood East subdivision. An inspection of the site by TDWR in July 1977 revealed that Tanglewood East was under construction on the western portion of the property and the former ponds had been drained and were being backfilled. Construction of Clarke Distributing Company started in 1978. During the summer of 1980, citizens complained of creosote odors from soils obtained at the site and used on various road projects around Montgomery County. Based on these complaints, an investigation was begun at the site in 1981. Three ground water monitoring wells were installed and soil and ground water samples taken. This investigation and later studies resulted in placement of the site on the National Priorities List of the Comprehensive Environmental Response, Compensation and Liability Act on September 1, 1983. A remedial investigation was begun by TDWR in 1984.

Analysis of contamination at any site will require knowledge of the origin the contaminants. At a facility no longer in operation, such as the UCC site, this type of information is not commonly available and must be extracted from other facilities currently in operation. Wood treating operations similar to the UCC facility typically consist of three major areas: a pole yard for storage of treated and untreated wood, a work area and a series of impoundments for disposal of waste water. The major equipment used includes
pressure retorts, a creosote still, various pumps, work tanks, and equipment for moving the wood. Many wood treating operations use both creosote and pentachlorophenol (PCP). The PCP is typically applied using diesel oil as a carrier. The treatment solution for both processes is generally referred to as the "oil". The typical treating operation involves first drying the wood to remove water and wood sugars from the sap wood and then replacing these liquids with the "oil". The drying operation is performed by first placing the wood in the retorts and then alternating high pressure stream and then vacuum until the liquids are removed. The retort is then filled with "oil" under pressure for approximately 12 hours. The drying operation generates a great deal of waste water containing wood sugars, inorganic salts from the wood and treating oil carried over from previous treatment cycle. This water was typically disposed of in ponds on the site property. Two sets of ponds are normally used: one for creosote and one for PCP. Creosote is heavier than water and is collected from the pond bottom and recycled. PCP present in the diesel oil floats and is also collected and reused.

Examination of areal photographs taken while the United Creosoting Company was in operation indicates that many of the facilities common to other creosoting operations were also used at this site. A creosote still, pressure
cylinders and two ponds are clearly visible. Field sampling of the soils and ground water has confirmed the presence of both PCP and creosote compounds indicating that both preservatives were used at the site. Monitoring of sediments within the former ponds suggests that the smaller western pond was used primarily for disposal of PCP wastes while the larger eastern pond was used for the disposal of creosote wastes. The major ground water contaminants are thought to have originated in these two ponds.

4.2 Site Geology and Hydrology

The UCC site is located in the Gulf Coastal Plain province of Texas. The Bureau of Economic Geology [1968] has characterized the surficial geology as unconsolidated sediments in alluvial fan deposits. These sediments are part of the Willis sand, the coarsest of the Pleistocene formations. This classification has been questioned by Rogers [1984] who suggested that the near surface sediments at the site are part of a prograding delta complex. The geology of the site is extremely complex consisting of interbedded discontinuous sand and clay lenses. These lenses can be grouped into four generalized geologic units. The first major unit encountered is a reddish brown sandy clay which reduced the infiltration from the former ponds and greatly restricts the recharge of rainwater to the
underlying formations. Underlying the surficial clay is a shallow water bearing sand which is sometime subdivided into two partially connected hydrologic units by a thin discontinuous clay. Water level and chemical measurements in these two zones indicate that they are interconnected. The upper portion of this shallow sand unit is unconfined while the lower portion appears to be semi-confined. Below the shallow sand unit is a thick impermeable clay which provides a hydrologic barrier preventing downward migration of contaminants to a deeper apparently continous sand. A north-south section through the site is shown in figure 4-1.

All work by Rice University has been restricted to the shallow unconfined and semi-confined zones. The location of monitoring wells penetrating the unconfined and semi-confined zones are show in Figure 4-2. Flow in the unconfined zone is to the south with a gradient of approximately 0.6%. The average permeability of this zone is 0.74 m/d based on slug tests in selected wells. Flow in the semi-confined zone is to the southwest. The permeability of this zone appears to be somewhat higher but has not been accurately measured.

4.3 Site Chemistry

The water chemistry of the shallow unconfined and semi-confined zones at the UCC site has been decribed by various
workers including Bedient et al.[1984], Wang et al.[1984] and more recently Weston [1985]. Their major findings are summarized here.

The natural ground water in the area is generally very soft, acidic and contains low dissolved solids. Well RU-3 is uncontaminated, has a pH = 4.0, alkalinity of zero, conductivity = 88 μmho/l and inorganic chloride of approximately 10 mg/l. The background dissolved oxygen is variable and ranges from 2.5 to 3.5 mg/l.

In the immediate vicinity and to the southwest of the former ponds, a plume of contaminated water is present. This plume is most easily identified by elevated chloride concentrations which range from background to a maximum of 150 mg/l. Within the chloride plume is a region of elevated organic contaminants, primarily polynuclear aromatic hydrocarbons (PNA) such as naphthalene, anthracene and phenanthrene. Naphthalene ranges from 10% of its solubility in water near the ponds (3.5 mg/l) to the analytical detection limit. PCP is present near the former ponds at trace levels (20 μg/l) but transport appears to be limited, possibly due to adsorption on to the soil matrix. Dissolved oxygen is close to zero in all areas where the PNA are present and rises to background at the perimeter of the chloride plume. The alkalinity and pH of the contaminant
plume is similar to background. Inorganic nutrients such as nitrogen and phosphorus species are in the 1.0 mg/l range. These high levels are probably due to the former ponds. Dissolved sulfide is low throughout the site. Dissolved iron levels range from 0.5 to 2.0 mg/l. There appears to be a weak correlation between dissolved iron and low dissolved oxygen in the contaminant plume. This indicates that, in some locations, iron may have been used as an alternative electron acceptor although the low levels of dissolved iron present suggest that iron reduction was not a major factor in the degradation of the wood sugars and hydrocarbon.

4.4 Site Microbiology

The UCC site is microbiologically very well characterized. Researchers from Rice University, EPA, Oklahoma State University, Cornell University and Florida State University have performed microbial studies on ground water and aquifer samples collected at the site. Wilson et al. [1983] describe the aseptic sampling technique used. The subsurface microflora at the site appears to be dominated by bacteria with few eucaryotes. Microbial populations are approximately $10^6$ to $10^7$ cells per gram aquifer material in contaminated areas with somewhat lower cell counts in uncontaminated areas [Webster et al., 1985].
Anywhere from zero to ten percent of the cells are metabolically active as indicated by a specialized staining technique [AOINT staining procedure, Webster et al., 1985]. Bacteria present below the water table in contaminated areas exhibited unbalanced growth indicated by the formation of poly beta-hydroxy alkanoate (PHA) storage granules [Smith et al., 1984].

Organisms in the contaminated areas appear to be well adapted to the wastes. Wilson et al. [1985] found rapid disappearance of naphthalene, 1 and 2-methylnaphthalene, dibenzofuran, fluorene and acenaphthene from contaminated aquifer material (below detection limit after one week) but very minimal disappearance in aquifer material from a pristine area on the site. Microbes have been isolated from aquifer material and ground water which could utilize anthracene, dibenzofuran, fluorene, and naphthalene as a sole carbon source. Pentachlorophenol was degraded although no organisms were isolated which could use PCP as a sole carbon source [Lee et al., 1984]. Lee and Ward [1984] demonstrated that lack of oxygen could limit degradation. Ground water samples treated with oxygen showed a rapid drop in all compounds to less 20 µg/l in 20 days. Samples maintained under a nitrogen atmosphere showed greatly reduced rates of disappearance. The small amount of degradation that did occur was probably due to the
introduction of oxygen during sample collection. Addition of inorganic nutrients (nitrogen, phosphorous and other trace nutrients) resulted in a slight increase in rates of disappearance.

The effect of oxygen limitation may also be examined by comparing oxygen and hydrocarbon concentrations in the sampling wells. Figure 4-3 shows observed oxygen and naphthalene concentrations in wells penetrating the contaminant plume (indicated by elevated chloride concentrations). Whenever oxygen is present above 0.3 mg/l, naphthalene is less than 100 μg/l. This data combined with the previous laboratory studies of Lee and Ward [1984] suggests that at the UCC site, the microorganisms will degrade naphthalene and presumably other hydrocarbons to below 100 μg/l whenever oxygen is present. There were no locations where high concentrations of oxygen and naphthalene were simultaneously observed indicating that the microbial kinetics at high concentrations are rapid relative to naphthalene and oxygen transport at the UCC site. The low levels of naphthalene and oxygen observed in some wells may be due to stratification in the aquifer (mass transport limitation) or due to the presence of some lower limit for degradation (microbial kinetic limitation). Identification of these limits will require much additional work and is beyond the limits of this research.
FIGURE 4-3

Observed Oxygen and Naphthalene Concentrations in wells penetrating the chloride plume
5.0 Field Measurement of Adsorption

The major objective of this portion of the research was to study in situ the relative importance of adsorption and biodegradation on the transport and fate of the organic contaminants present at the UCC site. A secondary objective was to evaluate the utility of this type of field testing for characterizing these processes at a typical hazardous waste site. In order to achieve these objectives, a three well injection-production test was performed at the UCC field site in Conroe, Texas. During the three well test chloride, a non-reactive tracer, and two organic compounds, naphthalene and paradichlorobenzene, were injected into a center well for twenty-four hours followed by clean ground water for six days. Ground water was continuously produced from two adjoining wells and monitored to observe the breakthrough of these compounds. Naphthalene was used as an organic tracer because: 1) it has moderate potential for adsorption; 2) it is readily biodegradable; 3) the microorganisms at the UCC site have been previously exposed to naphthalene; and 4) naphthalene is the most common organic contaminant in the aquifer. Paradichlorobenzene (pDCB) was also used as an organic tracer because: 1) it has a potential for adsorption similar to naphthalene; 2) it is more refractory; and 3) pDCB has never been observed at the UCC site. Data from the three well test was analyzed by
plotting normalized breakthrough curves and comparing the moments of the chloride and organics distributions.

5.1 Field and Laboratory Procedure

After many months of negotiations with the City of Conroe, EPA-Dallas, and the Texas Department of Water Resources (TDWR), permission was finally obtained for the three well injection-production test. The system finally approved for the test included pumping from the ground to a self contained treatment system. The treatment system included activated carbon, filtration and ion exchange and was designed to remove organics to less than 10 µg/l and chloride to background. Field testing showed naphthalene and pDCB were removed to below detection limits. The injection-production-treatment system used in the three well test at the United Creosoting Site is shown in Figure 5-1. Organic and inorganic tracers were prepared in solution, mixed with water produced from wells RU-28 and RU-29 (Figure 4-2) and then reinjected into the semi-confined aquifer via well RU-1 for 24 hours beginning at 4:50 p.m. on June 21, 1984. At the end of the 24 hours, the addition of the organic and inorganic tracers ended but pumping and reinjection of ground water was continued for an additional 6 days. All produced water was passed through the carbon and deionization columns prior to injection. The combined
flow rate from wells RÜ-28 and RU-29 ranged from 1.25 to 1.9 liters/min during the 7-day test.

Water was withdrawn from wells RÜ-28 and RU-29 using two stainless steel, 1/3 hp Grundfos submersible pumps. Water discharged from each pump passed through approximately 9 m of 2.5 cm threaded PVC pipe to a sampling tap and flow control valve. Prior to reinjection, the water was treated in an 0.2 m by 1.4 m activated carbon column (ICI Darco 12x20 mesh), an acid-base deionization column (Continental model 2921 mixed bed), and a 5 μm polypropylene cartridge filter.

Water samples from the production wells were taken from the PVC discharge lines after first wasting 100 to 200 mls to a collection vessel. Water samples from the injection stream were taken from the bottom of well RU-1 using a dedicated masterflex pump. All glassware was thoroughly washed and baked at 500°C prior to use.

Depth to water and conductivity were measured using a YSI 33 conductivity meter. Chloride was measured using a Chemetrics Kit (Model K2020) by the mercuric nitrate method. Dissolved oxygen was measured using a YSI model 57 oxygen meter.
Organics analyses were performed by gas chromatography after first concentrating 100 ml samples using Sep-Pak C_{18} cartridges (Waters) and then extracting the cartridges with 1.0 ml methylene chloride. A Tracor 560 gas chromatograph was used with a SGE DB-5 capillary column and FID detector. Helium carrier gas flow was 1.7 ml/min and the injection size was 1.0 μl. Detector and injection temperatures were 350°C and 250°C. The temperature program was 80°C for 5.0 minutes then increased 10°C per min. The retention times were 6.8 min for pDCB and 10.9 min for naphthalene.

The tracer injected during the first 24 hours was prepared by diluting a concentrated stock solution with produced water at a ratio of 1:15. The concentrated stock solution was prepared in the laboratory by adding an excess of pDCB and naphthalene to 375 liters deionized water and mixing for 24 hours. The chloride tracer was then added as a molar ratio of 1.5:1 calcium to sodium chloride. The stock solution was then passed through a 5 μm cartridge filter prior to transport to the field site in 19 liter glass jugs.

The calcium to sodium chloride ratio used in the tracer test was intended to match the ratio in the native ground water to reduce swelling of the clays. Some swelling of the clays probably did occur since a small reduction in flow
from the production wells occurred at approximately the same time as the chloride breakthrough. Flow rates gradually dropped during the course of the test from 1.9 to 1.25 liters/min.

During the seven days of the pump test, approximately 51% of the pDCB, 77% of the naphthalene and 67% of the injected chloride was recovered. After completion of the test, the injection-production-treatment system was operated for an additional twenty days. At the end of the twenty days samples were collected and analyzed by Rice University. These analyses showed that the area surrounding RU-1 contained no measurable pDCB and naphthalene concentrations were below the levels present prior to the field test. Later sampling as part of the Superfund characterization study confirmed that pDCB was below the analytical detection limit of 10 μg/l and naphthalene concentrations were less than levels previously observed by Rice University and the Texas Department of Water Resources.

5.2 Results and Statistical Data Analysis

Chloride, conductivity, pDCB and naphthalene concentrations observed during the course of the test are shown in Appendix A1. Breakthrough curves for chloride, conductivity, pDCB and naphthalene in each well (RU-28 and RU-29) are plotted in Figures 5-2a to 5-2d. No data is
FIGURE 5-2c
VARIATION IN NAPHTHALENE VERSUS TIME

NAPHTHALENE CONCENTRATION (ppb)

FIGURE 5-2d
VARIATION IN p-DICHLOROBENZENE VERSUS TIME

p-DICHLOROBENZENE CDNC. (ppb)
provided on the variation in dissolved oxygen (D.O.) since reaeration probably occurred in the wells (D.O. was strongly correlated with depth to water in each well).

As can be seen from the figures, RU-29 responded much more strongly to the injected tracers than RU-28. This is thought to be due to a high permeability zone to the north of RU-28 which would result in a dilution of the tracers. Analysis of slug test results and drawdown data taken during the seven day test confirms the higher permeabilities in the northern well, RU-28. Numerous attempts were made to simulate the flow field during the field test using commonly available transport models. A semi-analytical model was initially employed which calculates breakthrough curves by integrating along the stream lines. This approach assumes that the aquifer is homogeneous and could not predict the weak response in RU-28. Attempts were also made to simulate the field test using the USGS Solute Transport Model (Konikow and Bredehoeft, 1978) using both uniform and non-uniform permeability distributions. No combination of permeabilities could be found which adequately matched the observed flow rates, drawdowns and chloride breakthrough.

In order to overcome the difficulties inherent in studying transport in a highly nonhomogeneous aquifer, an alternative approach was selected which requires a minimum
of assumptions about transport processes in the subsurface. This approach involves the comparison of normalized recovery curves and analysis of their statistical properties. Because of the weak response of RU-28 to the tracers, most efforts have been focused on the analysis of the data from RU-29.

Direct comparison of the breakthrough curves for naphthalene, pDCB, chloride, and conductivity is complicated by differences in injection and background concentration. A convenient method of comparing data in these conditions is to plot the normalized concentration \( f \) where:

\[
f = \frac{\text{observed concentration} - \text{background concentration}}{\text{injection concentration} - \text{background concentration}}
\]

The observed background and injection concentrations are shown in Table 5-1 along with the statistical moments of the normalized concentration distributions for each compound. The statistical moments were calculated as

\[
E(0) = \int f(v)dv \quad (5-1)
\]

\[
E(v) = \int vf(v)dv \quad (5-2)
\]

\[
\mu = \frac{E(v)}{E(0)}
\]

where

\( f(v) = \) concentration of compound

\( v = \) produced volume

\( \mu = \) mean of distribution
Table 5-1

Summary of Normalized Recovery Data for 3-Well Test

Well RU-29

<table>
<thead>
<tr>
<th>Moments</th>
<th>Chloride</th>
<th>Conductivity</th>
<th>Naphthalene</th>
<th>pDCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0</td>
<td>31.80</td>
<td>36.49</td>
<td>11.10</td>
<td>16.68</td>
</tr>
<tr>
<td>E1</td>
<td>3650.</td>
<td>4287.</td>
<td>1312.</td>
<td>1848.</td>
</tr>
<tr>
<td>$\mu = \frac{E1}{E0}$</td>
<td>114.8</td>
<td>117.5</td>
<td>118.2</td>
<td>110.8</td>
</tr>
<tr>
<td>$R_{Cl}$</td>
<td>1.00</td>
<td>1.02</td>
<td>1.03</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Values used to calculate normalized concentration

- Background Conductivity = $303.9 \pm 60$ $\mu$mho/l
- Injection Conductivity = $2243. \pm 389$ $\mu$mho/l
- Background Chloride = $46.4 \pm 9$ mg/l
- Injection Chloride = $507. \pm 10$ mg/l
- Background Naphthalene = $113.8 \pm 54$ $\mu$g/l
- Injection Naphthalene = $1580. \pm 240$ $\mu$g/l
- Background pDCB = 0.0 $\mu$g/l
- Injection pDCB = $3500. \pm 650$ $\mu$g/l
The cumulative volume of water produced from each well was used as the ordinate in our analyses to eliminate the effects of small variations in pumping rate. Equations 5-1 and 5-2 were integrated between zero and the final produced volume using a Simpson's rule integration. Normalized concentration distributions are shown in Figure 5-3 for chloride and conductivity and in Figure 5-4 for chloride, naphthalene and pDCB.

Analysis of Figure 5-3 for RU-29 shows that the normalized concentration curves for chloride and conductivity are very similar as would be expected. The total volume under the curves (zero moment) and centroids of each distribution are also similar, although the conductivity curve does contain a slightly larger volume and delayed centroid. This is due to the distinct tailing of the conductivity curve. The reason for this tailing is unknown but could be due to exchange of cations on the clays. To eliminate the possible effects of ion exchange, chloride was used as the tracer in the analysis of the organic adsorption data.

The breakthrough curves for naphthalene and pDCB are also similar to each other and have the same general appearance as the chloride curve. Average retardation factors can be calculated by a variety of methods including comparing the
Figure 5-3
Normalized Concentration for Chloride and Conductivity

Chloride

Normalized Concentration

Conductivity

Produced Volume (cu. ft.)
FIGURE 6-4
NORMALIZED CONCENTRATION FOR
CHLORIDE, NAPHTHALENE, pDCB
WELL RU-29

CHLORIDE
NAPHTHALENE
pDCB

NORMALIZED CONCENTRATION

PRODUCED VOLUME (cu. ft.)
relative positions of the peak concentrations, the 50% breakthrough points or the first arrival of chloride and the adsorbing contaminant. The disadvantage of these procedures is that they are strongly dependent on only a few data points. The method chosen in this analysis was to compare the relative positions of the centroids of mass of chloride and the organic contaminants, naphthalene and pDCB \[ R = \frac{\mu(\text{organic})}{\mu(\text{chloride})} \]. This procedure uses the maximum available data and should give an unbiased estimate of the retardation factor. The estimated retardation factors for naphthalene and pDCB based on the normalized concentration curves are:

Naphthalene Retardation Factor - RU-29 = 1.03
pDCB Retardation Factor - RU-29 = 0.97

These low retardation factors clearly demonstrate that adsorption in not a major process controlling the transport of naphthalene and pDCB at the UCC Site. The low observed retardation cannot be explained as a kinetic effect since there is no significant tailing of either the naphthalene or pDCB curves. Various theoretical and experimental arguments have been proposed which indicate that when sorption-desorption kinetics are significant, the breakthrough curves will show a distinct tail [Valocchi, 1985; Pickens et al., 1981]. The low observed retardation is thought to be due to
the very low organic carbon content of the aquifer at the UCC Site. All measurements of soil organic carbon taken at the site during the Superfund characterization were below the analytical detection limit of 0.01% by weight.

An effective retardation factor for pentachlorophenol (PCP) of 3.5 was estimated during the Superfund characterization by comparing the transport of PCP with chloride in the ground water [Weston, 1985]. This retardation factor is equivalent to a partition coefficient (Kd) of 0.44 cm³/g. The effective Kd for naphthalene and pDCB can then be estimated if the ratio of Kd's is equal to the ratio of the octanol-water partition coefficients. By this procedure the effective retardation factors for naphthalene and pDCB were both estimated to be 1.06. These retardation factors are well within the range observed in the field.

The major difference between the chloride and organic curves is the much lower total area. Only 35% as much of the injected naphthalene and 52% as much of the pDCB were recovered as compared to chloride. This cannot be due to adsorption since there was no significant delay in the centroids of the naphthalene or pDCB curves. In fact, the centroid of the pDCB curve arrived slightly earlier than the chloride centroid. The lower total area under each curve
combined with the lack of appreciable retardation suggests the destruction or transformation of the organic compounds. Previous field studies at the UCC Site have shown that an active microbial population is present and is adapted to naphthalene [Lee et al., 1984a]. Paradichlorobenzene has never been observed at the site and is generally thought to be more refractory. The lower percent recovery of naphthalene than pDCB appears to agree with this.

Some indication of the potential for biodegradation can be obtained from mineralization studies performed by M. Lee under the direction of C.H. Ward [Lee, 1986]. These studies were performed on ground water samples collected from well RU-29 during the three well test. Ground water was amended with radiolabeled naphthalene and pDCB and monitored for the appearance of radiolabeled carbon dioxide. This type of study only provides information on the complete transformation of the organic compound to carbon dioxide and other inorganic products. Mineralization studies provide little information on the transformation of a compound to other organic intermediates. Results from the mineralization studies are shown in Table 5-2. Details of the experimental procedure can be found in Lee [1986]. Mineralization of naphthalene was rapid throughout the test and appeared to be dependent on concentration. The extent of naphthalene mineralization ranged from 3.8% to 34.3%
### Table 5-2
Mineralization of Naphthalene and pDCB in Ground Water from RU-29

<table>
<thead>
<tr>
<th>Sample Time (hrs)</th>
<th>Concentration (μg/l)</th>
<th>Percent Mineralized after 24 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Naphthalene</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>85</td>
<td>3.8</td>
</tr>
<tr>
<td>63</td>
<td>470*</td>
<td>22.3</td>
</tr>
<tr>
<td>111</td>
<td>270</td>
<td>34.3</td>
</tr>
<tr>
<td>159</td>
<td>70</td>
<td>9.0</td>
</tr>
</tbody>
</table>

| **pDCB**         |                      |                                 |
| 2                | 0                    | 0.68                            |
| 63               | 910*                 | 0.52                            |
| 111              | 450                  | 2.04                            |
| 159              | 35                   | 0.62                            |

* Estimated Concentration from two nearest observations.

after 24 hrs incubation. Mineralization of pDCB was much lower but also appeared to be concentration dependent and ranged from 0.6 to 2.0% after 24 hrs. The high naphthalene mineralization rates clearly confirm the potential for significant loss of naphthalene during the three well test. The slow mineralization of pDCB is somewhat surprising considering the large amount of pDCB apparently lost during the test. This apparent disparity can be easily explained if two factors are considered.

1) Only the fraction of the microbial population suspended in the groundwater was measured in the mineralization studies. The large microbial population present attached to the soil matrix could result in much higher rates of mineralization.

2) The mineralization studies only measured that fraction converted to carbon dioxide. Any pDCB converted to other organic intermediates would not be measured.

Disappearance of pDCB has been observed at other sites with little mineralization. Hutchins et al. [1984] observed greater than 98% removal of pDCB in a series of column tests used to study the loss of trace organics during rapid infiltration, yet observed only 6% mineralization in microcosms of soil used in the columns. The microcosm incubation time was approximately equal to the hydraulic residence time of the columns.
5.3 Summary

A three well injection-production test using an inorganic tracer, chloride, and two organic compounds, naphthalene and paradichlorobenzene (pDCB), was successfully performed at the United Creosoting Company, Inc. (UCC) superfund site in Conroe, Texas. Implementation of the test was initially delayed by the need to obtain approval from the Texas Department of Water Resources, the U.S. Environmental Protection Agency and the City of Conroe. Disposal of the contaminated ground water was a major stumbling block and was overcome by the development of a self contained system for the treatment and reinjection of the contaminated water. If this type of testing is to be performed at any other sites, on site treatment and disposal should be planned from the outset. Also, installation of additional non-pumping monitoring wells may aid in interpretation of the data.

Results from the field test showed a large increase in chloride, naphthalene, and pDCB in well RU-29 approximately 24 hrs after injection of the these compounds into well RU-1. Well RU-28 showed a much weaker response to to the injection. The large difference in response between these two wells is thought to be due to variations in permeability within the aquifer. Several different analytical and numerical models were used to try to explain the large
difference in response between these two wells. No simple combination of permeabilities could adequately match the observed chloride distributions in both wells. The exact mechanism which caused the strong response of RU-29 and the weak response of RU-28 is still unclear although variation in the permeability is thought to be the primary cause.

Analysis of the field data indicates that there was no significant retardation of the two organic compounds. Retardation factors for naphthalene and pDCB were 1.03 and 0.97, respectively. These retardation factors were calculated as the ratio of the centroid of the normalized organic and chloride concentration distributions. There is no evidence to indicate that the small observed retardation is due to a kinetic effect. Neither the naphthalene nor the pDCB concentration distribution showed any significant tailing. The low naphthalene and pDCB retardation closely corresponds with low observed retardation of pentachlorophenol in a ground water plume at the UCC site.

The fractional recovery of naphthalene and pDCB was much lower than that of chloride. Only 35% as much of the injected naphthalene and 52% as much of the pDCB were recovered as the chloride. This lower recovery is thought to be due to biotransformation by subsurface microorganisms. Rapid mineralization of naphthalene was observed in
laboratory studies on ground water collected from well RU-29 during the course of the three well test. Mineralization of pDCB was much slower. The slower mineralization of pDCB conforms with the smaller loss of pDCB observed during the three well test.
6.0 Numerical Simulation of Oxygen Limited Biodegradation

Recent field monitoring at the UCC site has shown that a plume of hydrocarbon contaminated ground water is present in the shallow aquifer and is thought to have originated in two former ponds used for disposal of waste water. A plume of elevated chloride concentrations is also present in the ground water but covers a much larger area. There are two possible causes for this difference in size: adsorption and biotransformation. Results from the three well injection-production test clearly indicate that adsorption is not significant in the shallow aquifer. Laboratory studies by Lee and Ward [1984] have demonstrated that an adapted microbial population is present in the shallow aquifer and is capable of rapidly degrading the hydrocarbons present given sufficient oxygen but that degradation is severely reduced in the absence of oxygen. Oxygen is present in uncontaminated areas of the shallow aquifer at low concentrations (approximately 3.0 mg/l) and is absent in highly contaminated areas. If oxygen transport into the hydrocarbon plume is slow, this could potentially explain why only limited biodegradation of the hydrocarbons has occurred in the 15 years since the UCC facility was closed. In order to investigate this hypothesis, a numerical model has been developed to simulate the transport and biodegradation of hydrocarbons under oxygen limiting
conditions. The equation formulation and preliminary testing of the model are described below. Results of the field testing are described in chapters 7 and 8.

6.1 Past Work

Most previous work in ground water modeling has been limited to simulation of abiotic processes although a few researchers have considered microbially mediated reactions. Sykes et al. [1982] studied the anaerobic degradation of a leachate plume at the Borden landfill using a galerkin finite element formulation of the advection dispersion equation. Microorganism growth, decay and substrate utilization were simulated using Monod kinetics. In an extensive series of studies at Stanford University, Rittman and McCarty [1980], Bouwer and McCarty [1984] and Kissel et al. [1984] have used the biofilm concept to simulate the removal of organics by attached organisms. This work has focused on mechanisms at the pore scale and has not been aimed at simulating large scale ground water transport. Baehr and Corapcioglu [1984] have presented a one dimensional model for simulating gasoline transport in the unsaturated zone which includes transport by air, water and free hydrocarbon phases with exchange between each phase and losses due to biodegradation.

6.2 Equation Formulation
In this work, the primary emphasis is placed on simulating the biodegradation of hydrocarbons and other organics which are degradable only in the presence of oxygen using as few model parameters as feasible. Compounds which require oxygen for degradation are common in nature and include many petroleum derivatives and polynuclear aromatics.

Growth of microorganisms and removal of hydrocarbon and oxygen are simulated using a modification of the Monod function where:

\[
\frac{dH}{dt} = - M_t \cdot k \cdot \left( \frac{H}{K_h + H} \right) \left( \frac{O}{K_o + O} \right) \quad (6-1)
\]

\[
\frac{dO}{dt} = - M_t \cdot k \cdot F \left( \frac{H}{K_h + H} \right) \left( \frac{O}{K_o + O} \right) \quad (6-2)
\]

\[
\frac{dM_t}{dt} = M_t \cdot k \cdot Y \left( \frac{H}{K_h + H} \right) \left( \frac{O}{K_o + O} \right) + k_c \cdot Y \cdot OC - b \cdot M_t \quad (6-3)
\]

where
- \( H \) = hydrocarbon concentration
- \( O \) = oxygen concentration
- \( M_t \) = total microbial concentration
- \( k \) = maximum hydrocarbon utilization rate per unit mass microorganisms
- \( Y \) = microbial yield coefficient (g cells/g hydrocarbon)
- \( K_h \) = hydrocarbon half saturation constant
- \( K_o \) = oxygen half saturation constant
- \( k_c \) = first order decay rate of natural organic carbon
- \( OC \) = natural organic carbon concentration
- \( b \) = microbial decay rate
- \( F \) = ratio of oxygen to hydrocarbon consumed
The use of the Monod function to model oxygen limitation was first proposed by Longmuir [1954] and has been used extensively by many others. Williamson and McCarty [1976] have suggested that using the minimum of the two terms \(\frac{H}{K_h+H}\) or \(\frac{O}{K_o+O}\) is preferable in trickling filter simulation since diffusion into the biofilm will be rate limiting. It is not clear that this holds in aquifers since the maximum biofilm thickness will be restricted by the formation pore size. The product of the two terms adopted in this work is the more commonly used form [Rich, 1973] and greatly simplifies the mathematical analysis.

The microorganisms are assumed to grow on both the foreign hydrocarbon and naturally occurring organic carbon such as humic and fulvic acids. These compounds are very slowly degradable but due to their relatively high concentrations can support a significant bacterial population. Growth of the microorganisms was assumed to be first order with respect to the natural organic carbon content. Decay rates used in this work would result in an organic carbon half life of 700 years and support a steady-state microbial population of \(10^5\) cells per ml pore water.

If equations 6-1 and 6-2 for oxygen and hydrocarbon removal are combined with the classic form of the advection dispersion equation [Bear, 1979] for a solute undergoing
linear instantaneous adsorption, the following equations are obtained:

\[
\begin{align*}
\frac{\partial H}{\partial t} &= \nabla \cdot (D \nabla H - vH) / R_h + M_t \cdot k \cdot \left( \begin{array}{c} H \\ K_h + H \end{array} \right) / \left( \begin{array}{c} O \\ K_o + O \end{array} \right) \\
\frac{\partial O}{\partial t} &= \nabla \cdot (D \nabla O - vO) + M_t \cdot k \cdot F \cdot \left( \begin{array}{c} H \\ K_h + H \end{array} \right) / \left( \begin{array}{c} O \\ K_o + O \end{array} \right)
\end{align*}
\]

(6-4) (6-5)

where

\begin{align*}
D &= \text{Dispersion tensor} \\
v &= \text{ground water velocity vector} \\
R_h &= \text{retardation factor for hydrocarbon}
\end{align*}

The movement of microorganisms in aquifers will be limited by filtration and the natural tendency of the organisms to adhere to the aquifer material. Most work to date has focused on the transport of foreign organisms. In these studies, filtration has been assumed to be the dominant mechanism [Gerba et al., 1975; Corapcioglu and Haridas, 1984]. The movement of naturally occurring organisms will also be limited by the tendency of the organisms to grow as microcolonies attached to the formation. In most aquifers, greater than 95 percent of the native organisms are attached [Thomas et al., 1985; Harvey et al., 1984]. Since filtration will only limit the movement of cells already in solution, the affinity of microorganisms for solid surfaces will control the transport of the total population. As a first approximation, we can assume that the exchange of microorganisms between the solid
surface and the free solution will be rapid and follow a linear relationship with total concentration. If this is correct, then the movement of the microorganisms can be simulated using a simple retardation factor approach [Freeze and Cherry, 1979].

\[
\frac{\partial M_s}{\partial t} = \nabla \cdot (D \nabla M_s - \nu M_s) / R_m + M_s \cdot k \cdot Y \left( \begin{array}{c} H \\ K_h+H \\ K_o+O \end{array} \right) - \frac{O}{K_h+H} + k_c \cdot Y \cdot OC - b M_s 
\]

(6-6)

where

- \( M_s \) = concentration of microbes in solution
- \( M_a \) = concentration of microbes attached to solids
- \( K_m \) = ratio of microbes attached to microbes in solution
- \( R_m \) = microbial retardation factor
- \( M_a = K_m \cdot M_s \)
- \( M_t = M_s + M_a = (1 + K_m) \cdot M_s = R_m \cdot M_s \)

In order to study the behavior of these equations and to identify the most significant parameters, several simple numerical models were developed to solve these equations in one and two dimensions. One-dimensional forms of equations 6-4, 6-5 and 6-6 were solved initially to study the general solution behavior and effect of microbial kinetics. Two-dimensional horizontal simulations were employed to study the effect of dispersion and adsorption on the transfer of oxygen into the contaminant plume. Finally, two-dimensional vertical simulations were used to examine the impact of oxygen transfer from the unsaturated zone on hydrocarbon degradation.
6.3 One-Dimensional Simulations: Effect of Microbial Kinetics

Equations 6-4, 6-5 and 6-6 were written in the following one-dimensional form.

\[
\frac{\partial H}{\partial t} = - \frac{1}{R_h} \left( \frac{\partial^2 H}{\partial x^2} - v \frac{\partial H}{\partial x} \right) - \frac{k \cdot M_L}{K_h + H} \left( \frac{H}{K_h + H} \right) \left( \frac{O}{K_0 + O} \right) \tag{6-7}
\]

\[
\frac{\partial O}{\partial t} = - \frac{1}{D_1} \left( \frac{\partial^2 O}{\partial x^2} - v \frac{\partial O}{\partial x} \right) - \frac{k \cdot M_L \cdot F}{K_h + H} \left( \frac{H}{K_h + H} \right) \left( \frac{O}{K_0 + O} \right) \tag{6-8}
\]

\[
\frac{\partial M_S}{\partial t} = - \frac{1}{R_m} \left( \frac{\partial^2 M_S}{\partial x^2} - v \frac{\partial M_S}{\partial x} \right) + \frac{k \cdot M_S \cdot Y}{K_h + H} \left( \frac{H}{K_h + H} \right) \left( \frac{O}{K_0 + O} \right) + K_C \cdot Y \cdot OC - b M_S \tag{6-9}
\]

and

\[
H(x,0) = H_b, \quad O(x,0) = O_b, \quad M_S(x,0) = M_b \quad \text{for} \quad x > 0;
\]

\[
H(0,t) = H_i, \quad O(0,t) = O_i, \quad M_S(0,t) = M_i \quad \text{for} \quad t > 0;
\]

\[
H(\infty,t) = H_b, \quad O(\infty,t) = O_b, \quad M_S(\infty,t) = M_b \quad \text{for} \quad t > 0;
\]

where

- \(D_1\) = longitudinal dispersion coefficient
- \(D_1 = a_L \cdot v\)
- \(a_L\) = longitudinal dispersivity
- \(x\) = coordinate in the direction of flow
- \(H_b, O_b, M_b\) = background solute concentrations of hydrocarbon, oxygen and microorganisms
- \(H_i, O_i, M_i\) = influent solute concentrations of hydrocarbon, oxygen and microorganisms

These equations were then solved numerically by approximating the transport terms as a series of completely mixed reactors (CMR). This is a special case of the fully upwinded finite difference solution corrected for numerical dispersion presented Van Genuchten and Wierenga [1974b]. At
early time and near the contaminant source, biodegradation rates are very high and a short time step is required. At later time and farther from the source, biodegradation rates are much lower and a longer time step is feasible. By employing the CMR approximation, a variable time step solver can be employed which significantly reduces computation time and cost. Bear [1960] has shown that a series of CMR's results in an outflow concentration distribution which is Poisson for a dirac input. By the central limit theorem as the number of reactors becomes large, this distribution becomes normal and approaches the analytical solution of the 1-D advection dispersion equation [Crank, 1956].

The series of ordinary differential equations which results from the CMR reactor approximation are stiff due to the very high rates of biodegradation at early time. These equations were solved using a standard simulation package with a adaptive time step solver for stiff equations [CSMP III; IBM, 1976]. The stiff solver performs an explicit integration of each equation. The time step is selected to maintain the relative and absolute error to less than 0.01%. The equations for each reactor and each component are solved sequentially. This results in a solution which is essentially continuous in time. Numerical dispersion associated with evaluation of the time derivative is negligible [Van Genuchten and Wierenga, 1974b]. Solution
accuracy was checked against the analytical solution of Ogata and Banks [1961] (Figure 6-1). In all cases the CMR procedure agreed with the analytical solution within one percent. A listing of the program is provided in Appendix B1.

6.3.1 Parameter Estimation

Estimates of the major physical and microbial parameters were obtained from field and laboratory studies on the UCC site in Conroe, Texas. Details of the field studies are described in chapter 4. Microbial parameters were estimated from degradation studies in Rice University laboratories. The microbial parameters are thought to be representative of conditions at a site where the hydrocarbon contamination has been present for some time and adaptation of the microorganisms has already occurred. No attempt was made to simulate \textit{in situ} adaptation since this process is very poorly understood. At sites where a small accidental spill has recently occurred or for poorly degradable compounds, these kinetic parameters may not be applicable. The ratio of oxygen to hydrocarbon consumed (F) was estimated assuming complete mineralization to carbon dioxide and water. Oxygen was assumed to be the only electron acceptor. The initial microbial population was estimated from aseptically collected aquifer samples [Lee et al., 1984]. The maximum
hydrocarbon utilization rate \( (k) \) and hydrocarbon half saturation constant \( (K_h) \) were obtained from a series of batch degradation studies in which the initial hydrocarbon concentration was varied from 4.9 to 798 \( \mu \text{g/l} \) [naphthalene used as model hydrocarbon, Thomas et al., 1985]. No data could be obtained from the UCC site on the oxygen half saturation constant \( (K_o) \), microbial yield \( (\gamma) \) or microbial decay coefficient \( (b) \). Values for these parameters were obtained from literature sources [Longmuir, 1954; Wodzinski and Johnson, 1968; Weston, 1971]. Background dissolved oxygen, organic carbon and hydrocarbon concentrations were measured on site. The physical and microbial parameters used in all simulations are provided in Table 6-1.

6.3.2 Simulation Results (1-D)

Preliminary studies with the one dimensional solution indicate that there are three general regions where different processes control the rate and extent of degradation. Figure 6-1 shows the location of these regions and the variation in oxygen and hydrocarbon with distance.

In the region closest to the contaminant source, the rate of biodegradation will be very high. A large microbial biomass will develop immediately adjoining the contaminant source and result in nearly complete removal of oxygen. The areal extent of this region will depend on the ground water
FIGURE 6-1
Variation in Hydrocarbon, Oxygen and Microorganism Concentration
(Time = 11,000 days)

Region 1
Region 2
Region 3

SOLUTE CONCENTRATION (mg/l)

DISTANCE FROM SOURCE (m)

Hydrocarbon
Analytical Solution: Chloride
CSMP Solution: Chloride
Microorganisms x 10
Oxygen
Table 6-1

Best Estimates of Physical and Kinetic Parameters

at the UCC site

Velocity (v)\(^1\) = 0.015 m/d
Longitudinal Dispersivity (a\(_L\))\(^1\) = 9.1 m
Transverse Dispersivity (a\(_T\))\(^1\) = 1.8 m
Maximum Hydrocarbon Utilization rate (k)\(^2\) = 1.7 /d
Ratio of oxygen to hydrocarbon consumed (F) = 3.0
Microbial yield coefficient (Y)\(^3\) = 0.5 g/g
Hydrocarbon half saturation constant (K\(_H\))\(^2\) = 0.13 mg/l
Oxygen half saturation constant (K\(_O\))\(^4\) = 0.10 mg/l
Microbial decay coefficient (b)\(^5\) = 0.01 /d
Background hydrocarbon conc. (H\(_B\))\(^1\) = 0.0 mg/l
Background oxygen concentration (O\(_B\))\(^1\) = 3.0 mg/l
Background microbial biomass (M\(_B\))\(^6\) = 0.1 mg/l
Background organic carbon (OC)\(^1\) (0.01% by wt.) = 750 mg/l
Influent hydrocarbon conc. (H\(_I\))\(^1\) = 4.5 mg/l
Influent oxygen conc. (O\(_I\))\(^1\) = 3.0 mg/l
Influent microbe conc. (M\(_I\))\(^1\) = 0.1 mg/l
Organic carbon utilization rate (k\(_C\))\(^1\) = 2.7 \cdot 10^{-6} /d
Hydrocarbon retardation factor (R\(_H\))\(^1\) = 1.0
Microbial retardation factor (R\(_m\))\(^6\) = 100.

\(^1\) Obtained from field data at the UCC site.
\(^2\) Unpublished data – M. Thomas.
\(^3\) Wodzinski and Johnson, 1968.
\(^4\) Longmuir, 1954.
\(^5\) Weston, 1971.
\(^6\) Thomas et al., 1985.
velocities. Near an injection well, the ground water velocity will be very high and this region of high biodegradation rates may cover a much larger area. The steady state microbial distribution within the region will depend on the flux of hydrocarbon and oxygen into the formation and the loss of microorganisms due to sloughing of the biofilm and endogenous decay. The mechanics of sloughing are still poorly understood, but it is clear that a heavy microbial biomass will develop near the hydrocarbon source and result in very rapid depletion of oxygen (Figure 6-1). Biodegradation in this region may also be limited by diffusion into the microbial biofilm and might be more accurately described using the more complex numerical model developed by Kissel et al. [1984] which includes biofilm kinetics.

In the body of the hydrocarbon plume, mass transfer between oxygen in the formation water and hydrocarbon in the plume will limit the rate of biodegradation. The primary mass transfer processes are horizontal mixing with oxygenated formation water, advective fluxes of oxygen due to the different adsorption affinities of oxygen and hydrocarbon, and vertical exchange with the unsaturated zone. In most aquifers, these fluxes will be slow relative to the capacity of the microorganisms to degrade the hydrocarbon. At the leading edge of the hydrocarbon plume,
a zone of reduced oxygen and hydrocarbon concentrations will develop between the hydrocarbon in the plume and the oxygenated formation water (Figure 6-1). The reduced oxygen and hydrocarbon concentrations are due to biodegradation by the microorganisms. As the plume moves, this zone of reduced oxygen and hydrocarbon will increase in size and further limit mass transfer.

In the third region downstream of the bulk hydrocarbon plume, oxygen is present in excess and hydrocarbon will be completely absent or present at only trace concentrations. Biodegradation in this region will not be limited by the oxygen concentration but may be limited by the hydrocarbon concentration and the population of organisms supported by naturally occurring organic carbon. Survival of microorganisms at low carbon concentrations is still very poorly understood and any simulation results in this region should be used with a great deal of caution.

6.3.3 Instantaneous Reaction Assumption

Sensitivity analyses performed with the 1-D model indicated that the various microbial parameters \((K_h, K_o, k, Y, F)\) had little or no effect on the hydrocarbon distribution in the body of the plume and on the time to hydrocarbon breakthrough. The sensitivity analyses were performed for a range of values representative of conditions
that might occur after the subsurface population had adapted to the contaminant. No attempt was made to include the impact of microbial adaptation since this process is still poorly understood and is not yet amenable to numerical simulation. The sensitivity analyses did indicate that variations in cell yield, substrate utilization rates and half saturation constants do have a slight effect on the hydrocarbon distribution near the contaminant source. The ground water velocity had a somewhat greater impact on transient concentration distributions, particularly near the source. This is not surprising considering the large variation in ground water velocities possible. Microbiological parameters typically vary over about one order of magnitude for easily degradable hydrocarbons while ground water velocities may vary over four or five orders of magnitude.

The weak sensitivity of the hydrocarbon distribution to microbial kinetics suggested that the consumption of hydrocarbon and oxygen by the microorganisms in the body of the plume (region 2) might be approximated as an instantaneous reaction between oxygen and hydrocarbon. In an explicit finite difference form, this approximation would be

\[ H(t+1) = H(t) - O(t)/F; \quad O(t+1) = 0 \text{ where } H(t) > O(t)/F \quad (6-10) \]
\[ O(t+1) = O(t) - H(t) \cdot F; \quad H(t+1) = 0 \text{ where } O(t) > H(t) \cdot F \quad (6-11) \]
H(t), H(t+1), O(t), O(t+1) are the hydrocarbon and oxygen concentrations at time t and t+1. Results obtained using this instantaneous reaction approximation are compared with the complete solution of equations 6-7, 6-8 and 6-9 in Figure 6-1. The hydrocarbon and oxygen distributions were obtained by solving the complete equations (lines) and by employing the instantaneous reaction assumption (symbols). The instantaneous reaction approximation closely matches the complete solution for the majority of the plume. Only in Region 1 near the hydrocarbon source is there any significant error. The width of this region will depend on the mixing properties of the aquifer near the contaminant source, the ground water velocity and the nature of the hydrocarbon. When ground water velocities are very high or for poorly degradable hydrocarbons the area in which the instantaneous reaction assumption is not applicable may be significant.

6.4 Horizontal 2-D Simulations: Effect of Adsorption and Horizontal Mixing

In the previous section, microbial consumption of hydrocarbon and oxygen was found to be rapid relative to ground water transport for the majority of the hydrocarbon plume. This allows equations 6-4 and 6-5 to be efficiently solved in two dimensions by employing the instantaneous
reaction assumption represented by equations 6-10 and 6-11. Simulation of microorganism concentration (equation 6-6) is no longer necessary since the reaction is assumed to be instantaneous. Under this assumption,

\[
\frac{\partial H}{\partial t} = \frac{1}{R_h} \left( \frac{\partial^2 H}{\partial x^2} + \frac{\partial^2 H}{\partial y^2} - \frac{\partial H}{\partial x} \right) - \frac{O/F}{F} \tag{6-12}
\]

\[
\frac{\partial O}{\partial t} = \frac{\partial^2 O}{\partial x^2} + \frac{\partial^2 O}{\partial y^2} - \frac{\partial O}{\partial x} - H \cdot F \tag{6-13}
\]

where

\[
D_t = \text{transverse dispersion coefficient}
\]

\[
\alpha_t = \text{transverse dispersivity}
\]

\[
D_t = \alpha_t \cdot \nu
\]

\[
y = \text{coordinate orthogonal to the flow}
\]

These equations were then solved using an explicit, fully upwinded, block centered finite difference solution. Velocity was uniform and oriented parallel to the x axis. Numerical dispersion effects were minimized by reducing the longitudinal dispersivity by the factor \((\Delta x - \nu \Delta t)/2\) as suggested by Lantz [1971]. The Courant number was maintained less than 1.0 and the corrected longitudinal dispersivity greater than zero. Grid orientation was not a problem since flow was always oriented along the the x axis. The accuracy of the general finite difference solution was checked by comparing with the analytical solution of Cleary and Ungs [1978]. The maximum error was 1.1 percent. A listing of the program is provided in Appendix B2.
The background concentrations \((H_b, O_b, M_b)\) were used as the initial conditions. Boundary conditions were implemented by locating the grid boundaries away from the contaminant plume and maintaining the concentrations at the boundaries at background \((H_b, O_b, M_b)\). Mass balance calculations were performed for a nonreactive tracer to ensure that mass was not being lost at boundaries.

Two dimensional simulations generate plumes with many of the same characteristics as in 1-D. A zone of reduced hydrocarbon and oxygen concentrations surrounds the plume on all sides limiting biodegradation. The most notable characteristic of the hydrocarbon plume is the small amount of lateral spread. Figure 6-2 shows a cross-section through the steady state hydrocarbon plume at 200 m from the source for a transverse dispersivity of 1.8 m. The contaminant source was simulated by maintaining a 30 m wide section of the upper boundary at the influent concentrations \((H_i = 3.5 \text{ mg/l, } O_i = 0.0 \text{ mg/l, and influent chloride } = 3.5 \text{ mg/l})\). The hydrocarbon plume has a somewhat lower peak concentration and is much narrower in cross-section than the plume for a non-reactive tracer such as chloride when the source concentration for both are equal. Long narrow plumes have been noted in the field at other gasoline spills [Twenter et al., 1983]. This is thought to be a direct consequence of biodegradation at the sides of the plume. An estimate of
transverse dispersivity \( (a_t) \) obtained by fitting a non-reactive solute transport model to the hydrocarbon data in Figure 6-2 would underestimate the actual \( a_t \) by 75%.

Adsorption of hydrocarbon to the aquifer can significantly increase the rate of biodegradation. This is due to the different transport velocities for oxygen and hydrocarbon which result in advective fluxes of oxygen into the hydrocarbon plume and enhance biodegradation. These effects are illustrated in Figure 6-3. The mass of hydrocarbon per unit length is plotted versus distance from the initial spill for \( R_h = 1.0, 2.0 \) and 3.0. The mass per unit length is calculated by integrating the hydrocarbon concentration in a plane orthogonal to the direction of flow and includes the material in solution and adsorbed to the aquifer. The saturated thickness was assumed to be 1.0 m. The movement of a pulse of hydrocarbon was simulated by setting \( R_h \cdot H_i = 100 \text{ mg/l} \) and \( O_i = 0.0 \text{ mg/l} \) for an area 15 m long by 30 m wide. The initial mass of hydrocarbon in each case was 14 kg. All transport parameters are the same as for Figure 6-2. The total mass of hydrocarbon (area under each curve) drops rapidly for \( R_h = 3.0 \) and is completely degraded in 19,000d while 22% of the original hydrocarbon is still present at this time for \( R_h = 1.0 \). The asymmetrical shape of the hydrocarbon distribution at 15,000d and \( R_h = 3.0 \) is due to the influx of oxygen from upstream and biodegradation at the upstream edge of the plume.
FIGURE 6-3

Variation in Hydrocarbon Mass per unit length

No Adsorption
$R_H = 1.0$

Moderate Adsorption
$R_H = 2.0$

Higher Adsorption
$R_H = 3.0$

MASS OF HYDROCARBON PER UNIT LENGTH (g/m)

DISTANCE FROM INITIAL SPILL (m)
For non-adsorbing hydrocarbons, transverse mixing appears to be the major source of oxygen to the plume. Longitudinal mixing has significantly less impact on oxygen exchange with the plume, possibly because of the small width of most plumes. Figure 6-4 shows the steady state variation in the mass of hydrocarbon per unit length versus distance from the source for various values of transverse dispersivity ($a_t$). The source term for this figure was identical to Figure 6-2. If there were no biodegradation, the curves in Figure 6-4 would all plot as horizontal lines since transverse mixing will reduce the peak concentrations but will not have any effect on the total mass in solution. These curves clearly illustrate the strong sensitivity of oxygen transport and resulting biodegradation to $a_t$. This sensitivity appears to be due to the large surface area available at the sides of the plume for mixing.

6.5 Vertical 2-D Simulations: Effect of Gas Exchange with the Unsaturated Zone

Vertical exchange of oxygen with the unsaturated zone could potentially result in significant fluxes of oxygen into a hydrocarbon plume. This exchange would be most important for contaminants such as gasoline which commonly occur at or near the water table. In order to gain some understanding of the rate limiting steps and to determine
FIGURE 6-4
Effect of Transverse Dispersivity on the Steady-State Hydrocarbon Distribution (longitudinal Dispersivity = 9.2m)

chloride $\alpha_t = 0.3 \text{ m to } 4.6 \text{ m}$

MASS OF HYDROCARBON PER UNIT LENGTH (g/m)

DISTANCE FROM SOURCE (m)
the potential significance of this process, the 2-D finite
difference solution previously described was modified to
simulate vertical transport in both the saturated and
unsaturated zones and exchange between the two zones. Only
exchange due to gaseous diffusion was considered in the
unsaturated zone. Vertical exchange in the saturated zone
was assumed to be due to dispersion only. Ground water flow
was assumed to be uniform and parallel to the horizontal (x)
axis. These assumptions were employed to gain some
understanding of the vertical exchange process for the
simplest case. Accurate description of field problems may
require a full three dimensional simulation including the
effects of stratification.

Oxygen and hydrocarbon transport in the unsaturated zone
were simulated by the following [Weeks et al., 1982].

\[
\frac{\partial O_g}{\partial t} = D_o \frac{\partial^2 O_g}{\partial z^2} - \beta - H_g \cdot F - \Delta o \quad (6-14)
\]

\[
\frac{\partial H_g}{\partial t} = D_h \frac{\partial^2 H_g}{\partial z^2} - \frac{O_g}{F} - \Delta h \quad (6-15)
\]

where

\( O_g \) = partial pressure of oxygen in soil gas  
\( H_g \) = partial pressure of hydrocarbon in soil gas  
\( z \) = vertical coordinate  
\( \beta \) = soil respiration rate  
\( D_o, h \) = effective gaseous diffusion coefficients for oxygen and hydrocarbon  
\( \Delta o, h \) = oxygen and hydrocarbon exchange with the saturated zone
Oxygen and hydrocarbon transport in the saturated zone were simulated as

\[
\begin{align*}
\frac{\partial O_s}{\partial t} &= D_v \frac{\partial^2 O_s}{\partial z^2} + D_1 \frac{\partial^2 O_s}{\partial x^2} - \frac{\partial O_s}{\partial x} - H_s \cdot F + \Delta O \tag{6-16} \\
\frac{\partial H_s}{\partial t} &= D_v \frac{\partial^2 H_s}{\partial z^2} + D_1 \frac{\partial^2 H_s}{\partial x^2} - \frac{\partial H_s}{\partial x} - \frac{O_s}{F} + \Delta h \tag{6-17}
\end{align*}
\]

where

- \( O_s \) = oxygen concentration in saturated zone
- \( H_s \) = hydrocarbon concentration in saturated zone
- \( D_v \) = vertical dispersion coefficient

At the water table interface, exchange is expected to be rapid and was simulated by maintaining the concentrations of hydrocarbon and oxygen immediately above and below the water table in equilibrium. This is equivalent to the two film approximation common in gas transfer. Equilibrium concentrations were calculated by Henry's Law

\[
\begin{align*}
O_s &= C_o \cdot O_g \tag{6-18} \\
H_s &= C_h \cdot H_g \tag{6-19}
\end{align*}
\]

where \( C_o \) and \( C_h \) are the Henry's law coefficients for oxygen and hydrocarbon.

Parameters used in the simulations were based on field conditions at the UCC site and are listed in Table 6-2. Naphthalene was used as a model compound for evaluating hydrocarbon behavior because it is intermediate in terms of volatility and solubility. The effective gaseous diffusion coefficients (\( D_g \)) were estimated as
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness Unsaturated Zone$^1$</td>
<td>7.6 m</td>
</tr>
<tr>
<td>Thickness Soil Zone$^1$</td>
<td>0.9 m</td>
</tr>
<tr>
<td>Thickness saturated zone$^1$ (B)</td>
<td>3.1 m</td>
</tr>
<tr>
<td>Soil respiration rate$^2$ (β)</td>
<td>4055 Pa O₂/d</td>
</tr>
<tr>
<td>Partial Pressure oxygen at soil surface$^3$</td>
<td>21176 Pa</td>
</tr>
<tr>
<td>Total Porosity$^1$ (θₜ)</td>
<td>0.262</td>
</tr>
<tr>
<td>Moisture content unsaturated zone$^1$ (θₘ)</td>
<td>0.125</td>
</tr>
<tr>
<td>Tortuosity$^1$ (T)</td>
<td>0.048</td>
</tr>
<tr>
<td>Gaseous Diffusion coef.-oxygen$^3$ (Dₘ)</td>
<td>0.0107 m²/d</td>
</tr>
<tr>
<td>Gaseous Diffusion coef.-hydrocarbon$^3$ (D)</td>
<td>0.0038 m²/d</td>
</tr>
<tr>
<td>Henry's Law coef. - oxygen$^3$ (C₀)</td>
<td>2290 Pa l/mg</td>
</tr>
<tr>
<td>Henry's Law coef. - hydrocarbon$^3$ (Cₜ)</td>
<td>841 Pa l/mg</td>
</tr>
<tr>
<td>Ground water velocity$^2$ (v)</td>
<td>0.02 m/d</td>
</tr>
<tr>
<td>Longitudinal dispersivity$^1$ (a₁)</td>
<td>9.1 m</td>
</tr>
<tr>
<td>Vertical dispersivity$^1$ (aᵥ)</td>
<td>0.05 m</td>
</tr>
</tbody>
</table>

$^1$ Obtained from field data at UCC site
$^2$ Grable and Siemer, 1968.
$^3$ Lyman et al., 1982.
\[ D_g = T (\theta_t - \theta_w) D_m \] 

where

\[ T = \text{soil tortuosity} \]
\[ \theta_t = \text{total porosity} \]
\[ \theta_w = \text{moisture content} \]
\[ D_m = \text{molecular diffusion coefficient} \]

Tortuosity was estimated using the equation developed by Grable and Siemer [1968]. Soil porosity and moisture content were measured at the UCC site. Molecular diffusion coefficients and Henry's law coefficients for hydrocarbon and oxygen were obtained from a standard text [Lyman et al., 1982].

One of the major uncertainties in evaluating vertical exchange is proper evaluation of vertical mixing in the saturated zone. Very few good measurements have been made of vertical dispersion. Sudicky et al. [1983] found in a detailed field study that the vertical transport of a non-reactive tracer was extremely limited. Vertical dispersion coefficients were much lower than those obtained by previous investigators and approximately equal to the molecular diffusion coefficients. Workers at Auburn University [Molz et al., 1985] have obtained similar results. This suggests that vertical mixing in the saturated zone will often be the rate limiting step in volatilization of hydrocarbons and oxygen exchange with the unsaturated zone.
A series of simulations were performed to study the major parameters affecting vertical exchange and resulting biodegradation. A typical vertical profile for oxygen and hydrocarbon is shown in Figure 6-5. Depending on the initial concentration of hydrocarbon, the contact point between oxygen and hydrocarbon may be above or below the water table. Contours of equal hydrocarbon concentration are shown in Figure 6-6a for a uniform initial source concentration of 1.0 mg/l. Figure 6-6b shows the variation in the vertically averaged concentration ($\bar{H}$) with distance. $\bar{H}$ follows an exponential decay suggesting that the effects of gas exchange with the unsaturated zone may be approximated as a first order decay in space and time since if

$$\frac{d\bar{H}}{dx} = - K' \bar{H}$$  \hspace{1cm} (6-21)

then

$$\frac{d\bar{H}}{dt} = \frac{dx}{dt} \frac{d\bar{H}}{dx} = - v K' \bar{H}$$  \hspace{1cm} (6-22)

where

$\bar{H}$ = vertically averaged hydrocarbon concentration  
$v$ = ground water velocity  
$K'$ = first order decay coefficient

In order to identify the parameters with the greatest impact on gas exchange, a series of sensitivity analyses
FIGURE 6-5

Typical Vertical Profile of Hydrocarbon and Oxygen in saturated and unsaturated zones

DEPTH BELOW LAND SURFACE (m)

HYDROCARBON AND OXYGEN CONCENTRATION (mg/l)
FIGURE 6-6a

Steady-State Hydrocarbon Distribution (concentrations in mg/l)

FIGURE 6-6b

Vertically averaged Hydrocarbon versus Distance

$\Delta$ - Simulated Values

Fitted Line: $\bar{H} = 0.86 \exp(-0.0016x)$ $r^2=0.999$
were performed. Vertical dispersion coefficient ($D_v$) and saturated thickness ($B$) had by far the greatest impact on the first order decay rate ($K'$). The decay coefficients were obtained from log transformed regressions. The correlation coefficients ($r^2$) were consistently greater than 0.98. Other parameters such as gaseous diffusion coefficients ($D_g$), ground water velocity, thickness of the unsaturated zone, and horizontal dispersion coefficients had little or no impact on $K'$. The initial hydrocarbon source strength had a slight affect on $K'$ indicating that the decay in $H$ is not exactly first order. In the concentration range of 1.0 to 10.0 mg/l hydrocarbon, $K'$ varied by less than a factor of 2.0. Uncertainties in vertical dispersion and saturated thickness may result in errors in several orders of magnitude for $K'$. Consequently a higher order representation of the decay process is not warranted. The effects of the major variables, $D_v$ and $B$, on $K'$ can be summarized in the regression function.

\[
K' = 2611D_v^{0.79} \exp \left[ \frac{-10.5 B}{B + 1.04} \right] \quad (r^2 = 0.99) \quad (6-23)
\]

$B = $ Saturated thickness (m)

$D_v =$ Vertical dispersion coefficient (m$^2$/d)

It should be emphasized that this function can only be used to estimate $K'$ for conditions similar to those at the UCC
site but should illustrate the general variation of $K'$ with $D_v$ and $B$ for a variety of conditions. Sensitivity analyses performed on the other parameters showed that these parameters could result in a change in the absolute value of $K'$ by a factor of 2 to 3, but the variation in $K'$ with $D_v$ and $B$ follows the same general form of equation 6-23.

6.6 Summary

Equations were presented for simulating the simultaneous growth, decay and transport of subsurface microorganisms as well as the transport and removal of oxygen and hydrocarbon. These equations were solved in one and two dimensions to study the impact of microbial kinetics, horizontal dispersion, adsorption and reaeration by vertical exchange with the unsaturated zone. These studies indicate that:

1. Biodegradation of a hydrocarbon plume will typically result in the development of a zone of reduced hydrocarbon and oxygen concentrations between the oxygenated formation water and the plume. This zone will limit exchange of oxygen with the plume and reduce the rate of biodegradation.

2. When exchange of oxygen with the hydrocarbon plume is rate limiting, the consumption of oxygen and hydrocarbon by microorganisms may be approximated as an
instantaneous reaction between oxygen and hydrocarbon. This greatly simplifies the mathematical analysis but may not be applicable for slowly degradable hydrocarbons or in situations where the native microbial population has not yet adapted to the foreign hydrocarbon.

3. In the region immediately adjoining the hydrocarbon source, a large microbial population will develop. In this region, the assumption of an instantaneous reaction between oxygen and hydrocarbon may not be appropriate and simulation of microbial kinetics may be required.

4. Hydrocarbon plumes will appear much narrower in plan view than commonly expected. This occurs as a result of transverse mixing with the oxygenated formation water and resulting biodegradation.

5. Transverse mixing will be the dominant source of oxygen for most hydrocarbon plumes when adsorption is not significant. Longitudinal mixing appears to have less effect on hydrocarbon biodegradation.

6. Adsorption to the aquifer material may significantly enhance the biodegradation of hydrocarbon spills. Oxygen, which is not retarded, will move into the more slowly moving hydrocarbon plume. When this occurs the hydrocarbon will be rapidly degraded.
7. Vertical exchange of oxygen and hydrocarbon with the unsaturated zone may significantly enhance the rate of biodegradation. Preliminary simulations indicate that vertical exchange will result in a first order decay in the vertically averaged hydrocarbon concentration. The first order decay rate is strongly dependent on the saturated thickness and the vertical dispersion coefficient.
7.0 Evaluation of Biodegradation Model: Field Scale

The USGS solute transport model was modified to simulate the transport and biodegradation of hydrocarbons based on the results of chapter 6. This model was then applied to the UCC field site to determine if model simulations results are actually representative of field conditions. The procedure used to modify the USGS model and results of the field calibration are described below.

7.1 Simulation Procedure

Two-dimensional horizontal simulations of the contaminant plume at the UCC site were developed using a method of characteristics solute transport model (USGS) originally developed by Konikow and Bredehoeft [1978] and later modified by Tracy [1982]. Only simulation of the bulk hydrocarbon concentration was necessary since most of the organic components have similar biodegradation rates and affinities for adsorption. PCP transport and biodegradation was not considered directly since PCP degrades very slowly and is present in the ground water at trace concentrations relative to the other compounds. The USGS model was first calibrated to the observed chloride distribution and then used to simulate hydrocarbon and oxygen transport. Aquifer dispersivities were obtained by matching the chloride distribution and used without further calibration in the hydrocarbon simulations.
The horizontal mixing of hydrocarbon within the contaminant plume with clean oxygenated formation water was simulated by taking advantage of the linear nature of the advection dispersion equation. In two horizontal dimensions the advection dispersion equation for a non-adsorbing solute can be written

\[
\frac{\partial c}{\partial t} + \frac{\partial c}{\partial x} - D_{1}\frac{\partial^2 c}{\partial x^2} - D_{t}\frac{\partial^2 c}{\partial y^2} = q(c) \tag{7-1}
\]

or

\[
L(c) = q(c) \tag{7-2}
\]

where

\[
L(\ ) = \frac{\partial}{\partial t} + \frac{\partial}{\partial x} - D_{1}\frac{\partial^2}{\partial x^2} - D_{t}\frac{\partial^2}{\partial y^2} = q(\ )
\]

\(x\) = coordinate along streamline
\(y\) = coordinate orthogonal to streamline
\(v\) = velocity along streamline

The reaction between hydrocarbon(H) and oxygen(O) has been shown to be rapid relative to ground water flow (see chapter 6) and consequently the oxygen and hydrocarbon loadings which include the effects of biodegradation, \(q(O)\) and \(q(H)\), will be

\[
q(H) = q(H') - \frac{q(O')}{F} \tag{7-3}
\]

\[
q(O) = q(O') - q(H')\cdot F \tag{7-4}
\]

where

\(q(O')\) = oxygen loading in the absence of biodegradation
\(q(H')\) = hydrocarbon loading in the absence of biodegradation
\(F\) = ratio of oxygen to hydrocarbon consumed by
the microorganisms

Therefore

\[ L(H) = q(H) = q(H') - q(O')/F \]

\[ L(H) = L(H') - L(O')/F \]  \hspace{1cm} (7-5)

and

\[ L(O) = L(O') - L(H') \cdot F \]  \hspace{1cm} (7-6)

This is essentially a statement of the principle of superposition. Superposition can be employed with the numerical simulations as long as the velocity field and all transport coefficients are identical for both oxygen and hydrocarbon simulations. This is possible at the UCC site because the major hydrocarbons are known to be very weakly affected by adsorption (see chapter 5).

The effects of oxygen and hydrocarbon exchange with the unsaturated zone were simulated as a first order decay in hydrocarbon concentration. In chapter 6 studies of the vertical exchange process showed that the change in vertically averaged hydrocarbon concentration can be approximated as a first order decay with time and distance. The decay rate \( K' \) at the UCC site was shown to be strongly dependent on the saturated thickness \( B \) and vertical dispersion coefficient \( D_v \) and an empirical equation was developed for estimating \( K' \) at the UCC site. This equation (eq. 6-23) was incorporated into the USGS solute transport model and was used to estimate \( K' \) for each node.
Quantitative simulation of the hydrocarbon and oxygen distributions required a two step procedure (see Appendix B5). The first step was to generate a hydrocarbon simulation which included the effects of reaeration (first order decay) and an oxygen simulation without biodegradation for a specific time. A short subroutine was then employed to perform the subtractions to generate oxygen and hydrocarbon distributions which reflect both the effects of biodegradation due to horizontal mixing and reaeration from the water table. Use of superposition is not rigorously applicable in this case since a decay term is present in the hydrocarbon equation and none is present in the oxygen equation. Nonetheless, the ease with which this procedure can be used with a wide variety of solute transport models makes it extremely useful and the errors introduced appear to be minimal considering the uncertainty involved in estimating the vertical and horizontal dispersivities. Work is currently underway to develop a more general simultaneous numerical solution which would allow simulation of hydrocarbons undergoing significant adsorption and vertical exchange with the unsaturated zone.

7.2 Parameter Estimation

The numerical model was applied to the shallow unconfined aquifer at the UCC site. The hydrology and geology of this
zone are described in chapter 4. The major uncertainty in any ground water simulation is proper estimation of the aquifer permeability. Other parameters such as porosity and hydraulic gradient typically show much less variability. Model simulations assumed the unconfined sand to have a uniform, isotropic permeability of 0.74 m/d with a small zone of low permeability near SW-2. This low permeability zone has been observed in geologic logs and in the slug test results. The mean permeability of 0.74 m/d was estimated from a series of slug tests on wells penetrating the shallow aquifer. The coefficient of variation for these tests was 1.40 suggesting that the true mean permeability could differ from the measured mean by up to a factor of three. This would result in a contaminant plume three times as large. Field measurements of the chloride plume have clearly shown that this is not the case and the average measured permeability is close to the total effective permeability of the aquifer. A retardation factor of 1.0 for the hydrocarbon has been used in all simulations (chapter 5).

The ratio of oxygen to hydrocarbon consumed by the microorganisms (F) was calculated assuming complete mineralization. Table 7-1 provides a summary of the parameters used in simulations.
Table 7-1
Simulation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>0.74 m/d</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.29</td>
</tr>
<tr>
<td>Saturated Thickness (B)</td>
<td>1.0 to 3.5 m</td>
</tr>
<tr>
<td>Hydrocarbon Retardation Factor</td>
<td>1.0</td>
</tr>
<tr>
<td>Background Oxygen Conc.</td>
<td>3.0 mg/l</td>
</tr>
<tr>
<td>Ratio Oxygen to Hydrocarbon consumed (F)</td>
<td>3.0</td>
</tr>
<tr>
<td>Longitudinal Dispersivity (a₁)</td>
<td>9.1 m</td>
</tr>
<tr>
<td>Transverse Dispersivity (aₜ)</td>
<td>1.8 m</td>
</tr>
<tr>
<td>Vertical Dispersivity (aᵥ)</td>
<td>3.5 cm</td>
</tr>
</tbody>
</table>
The organics distribution in the shallow aquifer was obtained from field monitoring by Rice University [Bedjent et al., 1984] and as part of a superfund characterization study [Weston, 1985]. During the superfund characterization, not all hydrocarbon components were quantified. Consequently, it was necessary to estimate the total hydrocarbon concentration based on selected contaminants. Naphthalene was chosen as the best indicator of total hydrocarbon because: 1) it is present in the highest concentrations; 2) it was measured by both Rice University and during the superfund characterization; and 3) it's volatility and biodegradability are typical of the hydrocarbons present. A log-log regression between naphthalene and total hydrocarbon ($r^2 = 0.99$) was used to estimate the total hydrocarbon concentration from the superfund data.

Oxygen measurements were taken in wells penetrating the unconfined unit whenever possible. Oxygen measurements in several of the recently installed wells (SW-7 and SW-8) were not possible because of access restrictions. Accurate measurement of oxygen in SW-2 was not possible because of the very low permeability in this area. Prior to collecting a sample for oxygen analysis, the well casings were purged with argon or nitrogen gas followed by pumping 3 well volumes. Dissolved oxygen was then measured by the membrane
electrode procedure (YSI model # 57) or the phenylarsine oxide modification of the Winkler test (Hach Chemical Co., Loveland CO). Monitoring data for chloride, oxygen, naphthalene and total hydrocarbon in all wells are shown in Table 7-2.

7.3 Chloride Simulations

Solute transport was simulated using the USGS code as modified by Tracy [1982]. An accurate water table match was obtained by assuming constant head hydraulic sources and sinks at the northern and southern boundaries of the site. A small ditch runs near the eastern boundary of the site and was simulated as a weak recharge area. In addition, a small leakage to the underlying aquifer was simulated near SW-5 to match the observed transport of organics into the deeper aquifer. Simulated and observed water table elevations are shown in Table 7-3. In general the match is very good.

The chloride and organics plumes were simulated by assuming loading rates for the period 1947 to the present. During the period 1947 to 1972 when the plant was in operation, the two ponds were assumed to recharge water to the shallow aquifer at a combined rate of 5.0 m³/d. This resulted in a significant water table mound (2.0 m rise) and a radial flow field when the ponds were in operation. The small western pond was assumed to contain a higher
Table 7-2
Chloride, Oxygen and Organic Concentrations in
Selected Wells at the UCC site

<table>
<thead>
<tr>
<th>Well</th>
<th>Chloride&lt;sup&gt;1&lt;/sup&gt; (mg/l)</th>
<th>Oxygen&lt;sup&gt;2&lt;/sup&gt; (mg/l)</th>
<th>Naphthalene&lt;sup&gt;1&lt;/sup&gt; (µg/l)</th>
<th>Total Hydrocarbon (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-1</td>
<td>15 ±3</td>
<td>2.9 ±0.06</td>
<td>ND&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>SW-2</td>
<td>77 ±9</td>
<td>---</td>
<td>43&lt;sup&gt;6&lt;/sup&gt; ±10</td>
<td>62&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>SW-3</td>
<td>84 ±6</td>
<td>0.7</td>
<td>ND&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>SW-4</td>
<td>71 ±8</td>
<td>1.2</td>
<td>70&lt;sup&gt;3&lt;/sup&gt; ±170</td>
<td>108&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>SW-5</td>
<td>152 ±6</td>
<td>0.3</td>
<td>33&lt;sup&gt;3&lt;/sup&gt; ±55</td>
<td>46&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>SW-7</td>
<td>19</td>
<td>---</td>
<td>ND&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>SW-8</td>
<td>26</td>
<td>---</td>
<td>ND&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>SW-9</td>
<td>41</td>
<td>0.7 ±0.02</td>
<td>56&lt;sup&gt;3&lt;/sup&gt;</td>
<td>84&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>RU-2</td>
<td>59 ±1</td>
<td>0.2</td>
<td>650&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1972&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>RU-3</td>
<td>8 ±1</td>
<td>1.4</td>
<td>ND&lt;sup&gt;4&lt;/sup&gt;</td>
<td>0</td>
</tr>
</tbody>
</table>

ND = less than detection limit of 10 µg/l
<sup>2</sup>Precision calculated by multiple day sampling
<sup>3</sup>Precision calculated by single sample replicates
<sup>4</sup>Obtained from superfund characterization
<sup>5</sup>Measured by Rice University
<sup>6</sup>Estimated by the relationship
Total hydrocarbon = 0.8342(Naphthalene)<sup>1</sup> 146
<sup>6</sup>Accuracy of measurement uncertain due to very low permeability
Table 7-3
Comparison of Simulated and Observed Water Table Elevations

<table>
<thead>
<tr>
<th>Well</th>
<th>Observed (m)</th>
<th>Simulated (m)</th>
<th>Error (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-1</td>
<td>65.44</td>
<td>65.44</td>
<td>0.00</td>
</tr>
<tr>
<td>SW-2</td>
<td>64.07</td>
<td>64.08</td>
<td>0.01</td>
</tr>
<tr>
<td>SW-3</td>
<td>64.11</td>
<td>64.08</td>
<td>-0.03</td>
</tr>
<tr>
<td>SW-4</td>
<td>63.60</td>
<td>63.62</td>
<td>0.02</td>
</tr>
<tr>
<td>SW-5</td>
<td>64.29</td>
<td>64.31</td>
<td>0.02</td>
</tr>
<tr>
<td>SW-7</td>
<td>63.58</td>
<td>63.56</td>
<td>-0.02</td>
</tr>
<tr>
<td>SW-8</td>
<td>64.16</td>
<td>64.18</td>
<td>0.02</td>
</tr>
<tr>
<td>SW-9</td>
<td>64.58</td>
<td>64.56</td>
<td>-0.02</td>
</tr>
<tr>
<td>RU-2</td>
<td>64.68</td>
<td>64.69</td>
<td>0.01</td>
</tr>
<tr>
<td>RU-3</td>
<td>64.77</td>
<td>64.76</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Root Mean Squared Error = \( (\text{Error}^2)^{1/2} \)

Root Mean Squared Error = \( \frac{\text{Error}^2}{n} \)
concentration of chloride since it was used primarily for disposal of PCP wastes. The larger eastern pond was used for disposal of creosote wastes and was assumed to contain a lower chloride concentration. The hydrocarbon concentration in both ponds was assumed to be equal. Flow rates out of each pond were apportioned by surface area.

Following closure of the plant in 1972, the ponds were drained but not backfilled and probably continued to add a small recharge to the shallow aquifer. During this period, recharge water was assumed to contain little chloride but to leach hydrocarbon from the sludges deposited in the bottom of the pond. In 1977 the ponds were backfilled. From 1977 to the present, the ponds were assumed to result in negligible recharge but to continue to leach hydrocarbons at a rate of 820 g/yr. Borings into the shallow aquifer in the immediate vicinity of the ponds frequently show heavy black organic deposits indicating that nonaqueous creosote has reached the shallow system and will probably continue to leach soluble hydrocarbon for some years to come. No attempt has been made to simulate the dissolution of hydrocarbon since this process will be dependent on local concentrations, flow rates and microbial activity. In our simulations the soluble hydrocarbon has been assumed to be distributed throughout the water column within a short distance from the former ponds. The proposed loading scenario is outlined in Table 7-4.
<table>
<thead>
<tr>
<th></th>
<th>Small Pond</th>
<th>Large Pond</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injection Rate</strong></td>
<td>0.9 m$^3$/d</td>
<td>4.1 m$^3$/d</td>
</tr>
<tr>
<td>Chloride Conc.</td>
<td>270 mg/l</td>
<td>45 mg/l</td>
</tr>
<tr>
<td>Oxygen Conc.</td>
<td>0.0 mg/l</td>
<td>0.0 mg/l</td>
</tr>
<tr>
<td>Hydrocarbon Conc.</td>
<td>45 mg/l</td>
<td>45 mg/l</td>
</tr>
<tr>
<td><strong>1972-1977</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection Rate</td>
<td>0.09 m$^3$/d</td>
<td>0.41 m$^3$/d</td>
</tr>
<tr>
<td>Chloride Conc.</td>
<td>10 mg/l</td>
<td>10 mg/l</td>
</tr>
<tr>
<td>Oxygen Conc.</td>
<td>0.0 mg/l</td>
<td>0.0 mg/l</td>
</tr>
<tr>
<td>Hydrocarbon Conc.</td>
<td>45 mg/l</td>
<td>45 mg/l</td>
</tr>
<tr>
<td><strong>1977-1986</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection Rate</td>
<td>0.01 m$^3$/d</td>
<td>0.04 m$^3$/d</td>
</tr>
<tr>
<td>Chloride Conc.</td>
<td>10 mg/l</td>
<td>10 mg/l</td>
</tr>
<tr>
<td>Oxygen Conc.</td>
<td>0.0 mg/l</td>
<td>0.0 mg/l</td>
</tr>
<tr>
<td>Hydrocarbon Conc.</td>
<td>45 mg/l</td>
<td>45 mg/l</td>
</tr>
</tbody>
</table>
Estimates of longitudinal ($a_1$) and transverse dispersivity ($a_t$) were obtained by matching the simulated and observed chloride plumes. Dispersion coefficients were calculated as

$$D_1 = a_1 \cdot |V| \quad D_t = a_t \cdot |V|$$

Estimated values of $a_1$ and $a_t$ are 9.1 and 1.8 m.

The simulated chloride plume as of 1985 is shown in Figure 7-1. Simulated and observed chloride concentrations compare reasonably well (Table 7-5). The root mean squared error (RMSE) is 9 mg/l which is approaching the precision of the analytical measurements.

7.4 Hydrocarbon and Oxygen Simulations

Hydrocarbon and oxygen simulations were generated using the superposition procedure previously described. The background oxygen concentration varies from 2.5 to 3.5 mg/l and was simulated using a uniform concentration of 3.0 mg/l. The vertical dispersivity ($a_v$) was estimated by fitting to the observed hydrocarbon data since no independent estimate of $a_v$ could be obtained. The estimated $a_v$ at this site is 3.5 cm which results in a vertical dispersion coefficient which is approximately an order of magnitude higher than the molecular diffusion coefficient. Recent field tests at the University of Waterloo [Sudicky et al., 1983] and Auburn
FIGURE 7-1
Simulated Chloride Plume - 1986
Table 7-5

Comparison of Simulated and Observed Chloride Concentrations

<table>
<thead>
<tr>
<th>Well</th>
<th>Observed (mg/l)</th>
<th>Simulated (mg/l)</th>
<th>Error (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-1</td>
<td>15</td>
<td>10</td>
<td>-5</td>
</tr>
<tr>
<td>SW-2</td>
<td>77</td>
<td>83</td>
<td>6</td>
</tr>
<tr>
<td>SW-3</td>
<td>84</td>
<td>96</td>
<td>12</td>
</tr>
<tr>
<td>SW-4</td>
<td>71</td>
<td>66</td>
<td>-5</td>
</tr>
<tr>
<td>SW-5</td>
<td>152</td>
<td>152</td>
<td>0</td>
</tr>
<tr>
<td>SW-7</td>
<td>19</td>
<td>30</td>
<td>11</td>
</tr>
<tr>
<td>SW-8</td>
<td>26</td>
<td>10</td>
<td>-16</td>
</tr>
<tr>
<td>SW-9</td>
<td>41</td>
<td>44</td>
<td>3</td>
</tr>
<tr>
<td>RU-2</td>
<td>59</td>
<td>49</td>
<td>-10</td>
</tr>
<tr>
<td>RU-3</td>
<td>8</td>
<td>17</td>
<td>9</td>
</tr>
</tbody>
</table>

Root Mean Squared Error $= 9$
University [Molz, 1985] found vertical dispersion coefficients which were approximately equal to the molecular diffusion coefficient. The higher vertical mixing at this site may be due to the heterogeneous nature of the aquifer. Rigorous testing of this modeling procedure will require a much larger data set and independent evaluations of $a_l$, $a_t$, and $a_y$. Even considering the small data base available and the heterogeneous nature of the aquifer, the fit between observed and simulated hydrocarbon concentrations is quite good.

Simulated and observed hydrocarbon concentrations are compared in Table 7-6. The presence or absence of hydrocarbon was accurately simulated in all wells with the exception of SW-9. The reason for this error is not clear. Both oxygen and hydrocarbon were observed in this well. The observed hydrocarbon could be a sampling error or could be due to stratification in the aquifer. Stratification could result in contaminated water being withdrawn from one layer and clean oxygenated water being withdrawn from another layer. The largest numerical difference between simulated and observed concentrations occurred at SW-2. This difference could be due to sampling error since SW-2 is located in a zone of very low permeability (slug test results indicate permeability is two orders of magnitude below all other values). Consequently, long time periods
Table 7-6
Comparison of Simulated and Observed Total Hydrocarbon Concentrations

<table>
<thead>
<tr>
<th>Well</th>
<th>Observed (µg/l)</th>
<th>Simulated (µg/l)</th>
<th>Error (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-1</td>
<td>ND</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SW-2</td>
<td>62¹</td>
<td>285</td>
<td>223</td>
</tr>
<tr>
<td>SW-3</td>
<td>ND</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SW-4</td>
<td>108</td>
<td>40</td>
<td>-68</td>
</tr>
<tr>
<td>SW-5</td>
<td>46</td>
<td>87</td>
<td>-41</td>
</tr>
<tr>
<td>SW-7</td>
<td>ND</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SW-8</td>
<td>ND</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SW-9</td>
<td>84</td>
<td>0</td>
<td>-84</td>
</tr>
<tr>
<td>RU-2</td>
<td>5352</td>
<td>5334</td>
<td>-18</td>
</tr>
<tr>
<td>RU-3</td>
<td>14</td>
<td>0</td>
<td>-14</td>
</tr>
</tbody>
</table>

Root Mean Squared Error = 80

ND = not detected

¹Accuracy of measurement uncertain due to very low permeability
are necessary for sample collection and there is significant opportunity for hydrocarbon loss and oxygen addition. Simulated and observed oxygen concentrations are compared in Table 7-7. Again, the numerical simulation provides a fairly good explanation of the observed data. The largest errors occur at SW-4 and SW-9. Both of these wells are located at the perimeter of the hydrocarbon plume where microbial activity is expected to be greatest and the effects of stratification within the aquifer most pronounced. If there is some type of stratification, this could result in an apparent kinetic effect in which both oxygen and hydrocarbon were observed in the same well. The average difference between simulated and observed oxygen concentrations is 0.7 mg/l and is somewhat larger than expected even considering the large natural variation in background oxygen. This large average error in oxygen concentration is primarily due to the large errors at SW-4 and SW-9. These errors are believed to be primarily due to stratification within the aquifer which the current model is not capable of accurately simulating. Future work should be directed towards explaining these errors and describing the effects of vertical stratification on the kinetics of hydrocarbon degradation.

In order to examine the relative importance of various processes supplying oxygen to the hydrocarbon plume, a
Table 7-7

Comparison of Simulated and Observed Oxygen Concentrations

<table>
<thead>
<tr>
<th>Well</th>
<th>Observed (mg/l)</th>
<th>Simulated (mg/l)</th>
<th>Error (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-1</td>
<td>2.9</td>
<td>2.9</td>
<td>0.0</td>
</tr>
<tr>
<td>SW-2</td>
<td>---</td>
<td>0.0</td>
<td>---</td>
</tr>
<tr>
<td>SW-3</td>
<td>0.7</td>
<td>0.6</td>
<td>-0.1</td>
</tr>
<tr>
<td>SW-4</td>
<td>1.2</td>
<td>0.0</td>
<td>-1.2</td>
</tr>
<tr>
<td>SW-5</td>
<td>0.3</td>
<td>0.0</td>
<td>-0.3</td>
</tr>
<tr>
<td>SW-7</td>
<td>---</td>
<td>1.4</td>
<td>---</td>
</tr>
<tr>
<td>SW-8</td>
<td>---</td>
<td>3.0</td>
<td>---</td>
</tr>
<tr>
<td>SW-9</td>
<td>0.7</td>
<td>2.1</td>
<td>1.4</td>
</tr>
<tr>
<td>RU-2</td>
<td>0.2</td>
<td>0.0</td>
<td>-0.2</td>
</tr>
<tr>
<td>RU-3</td>
<td>1.4</td>
<td>1.8</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Root Mean Squared Error = 0.7
series of simulations were performed in which the effects of exchange with the unsaturated zone and horizontal mixing with formation water were eliminated. Figure 7-2 shows contours of equal hydrocarbon concentration for three cases. Case 1 is our best simulation of conditions at the UCC site. Case 2 assumes that exchange with the unsaturated zone is eliminated. Case 3 assumes that no biodegradation at all occurs. At the UCC site, horizontal mixing with oxygenated formation water results in biodegradation of trace quantities of hydrocarbon at the plume edges and reduces the area of the plume but has little effect on the high hydrocarbon concentrations in the plume center. Exchange with the unsaturated zone appears to be the major source of oxygen to the plume center. The observed hydrocarbon distribution could not be simulated with classical adsorption, dispersion and first order decay models, since any possible combination of simulation parameters would still result in trace hydrocarbon concentrations at the plume edges.

7.5 Summary

The field observations of the hydrocarbon plume show that it is much smaller than the observed chloride plume. The previous field test of adsorption has shown that retardation of hydrocarbon is not significant. Leakage of water to
FIGURE 7-2
Simulated Hydrocarbon Distribution - 1986

a) Case 1
Best Estimate of Hydrocarbon Distribution

b) Case 2
No Reaeration

c) Case 3
No Biodegradation
deeper formations cannot explain this loss since leakage would also result in a loss of chloride. The only available explanation is that biodegradation reduces the areal extent of the plume. The oxygen limited biodegradation model appears to provide a reasonably good description of this process although there is insufficient data to rigorously test the model. The major current weakness in the model appears to be in the description of the effects of vertical stratification due to variations in permeability and vertical exchange with the unsaturated zone and the effects of this stratification on the biodegradation.
8.0 Evaluation of Biodegradation Model: Push-Pull Tests

A pair of push pull tests were performed at the UCC site in Conroe, TX to measure the potential for in situ biodegradation of hydrocarbons and to provide a data set for testing of the oxygen limited biodegradation model. In the tests, contaminated ground water containing a variety of polycyclic aromatic hydrocarbons was withdrawn from RU-2, chloride was added, and then the water was injected into RU-1. The same injection well used in the three well test was used in this test since the adsorption characteristics of this portion of the aquifer were now known. The push-pull test was performed twice. During the first test, the contaminated water was maintained in an anoxic state. During the second test, the contaminated water was oxygenated prior to injection to measure the effect of oxygen in enhancing in situ biodegradation. This data set was then used to test the suitability of the model developed in chapter 6 for simulating enhanced in situ biodegradation.

8.1 Field and Laboratory Procedure

Two single well push-pull tests were performed during September 1984 to study the effects of oxygen addition on the degradation of creosote compounds in an aquifer. The tests were performed jointly with Michael D. Lee under the direction of C.H. Ward. During the first test, 416 liters
of water were withdrawn from a highly contaminated portion of the aquifer (well RU-2) and then amended with 280 mg/l chloride. Nitrogen was bubbled through the water to degas any oxygen. This water was then rapidly injected into well RU-1. Water was produced from well RU-1 at a rate of 72 l/d for eight days. Dissolved oxygen, chloride and organics were measured periodically during the test. The second test followed an essentially identical procedure except air was bubbled through the contaminated water to increase the dissolved oxygen concentration to 6 mg/l prior to injection. Dissolved oxygen, chloride and organics concentrations were measured using the same procedures as used in the three well test. During both tests, no new organic compounds were injected into the ground water. All water originated in an already contaminated portion of the aquifer. During the course of the tests, this water was withdrawn and transported off site for final disposal, resulting in a reduction in the total amount of contaminants in the aquifer.

8.2 Results and Statistical Data Analysis

Normalized concentration curves for the anoxic and oxygenated push-pull tests are shown in Figures 8-1 and 8-2. Injection and background concentrations used to calculate these curves are shown in Table 8-1. PNA (polynuclear
FIGURE 8-1
NORMALIZED CONCENTRATION DISTRIBUTION
FOR ANOXIC PUSH-PULL TEST

- □ chloride
- ○ conductivity
- △ pna's

Normalized Concentration

Volume Produced (ft³)
FIGURE 8-2
NORMALIZED CONCENTRATION DISTRIBUTION FOR OXYGENATED PUSH-PULL TEST

- □ chloride
- ○ conductivity
- △ pna's
- ◆ oxygen

Normalized Concentration

Volume Produced (ft³)
Table 8-1
Injection and Background Concentrations during Push-pull Tests

**Anoxic Test**

<table>
<thead>
<tr>
<th></th>
<th>Injection</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>280 mg/l</td>
<td>70 mg/l</td>
</tr>
<tr>
<td>Total PNA</td>
<td>0.950 mg/l</td>
<td>0.095 mg/l</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.7 mg/l</td>
<td>0.7 mg/l</td>
</tr>
<tr>
<td>Conductivity</td>
<td>830 µmho/l</td>
<td>248 µmho/l</td>
</tr>
</tbody>
</table>

**Oxygenated Test**

<table>
<thead>
<tr>
<th></th>
<th>Injection</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>290 mg/l</td>
<td>75 mg/l</td>
</tr>
<tr>
<td>Total PNA</td>
<td>0.936 mg/l</td>
<td>0.114 mg/l</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.0 mg/l</td>
<td>0.7 mg/l</td>
</tr>
<tr>
<td>Conductivity</td>
<td>905 µmho/l</td>
<td>293 µmho/l</td>
</tr>
</tbody>
</table>
aromatic hydrocarbons) is the sum of naphthalene, 1-methylnaphthalene, dibenzofuran, and fluorene. These four compounds occur in the highest concentrations at the site and generally constitute 70 to 80% of the total hydrocarbons. Normalized oxygen concentration is not plotted in Figure 8-1 for the anoxic test since the injection and background concentrations were approximately equal. Under these conditions minor analytical errors result in large shifts in the normalized concentration which are not significant. A summary of the measured values is provided in Appendix A2.

Chloride concentration and conductivity decreased rapidly during both tests, returning to background after approximately 354 l had been produced. This is somewhat surprising since approximately 416 l of water were injected during both tests. Classical advection dispersion theory would predict that the normalized concentration of chloride and conductivity would be greater than 0.50 until at least one injection volume had been produced. Various hypotheses were examined to try to explain this apparent inconsistency. The only hypothesis found which adequately matched the chloride and conductivity data assumes that a fraction of the injection fluid was somehow lost. During the push-pull tests, the injection rates were very high to avoid loss of the organics during the injection phase. These high injection rates may have forced some of the injection water
through the semi-confining layer where it could not be recovered. In all further data analysis, a fraction of the injection volume has been assumed to be lost from the system.

The normalized PNA concentration closely matched the normalized chloride and conductivity concentrations during the anoxic test indicating little or no biotransformation. During the second oxygenated test, the concentration of the PNA dropped very rapidly to below the background concentration by the first day. The concentration of PNA then gradually returned to the background concentration due to dilution by formation water. The oxygen concentration closely matched the PNA. Oxygen dropped rapidly to background and then remained relatively constant. This test clearly illustrates the potential for rapid biotransformation of the 4 PNA (naphthalene, 1-methylnaphthalene, dibenzofuran and fluorene) when oxygen is added. The only surprising result is the minimal transformation that occurred during the anoxic test. The field sampling indicated that the injection and formation water contained approximately 0.7 mg/l dissolved oxygen during the anoxic test yet little or no disappearance of the PNA was observed and no drop in oxygen was observed. The exact cause of this apparent oxygen threshold is not clear. In most biological systems, 0.7 mg/l oxygen is considered to
be quite sufficient for aerobic growth. This may not be true for the biotransformation of hydrocarbons.

8.3 Numerical Simulation of Push Pull Tests

The transport of aromatic hydrocarbons during the push-pull tests was simulated using the biodegradation model developed in Chapter 6. Equations 6-4 and 6-5 were written in one dimensional radial coordinates

\[
\frac{\partial H}{\partial t} = \frac{\partial}{\partial r} \left( \frac{\partial H}{\partial r} - v H \right) - M_t \cdot k \cdot \left( \frac{H}{K_h + H} \left( \frac{1}{K_o + O} \right) \right)
\]

\[
\frac{\partial O}{\partial t} = \frac{\partial}{\partial r} \left( \frac{\partial O}{\partial r} - v O \right) - M_t \cdot k \cdot F \cdot \left( \frac{H}{K_h + H} \left( \frac{1}{K_o + O} \right) \right)
\]

where

\[D_l = a_1\]

\[v = q / 2\pi r B \theta\]

and solved using an upwind finite difference solution.

Transport of the microorganisms was assumed to be negligible \((R_m = \infty)\) and the variation in \(M_t\) was calculated using eq. 6-3. Numerical dispersion was accounted for using the correction factor suggested by Lantz [1971]. This procedure was compared with the analytical solution of Gelhar and Collins [1971] and closely agreed. A listing of the program is provided in the Appendix B3.

The transport portion of the biodegradation model was first calibrated by matching the chloride recovery curves.
The effective injection volume was estimated as the produced volume where the normalized chloride concentration equaled 0.50. An effective injection volume was used because of the apparent loss of a portion of the injection fluid to the overlying unconfined unit. The longitudinal dispersivity \( a_1 \) was then adjusted to match the observed chloride recovery curves. The best estimate of \( a_1 \) was 0.3 m for both the anoxic and oxygenated tests. Simulated and observed chloride recovery curves are shown in Figures 8-3 and 8-4.

The recovery curves for oxygen and the polynuclear aromatics (PNA) were simulated using the parameters listed in Table 8-2. The initial microbial biomass was estimated by matching the PNA recovery curve. All other microbial parameters are identical to those used in chapter 6.

Preliminary simulations of the oxygenated push-pull test closely matched the field data during the early portion of the test. During the later portion of the test the numerical simulations began to diverge from the field data. This occurred at approximately the same time as the observed oxygen concentration approached 0.7 mg/l. The computer simulations suggested that the PNA concentration should remain close to zero whenever oxygen is present yet during the later portion of the test, the PNA concentration rose while the dissolved oxygen concentration remained relatively
FIGURE 8-3
NUMERICAL SIMULATION OF ANOXIC PUSH-PULL TEST

- ○ chloride
- ○ oxygen
- ▲ pH's

Dissolved Oxygen and pH Concentration (mg/l)

Chloride Concentration (mg/l)

Time From Injection (days)
FIGURE 8-4
NUMERICAL SIMULATION OF OXYGENATED PUSH-PULL TEST

- □ chloride
- ○ oxygen
- △ pna's

Dissolved Oxygen and pNA Concentration (mg/l)

Chloride Concentration (mg/l)

Time From Injection (days)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Anoxic Test</th>
<th>Oxygenated Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Volume (l)</td>
<td>115</td>
<td>126</td>
</tr>
<tr>
<td>Dispersivity (m)</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Saturated Thickness (m)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ratio total hydrocarbon PNA</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Background Oxygen (mg/l)</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Background PNA (mg/l)</td>
<td>0.095</td>
<td>0.114</td>
</tr>
<tr>
<td>Background Chloride (mg/l)</td>
<td>70.</td>
<td>75.</td>
</tr>
<tr>
<td>Injection Oxygen (mg/l)</td>
<td>0.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Injection PNA (mg/l)</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>Injection Chloride (mg/l)</td>
<td>280</td>
<td>290</td>
</tr>
</tbody>
</table>
constant at approximately 0.7 mg/l. Three hypotheses were developed which could potentially explain this apparent discrepancy.

Hypothesis 1) The dissolved oxygen measurements are in error. The detection limit for dissolved oxygen by this procedure is 0.7 mg/l.

Hypothesis 2) Degradation of the PNA does not proceed below some minimum oxygen concentration, in this case 0.7 mg/l.

Hypothesis 3) There is a layering within the formation such that oxygen but no PNA are present in one layer and PNA but no oxygen are present in another layer. When the well is pumped, water from the two layers mix resulting in the observed concentrations of oxygen and PNA.

Hypothesis 1, oxygen introduction during sampling is not thought to have occurred for the following reasons: 1) the minimum dissolved oxygen (D.O.) ever observed in this well is 0.7 mg/l while less than 0.1 mg/l has been observed in other wells; 2) 0.7 mg/l D.O. was observed in the injection water using a different sampling procedure; and 3) the variability in oxygen measurements from sample to sample during the anoxic test was very low (s = 0.14 mg/l). Computer models were developed to simulate hypotheses 2 and
3. In Hypothesis 2, the biological reaction terms were modified as follows:

\[
\frac{\text{d}H}{\text{d}t} = -M_t \cdot k \cdot \left( \frac{H}{K_h + H} \right) \left( \frac{O_{\text{min}} - O}{O} \right) \tag{8-3}
\]

\[
\frac{\text{d}O}{\text{d}t} = -M_t \cdot k \cdot F \left( \frac{H}{K_h + H} \right) \left( \frac{O_{\text{min}} - O}{O} \right) \tag{8-4}
\]

\[
\frac{\text{d}M_t}{\text{d}t} = M_t \cdot Y \left( \frac{H}{K_h + H} \right) \left( \frac{O_{\text{min}} - O}{O} \right) + k_c \cdot Y \cdot \text{OC} - b \cdot M_t \tag{8-5}
\]

In Hypothesis 3, the aquifer was assumed composed of two layers of equal thickness. In the first layer the oxygen concentration was assumed to be zero and the concentration of PNA to be double the observed background concentration. In the second layer, the oxygen concentration was assumed to be double the observed background concentration and the PNA were assumed to be zero. Fifty percent of the flow was assumed to come from each layer.

Numerical simulations under both Hypotheses 2 and 3 were able to adequately match the field data for the oxygenated test although Hypothesis 2 gave a slightly better fit. The major difference occurs when the anoxic test is simulated. There was no set of parameters which would result in an adequate fit of the layered hypothesis to the anoxic test data. The injection water during the anoxic test was observed to have a dissolved oxygen concentration of 0.7
mg/l. This water was injected into all layers independent of the background concentration in that layer. If there is no minimum oxygen concentration, the oxygen and PNA concentrations should have dropped during the early part of the anoxic test. This was not observed.

Hypothesis 2 assuming a minimum oxygen concentration of 0.7 mg/l for degradation gave a good fit to the field data for both the anoxic and oxygenated tests. Numerical simulation results are compared with the data in Figures 8-3 and 8-4. This minimum oxygen concentration for degradation is somewhat contradictory to observations in other systems. Aerobic biodegradation of wastewater commonly occurs to below 0.1 mg/l oxygen. The apparent minimum dissolved oxygen concentration observed during the push-pull tests may only occur for hydrocarbons or for these specific PNA. An apparent minimum dissolved oxygen concentration has been observed in laboratory studies at Rice University [Lee, personal communication] although controls may not have been adequate to completely eliminate the possibility of oxygen introduction during sampling.

8.4 Summary

Two single well push-pull tests were performed by injecting ground water containing polycyclic aromatic hydrocarbons and chloride into well RU-1. During the second
test oxygen was added to the injection water. These tests have clearly demonstrated the importance of oxygen in hydrocarbon biotransformation. When oxygen was added to the injection water, the hydrocarbon rapidly dissappeared. When no oxygen was added, there was no significant loss of hydrocarbon. A numerical model which assumes that oxygen limitation follows Monod type kinetics was applied to the field data from the two push-pull tests. This model was not capable of adequately matching the field data. The model was then modified to eliminate biotransformation below 0.7 mg/l dissolved oxygen. With this modification, the model was able to very closely match the field data. No other modifications including layering within the aquifer were able to adequately match the observed data. More detailed laboratory studies will be need to determine if a minimum dissolved oxygen concentration exists below which hydrocarbon transformation does not occur.
9.0 Management of Ground Water Contamination at the United Creosoting Company, Inc. Superfund Site

In order to assess the effect of biodegradation on ground water management and clean up alternatives, a series of simulations were performed using the modified version of the USGS Solute Transport model developed in chapter 7. The simulated hydrocarbon and oxygen distributions developed in chapter 7 were used as the initial condition. All parameters are identical to those used in chapter 7. Simulation results in this chapter are shown by plotting the actual hydrocarbon concentrations for a subdomain of the simulation grid. Figure 9-1 shows the simulated hydrocarbon distribution as of 1986 and the subdomain of the grid shown in all other figures.

9.1 Clean Up Alternatives

A variety of clean up alternatives were considered ranging from no action to pumping and injection of oxygenated water. The major aspects of each alternative are outline in Table 9-1. The first alternative considered was no action. Under this alternative, the hydrocarbon sludges deposited in the former ponds would be left in place and would continue to leach soluble hydrocarbons for the foreseeable future. Model simulations indicate that the area with elevated hydrocarbon concentrations can be
FIGURE 9-1
Simulated 1986 Hydrocarbon Distribution

subdomain shown in FIG. 9-2 to 9-9
Table 9-1
UCC Site Clean Up Alternatives

<table>
<thead>
<tr>
<th>Alternative</th>
<th>Action</th>
<th>Simulation Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No Action</td>
<td>Continue simulation with existing hydrocarbon source.</td>
</tr>
<tr>
<td>2</td>
<td>Excavate former ponds</td>
<td>Reduce hydrocarbon source by 90%.</td>
</tr>
<tr>
<td>3</td>
<td>Clay Cap/Slurry Wall</td>
<td>Reduce permeability in pond to $8 \times 10^{-7}$ cm/s. Set hydrocarbon loading to 0.</td>
</tr>
<tr>
<td>4a</td>
<td>Pumping and injection of clean water at 0.38 l/m</td>
<td>Set hydrocarbon loading to 0. Produce water from 20 wells at 0.38 l/m. Inject water in 11 wells at 0.38 l/m. Injection oxygen = 0.0 mg/l.</td>
</tr>
<tr>
<td>4b</td>
<td>Pumping and injection of clean water at 1.9 l/m</td>
<td>Set hydrocarbon loading to 0. Produce water from 20 wells at 1.9 l/m. Inject water in 11 wells at 1.9 l/m. Injection oxygen = 0.0 mg/l.</td>
</tr>
<tr>
<td>5a</td>
<td>Pumping and injection of oxygenated water at 0.38 l/m</td>
<td>Set hydrocarbon loading to 0. Produce water from 20 wells at 0.38 l/m. Inject oxygenated water in 11 wells at 0.38 l/m. Injection oxygen = 6.0 mg/l.</td>
</tr>
<tr>
<td>5b</td>
<td>Pumping and injection of oxygenated water at 1.9 l/m</td>
<td>Set hydrocarbon loading to 0. Produce water from 20 wells at 1.9 l/m. Inject oxygenated water in 11 wells at 1.9 l/m. Injection oxygen = 6.0 mg/l.</td>
</tr>
</tbody>
</table>
expected to increase somewhat over the next 40 yrs as the plume of reduced oxygen concentration moves down gradient and away from the former ponds (Figure 9-2). After the low oxygen plume passes, the area of hydrocarbon contamination should then shrink slightly, reaching a steady-state configuration after approximately 80 years.

The second alternative considered was removal of the hydrocarbon sludges, but no active cleanup of the contaminated ground water. Removal of these sludges was assumed to result in a 90% reduction in the hydrocarbon loading to the ground water. Complete removal of the hydrocarbon source would be preferable but is probably not feasible considering the available technology. The model simulations shown in Figure 9-3 indicate that the aquifer has the capacity to assimilate approximately 10% of the current hydrocarbon loading and that the remaining contaminated ground water would be renovated by natural processes within 60 years.

The third alternative considered was enclosure of the former ponds by a low permeability slurry wall ($10^{-8}$ cm/s) and covering with a clay cap to eliminate infiltration. The hydrocarbon loading from the surface was assumed to be zero but a small amount of hydrocarbon would continue to leak through the slurry wall. Under this alternative, the
FIGURE 9-2
Simulated Hydrocarbon Distributions - No Action Alternative

<table>
<thead>
<tr>
<th>0 years</th>
<th>20 years</th>
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</thead>
<tbody>
<tr>
<td>0 0 0 0 0 1810 4403 2490 90 0</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 2570 6383 4280 170 0</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 103 2107 7517 5397 1077 0</td>
<td></td>
</tr>
<tr>
<td>0 63 837 2780 4777 3517 307 0</td>
<td></td>
</tr>
<tr>
<td>0 137 910 2240 2377 1123 0 0</td>
<td></td>
</tr>
<tr>
<td>0 287 283 1587 1057 120 0 0</td>
<td></td>
</tr>
<tr>
<td>0 280 240 823 363 0 0 0</td>
<td></td>
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<td>0 283 183 83 0 0 0 0</td>
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</tr>
<tr>
<td>0 47 83 0 0 0 0 0</td>
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</tr>
<tr>
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<table>
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<td>0 0 0 0 688 2691 1407 0 0</td>
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</tr>
<tr>
<td>0 0 0 0 1554 5182 2405 0 0</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 677 8085 3300 0 0</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 957 2927 2218 0 0</td>
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</tr>
<tr>
<td>0 0 0 0 844 1281 175 0 0</td>
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</tr>
<tr>
<td>0 0 0 0 883 285 0 0 0</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 586 68 0 0 0</td>
<td></td>
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<td>0 0 0 0 0 0 0 0 0</td>
<td></td>
</tr>
<tr>
<td>0 0 0 0 0 0 0 0 0</td>
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</table>
### FIGURE 9-3
Simulated Hydrocarbon Distributions - Excavate Former Ponds

<table>
<thead>
<tr>
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<table>
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<tbody>
<tr>
<td><img src="image" alt="Table" /></td>
<td><img src="image" alt="Table" /></td>
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</tbody>
</table>
hydrocarbon concentrations remain high within the slurry wall but drop rapidly outside with complete renovation within 60 years (Figure 9-4).

The fourth alternative considered assumed complete removal of the source followed by pumping, treatment by activated carbon adsorption and reinjection of the contaminated water. The injection production pattern used in the simulations is shown in Figure 9-5. Two different flow rates were considered: 0.38 l/m and 1.9 l/m for each well. The injection water was assumed to have been treated to remove all hydrocarbon but to contain zero dissolved oxygen. Simulated hydrocarbon plumes are shown in Figures 9-6 and 9-7 for injection rates of 0.38 and 1.9 l/m. At an injection rate of 1.9 l/m, the hydrocarbon plume dissipates rapidly and is below 10 µg/l in all locations within 5 yrs while at 0.38 l/m significant concentrations of hydrocarbon persist for over 20 years.

The fifth alternative considered was identical to alternative 4 except the injection water was assumed to contain a dissolved oxygen concentration of 6.0 mg/l. This could easily be accomplished by bubbling air through the injection stream following carbon adsorption. Simulated hydrocarbon plumes are shown in Figures 9-8 and 9-9 for injection rates of 0.38 and 1.9 l/m. At an injection rate
FIGURE 9-4
Simulated Hydrocarbon Distributions - Slurry Wall/Clay Cap

0 years

20 years

40 years

60 years
FIGURE 9-5
Well Locations for Alternatives 4 and 5

- ○ pumping well
- ● injection well

Legend:
- Pond
- Source
- Nodal
FIGURE 9-6
Simulated Hydrocarbon Distributions - Pump/Injection at 0.38 l/m
DO=0.0 mg/l

0 years

```
0 0 0 0 0 0 0 0 0
0 0 0 0 1610 4403 2490 80 0
0 0 0 0 2870 8392 4280 170 0
0 0 0 0 102 2107 7517 8287 1077 0
0 0 83 837 2780 4777 3517 307 0
0 0 137 910 2240 2377 1133 0 0
0 0 367 283 1597 1057 120 0 0
0 0 280 240 823 353 0 0 0
0 0 283 182 83 0 0 0 0
0 0 47 83 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
```

5 years

```
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 184 419 887 0 0
0 0 0 0 0 884 832 1955 0 0
0 0 0 0 106 712 238 917 0 0
0 0 0 0 230 1108 833 1017 0 0
0 0 0 0 28 855 49 0 0 0
0 0 27 75 515 231 0 0 0
0 0 23 155 90 0 0 0 0
0 0 0 71 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
```

10 years

```
0 0 0 0 0 0 0 0 0
0 0 0 0 82 200 0 0 0
0 0 0 0 6 172 283 0 0
0 0 0 0 248 61 322 0 0
0 0 0 48 315 178 278 0 0
0 0 0 7 218 19 0 0 0
0 0 22 289 149 0 0 0
0 0 35 100 0 0 0 0
0 0 42 41 0 0 0 0
0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0
```

20 years

```
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0
0 0 0 0 2 0 0 0 0
0 0 0 0 0 2 0 0 0
0 0 0 0 25 0 0 0 0
0 0 0 0 47 11 0 0 0
0 0 0 0 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
```
FIGURE 9-7
Simulated Hydrocarbon Distributions - Pump/Inject at 1.9 l/m
DO = 0.0 mg/l

0 years

2.5 years

years
FIGURE 9-8
Simulated Hydrocarbon Distributions - Pump/Inject at 0.38 l/m
DO=6.0 mg/l

0 years

2.5 years

5 years

10 years
**FIGURE 9-9**
Simulated Hydrocarbon Distributions - Pump/Inject at 1.9 l/m
DO=6.0 mg/l

<table>
<thead>
<tr>
<th>Years</th>
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<th>2.5 years</th>
</tr>
</thead>
<tbody>
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<table>
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<tr>
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</tr>
</tbody>
</table>

Note: The values represent concentrations or measurements of hydrocarbons, with '0' indicating non-detectable levels or zero concentration.
of 1.9 1/m, the hydrocarbon plume dissipates very rapidly and is completely degraded within 2.5 yrs. At 0.38 1/m, removal of the hydrocarbon is much more rapid than without oxygen addition but some hydrocarbon continues to persist for up to 10 yrs.

9.2 Summary

The modified version of the USGS model developed and calibrated in chapter 7 was used to simulate the effects of various clean up alternatives including no action, excavation of the former ponds, enclosure of the pond area in a slurry wall and various combinations of pumping and injection wells. Under the no action alternative, the hydrocarbon plume reached a steady state length of approximately 150 m after 80 years. Excavation of the former ponds or enclosure in a slurry wall both resulted in essentially complete clean up of the hydrocarbon plume within 60 years. These results should not be interpreted as indicating complete clean up in the immediate vicinity of the former ponds because of the approximations inherent in simulating the hydrocarbon source. Pumping and injection of oxygenated water (6.0 mg/l D.O.) was able to reduce by 50% the time to clean up compared to pumping and injection of water containing no oxygen. In aquifers where adsorption of
hydrocarbon is significant, this difference may be even more
dramatic.
10.0 Conclusions and Recommendations

10.1 Conclusions

Past research at Rice University and the R.S. Kerr Environmental Research Laboratory had shown that a plume of hydrocarbon contaminated ground water was present in the shallow aquifer beneath the UCC site. The hydrocarbon plume was observed to be somewhat smaller than a plume of elevated chloride concentrations which appears to have originated from the same source. This difference in size could be due to two processes: adsorption and biodegradation. A series of field experiments and numerical simulations were performed to examine the relative importance of these two processes and their impact on ground water contamination at the UCC site. The major conclusions from this work are listed below.

1. A three well injection production test was successfully performed at the UCC site. Use of an onsite treatment system was very helpful in gaining regulatory approvals and in final clean up of the contaminated ground water.

2. Results from the three well test clearly demonstrated that adsorption of naphthalene and similar compounds is not significant at the UCC site. This conclusion corresponds with the observed movement of a PCP plume also present at the site.
3. A significant loss of both naphthalene and pDCB was observed during the three well test. This mass loss was apparently due to biotransformation of these organics.

4. Equations have been developed for simulating the oxygen limited biodegradation of dissolved hydrocarbons in ground water. These equations have been incorporated into several models for simulating the biodegradation process for a variety of conditions.

5. Numerical simulations developed using the biodegradation models suggest that when an adapted microbial population is present, the microbial kinetics will be fast relative to ground water flow and mass transport of oxygen into the hydrocarbon plume will often be rate limiting.

6. The primary sources of oxygen to a hydrocarbon plume will be transverse mixing with oxygenated formation water and vertical exchange with the unsaturated zone. Where hydrocarbon plumes occur at or near the water table as is typical for gasoline spills, exchange with the unsaturated zone may be the major source of oxygen.

7. The USGS solute transport model was modified to simulate oxygen limited biodegradation in two horizontal dimensions when adsorption is not significant. This model provided a good description of the hydrocarbon and
oxygen distributions observed at the UCC site. A significantly more detailed field test of the model under controlled conditions will be necessary to verify that the model accurately simulates the process of hydrocarbon biodegradation.

8. The biodegradation model was not able to accurately simulate the observed oxygen and hydrocarbon distributions for two wells at the UCC site. These wells contain both hydrocarbon and oxygen and are located near the perimeter of the hydrocarbon plume. The simultaneous presence of oxygen and hydrocarbon in a single well is thought to be due to vertical stratification within the aquifer. The existing biodegradation model is not capable of simulating vertical stratification.

9. A field test of enhanced biodegradation was performed at the UCC field site. Results of this test clearly demonstrate the potential for rapid biotransformation of creosote compounds in the subsurface when oxygen is added. A modification of the original biodegradation model was able to closely match the field results.

10. The calibrated version of the USGS solute transport model including the biodegradation modifications was used to simulate various remedial actions at the UCC
site. If no action were taken to clean up the site, a steady state hydrocarbon plume approximately 150 m long can be expected to develop, while a 90% reduction in the hydrocarbon source would completely eliminate the plume. Various pumping and injection alternatives were also considered. Injection of oxygenated water resulted in a 50% reduction in the time to clean up compared to pump and injection of water containing zero oxygen.

10.2 Recommendations

The field experiments and numerical studies performed as part of this research have explained much of the observed behavior of the hydrocarbon plume present at the UCC site but have also emphasized the gaps in our understanding of the transport and fate of organics in the subsurface. Further research should be directed towards filling these gaps. In particular:

1. The equations developed in this thesis for simulating oxygen limited biodegradation should be tested against one or more data sets from carefully controlled and instrumented field tests to determine if the equations do accurately simulate the hydrocarbon biodegradation process.
2. Additional experimental and numerical studies should be performed on the effects of spatial variations in permeability and oxygen content on oxygen limited biodegradation. These studies will hopefully improve our understanding of the kinetics of biodegradation, the uncertainty in any prediction, and explain apparent anomalies in the field data.

3. Additional experimental and numerical studies should be performed on the effects of oxygen/gas exchange with the unsaturated zone with particular emphasis on mass transport through the capillary fringe.

4. Additional laboratory studies should be performed on the kinetics of creosote biotransformation at low oxygen concentrations.

5. A more general user friendly version of the biodegradation model should be developed which would allow simulation of a variety of field sites where oxygen limited biodegradation may be significant.
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APPENDIX A1: Three well Test Results

Water Quality Data from 3-well Test - Well RU-29

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<tr>
<th>Time (hrs)</th>
<th>Cond. (°Mhos/1)</th>
<th>pDCB (µg/l)</th>
<th>Naphth (µg/l)</th>
<th>Flow (gpm)</th>
<th>Chloride (mg/l)</th>
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</thead>
<tbody>
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<td>305.</td>
<td>na</td>
<td>na</td>
<td>0.180</td>
<td>80</td>
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APPENDIX A1: Three well Test Results (continued)

Water Quality Data from 3-well Test - Well RU-29

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### APPENDIX A1: Three well Test Results (continued)

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<td>na</td>
<td></td>
</tr>
<tr>
<td>87.1</td>
<td>385. na</td>
<td>na</td>
<td>0.340</td>
<td>76.</td>
<td></td>
</tr>
<tr>
<td>91.1</td>
<td>390. na</td>
<td>na</td>
<td>0.322</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>93.1</td>
<td>370. 120.</td>
<td>230. na</td>
<td>0.304</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>95.1</td>
<td>420. na</td>
<td>na</td>
<td>0.292</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>97.1</td>
<td>375. na</td>
<td>na</td>
<td>0.280</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>99.1</td>
<td>395. 110.</td>
<td>250. 0.287</td>
<td>80.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101.1</td>
<td>375. na</td>
<td>na</td>
<td>0.255</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>103.1</td>
<td>380. na</td>
<td>na</td>
<td>0.252</td>
<td>na</td>
<td></td>
</tr>
</tbody>
</table>
### APPENDIX A1: Three well Test Results (continued)

#### Water Quality Data from 3-well Test - Well RU-28

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Cond. (μmho/1)</th>
<th>pDCB (μg/l)</th>
<th>Naphth (μg/l)</th>
<th>Flow (gpm)</th>
<th>Chloride (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105.1</td>
<td>330.</td>
<td>na</td>
<td>200.</td>
<td>0.249</td>
<td>na</td>
</tr>
<tr>
<td>107.1</td>
<td>380.</td>
<td>na</td>
<td>na</td>
<td>0.248</td>
<td>na</td>
</tr>
<tr>
<td>109.1</td>
<td>350.</td>
<td>na</td>
<td>na</td>
<td>0.243</td>
<td>na</td>
</tr>
<tr>
<td>111.1</td>
<td>345.</td>
<td>80.</td>
<td>230.</td>
<td>0.240</td>
<td>53.</td>
</tr>
<tr>
<td>113.1</td>
<td>365.</td>
<td>28.</td>
<td>180.</td>
<td>0.238</td>
<td>na</td>
</tr>
<tr>
<td>115.1</td>
<td>315.</td>
<td>na</td>
<td>na</td>
<td>0.238</td>
<td>na</td>
</tr>
<tr>
<td>117.1</td>
<td>330.</td>
<td>na</td>
<td>na</td>
<td>0.238</td>
<td>na</td>
</tr>
<tr>
<td>119.1</td>
<td>320.</td>
<td>na</td>
<td>na</td>
<td>0.235</td>
<td>na</td>
</tr>
<tr>
<td>121.1</td>
<td>300.</td>
<td>na</td>
<td>na</td>
<td>0.233</td>
<td>na</td>
</tr>
<tr>
<td>123.1</td>
<td>330.</td>
<td>na</td>
<td>na</td>
<td>0.232</td>
<td>53.</td>
</tr>
<tr>
<td>125.1</td>
<td>340.</td>
<td>60.</td>
<td>240.</td>
<td>0.230</td>
<td>na</td>
</tr>
<tr>
<td>127.1</td>
<td>325.</td>
<td>na</td>
<td>na</td>
<td>0.229</td>
<td>na</td>
</tr>
<tr>
<td>129.1</td>
<td>350.</td>
<td>na</td>
<td>na</td>
<td>0.227</td>
<td>na</td>
</tr>
<tr>
<td>131.1</td>
<td>350.</td>
<td>na</td>
<td>na</td>
<td>0.226</td>
<td>na</td>
</tr>
<tr>
<td>133.1</td>
<td>340.</td>
<td>na</td>
<td>na</td>
<td>0.224</td>
<td>na</td>
</tr>
<tr>
<td>135.1</td>
<td>330.</td>
<td>28.</td>
<td>180.</td>
<td>0.223</td>
<td>51.</td>
</tr>
<tr>
<td>137.1</td>
<td>330.</td>
<td>na</td>
<td>na</td>
<td>0.221</td>
<td>na</td>
</tr>
<tr>
<td>139.1</td>
<td>340.</td>
<td>na</td>
<td>na</td>
<td>0.220</td>
<td>na</td>
</tr>
<tr>
<td>143.1</td>
<td>340.</td>
<td>na</td>
<td>na</td>
<td>0.219</td>
<td>50.</td>
</tr>
<tr>
<td>147.1</td>
<td>320.</td>
<td>na</td>
<td>na</td>
<td>0.218</td>
<td>na</td>
</tr>
<tr>
<td>151.1</td>
<td>340.</td>
<td>na</td>
<td>na</td>
<td>0.217</td>
<td>na</td>
</tr>
<tr>
<td>155.1</td>
<td>340.</td>
<td>43.</td>
<td>170.</td>
<td>0.216</td>
<td>42.</td>
</tr>
<tr>
<td>159.1</td>
<td>340.</td>
<td>na</td>
<td>na</td>
<td>0.194</td>
<td>na</td>
</tr>
<tr>
<td>163.1</td>
<td>270.</td>
<td>na</td>
<td>na</td>
<td>0.194</td>
<td>na</td>
</tr>
<tr>
<td>167.1</td>
<td>280.</td>
<td>31.</td>
<td>36.</td>
<td>0.172</td>
<td>na</td>
</tr>
</tbody>
</table>

*na - not available*
## APPENDIX A2: Push-Pull Test Results

### ANOXIC TEST RESULTS

**Water Quality Data from Anoxic Test**

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Cond. (µmhos/1)</th>
<th>O2 (mg/l)</th>
<th>Total (mg/l)</th>
<th>Flow (Ft³/d)</th>
<th>Chloride (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>980.</td>
<td>0.85</td>
<td>1.175</td>
<td>2.441</td>
<td>280.</td>
</tr>
<tr>
<td>1.129</td>
<td>800.</td>
<td>0.70</td>
<td>0.521</td>
<td>2.441</td>
<td>188.</td>
</tr>
<tr>
<td>2.042</td>
<td>650.</td>
<td>0.70</td>
<td>0.270</td>
<td>2.721</td>
<td>129.</td>
</tr>
<tr>
<td>2.948</td>
<td>na</td>
<td>0.80</td>
<td>0.208</td>
<td>2.385</td>
<td>99.</td>
</tr>
<tr>
<td>3.813</td>
<td>388.</td>
<td>0.80</td>
<td>0.158</td>
<td>2.441</td>
<td>77.</td>
</tr>
<tr>
<td>5.900</td>
<td>300.</td>
<td>0.40</td>
<td>0.120</td>
<td>0.0</td>
<td>83.</td>
</tr>
<tr>
<td>7.800</td>
<td>344.</td>
<td>na</td>
<td>0.170</td>
<td>2.870</td>
<td>74.</td>
</tr>
</tbody>
</table>

### Water Quality Data from Oxygenated Test

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Cond. (mg/l)</th>
<th>O2 (mg/l)</th>
<th>Total (mg/l)</th>
<th>Flow (Ft³/d)</th>
<th>Chloride (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>na</td>
<td>4.00</td>
<td>0.935</td>
<td>2.492</td>
<td>na</td>
</tr>
<tr>
<td>0.975</td>
<td>700.</td>
<td>0.80</td>
<td>0.075</td>
<td>2.492</td>
<td>229.</td>
</tr>
<tr>
<td>1.740</td>
<td>540.</td>
<td>0.70</td>
<td>0.080</td>
<td>2.492</td>
<td>188.</td>
</tr>
<tr>
<td>2.687</td>
<td>418.</td>
<td>0.80</td>
<td>0.121</td>
<td>2.441</td>
<td>119.</td>
</tr>
<tr>
<td>4.887</td>
<td>348.</td>
<td>0.90</td>
<td>0.106</td>
<td>2.467</td>
<td>88.</td>
</tr>
</tbody>
</table>

**na** - not available
APPENDIX B1: 1-D CSMP Model

TITLE BIO1 - ONE DIMENSIONAL SIMULATION OF BIODEGRADATION

* PROGRAM CALCULATES DEGRADATION OF CONTAMINANT, REMOVAL OF OXYGEN
  * AND GROWTH OF BACTERIA IN A SERIES OF CSTR.
  * FIFTY PERCENT BREAKTHROUGH OCCURS AT CELL N=1/THETA
  * THIS IS EQUIVALENT TO AN UPWINDED FINITE DIFFERENCE
  * SOLUTION IN WHICH THE NUMERICAL DISPERSION IS DECREASED
  * BY DELTA X/2.
  * MICROBES ARE SUPPORTED BY THE SLOW DEGRADATION OF NATURALLY
  * OCCURRING ORGANIC CARBON
  *
  * THETA, THE DETENTION TIME OF EACH CELL IS IS BASED ON THE
  * PECLET NUMBER (PE). INDIVIDUAL CELL LENGTH(L)= 2.0=ALFA
  * THETA = L/V = 2.0=ALFA/V
  *
  *
  ******************************* PARAMETERS *******************************
  *
  * S = SUBSTRATE (MG/L)
  * O = OXYGEN(MG/L)
  * M = MICROBES(MG/L)
  * C = NATURALLY OCCURRING ORGANIC CARBON(MG/L)
  * V = VELOCITY(M/D)
  * ALFA = DISPERSIVITY(M)
  * X = DISTANCE TRAVELED(M)
  * T = TIME(DAYS)
  * K1= MAXIMUM SUBSTRATE UTILIZATION RATE(1/D)
  * KC= NATURAL CARBON UTILIZATION RATE (1/D)
  * F = RATIO OF OXYGEN TO SUBSTRATE CONSUMED
  * Y = MICROBE YIELD COEFFICIENT(MG/MG)
  * K5= SUBSTRATE HALF SATURATION CONSTANT(MG/L)
  * KD= OXYGEN HALF SATURATION CONSTANT(MG/L)
  * LOSS = FRACTION MICROBES LOST TO NEXT CELL(DIMENSIONLESS)
  * B = MICROBE DECAY COEFFICIENT(1/D)
  * SMIN = MINIMUM SUBSTRATE CONCENTRATION(MG/L)
  *
MACRO X,T,O,S,M =CSTR(XIN,SIN,OIN,TIN,MIN)
  X = XIN + L
  MONOD = (O+S)/((K0+O)*(K0+S))
  DSDT = (SIN/THETA - S/THETA)/RS -K1*M*RM*MONOD
  S = INTGRAL(SZERO,DSDT)
  DDT = (OIN/THETA - O/THETA)/RO - K1*F*M*RM*MONOD
  O = INTGRAL(OZERO,DDT)
  DTDT = T/THETA
  T = INTGRAL(TZERO,DTDT)
  DMDT = (MIN/THETA-M/THETA)/RM + K1*Y*M*MONOD + KC+Y+C -B*M
  M = INTGRAL(MZERO,DMDT)
ENDMAC

* FLOW PARAMETERS
PARAM V=0.05, ALFA=30.0

* INITIAL CONDITIONS
PARAM SZERO=0.000, ZERO=3.0, TZERO= 0., MZERO=0.1
= INFLOW CONCENTRATIONS
PARAM SIN=4.500, DIN=3.0, TIN=100., MIN=0.1
= KINETIC PARAMETERS
PARAM K1=1.70, F=3.0, KS=0.13, KG=0.10, Y=5., B=0.01, KC=3.38E-6
PARAM C = 800.00
= RETARDATION FACTORS
PARAM RS = 1.0, RO =1.0, RM = 100.0
=
INITIAL
THETA = 2.0 * ALFA/V
L = V/THETA
XIN=0.0
=
DYNAMIC
X1, T1, O1, S1, M1 = CSTR(XIN, SIN, DIN, TIN, MIN)
X2, T2, O2, S2, M2 = CSTR(X1, S1, O1, T1, M1)
X3, T3, O3, S3, M3 = CSTR(X2, S2, O2, T2, M2)
X4, T4, O4, S4, M4 = CSTR(X3, S3, O3, T3, M3)
X5, T5, O5, S5, M5 = CSTR(X4, S4, O4, T4, M4)
X6, T6, O6, S6, M6 = CSTR(X5, S5, O5, T5, M5)
X7, T7, O7, S7, M7 = CSTR(X6, S6, O6, T6, M6)
X8, T8, O8, S8, M8 = CSTR(X7, S7, O7, T7, M7)
X9, T9, O9, S9, M9 = CSTR(X8, S8, O8, T8, M8)
X10, T10, O10, S10, M10 = CSTR(X9, S9, O9, T9, M9)
X11, T11, O11, S11, M11 = CSTR(X10, S10, O10, T10, M10)
X12, T12, O12, S12, M12 = CSTR(X11, S11, O11, T11, M11)
X13, T13, O13, S13, M13 = CSTR(X12, S12, O12, T12, M12)
X14, T14, O14, S14, M14 = CSTR(X13, S13, O13, T13, M13)
X15, T15, O15, S15, M15 = CSTR(X14, S14, O14, T14, M14)
X16, T16, O16, S16, M16 = CSTR(X15, S15, O15, T15, M15)
X17, T17, O17, S17, M17 = CSTR(X16, S16, O16, T16, M16)
X18, T18, O18, S18, M18 = CSTR(X17, S17, O17, T17, M17)
X19, T19, O19, S19, M19 = CSTR(X18, S18, O18, T18, M18)
X20, T20, O20, S20, M20 = CSTR(X19, S19, O19, T19, M19)
=
TERMINAL
TIMER FINTIN=10000., PRDEL=10000., OUTDEL=1000., DELT=1000.
METHOD STIFF
PRINT S3, O3, T3,....
S4, O4, T4,....
S5, O5, T5,....
S6, O6, T6,....
S7, O7, T7,....
S8, O8, T8,....
S9, O9, T9,....
S10, O10, T10,....
S11, O11, T11,....
S12, O12, T12,....
S13, O13, T13,....
S14, O14, T14,....
S15, O15, T15,....
S16, O16, T16,....
S17, O17, T17,....
S18, O18, T18,....
S19, O19, T19,...
S20, O20, T20
OUTPUT S9, T9, M9, Q9
END
STOP
ENDJOB
APPENDIX B2: 2-D Horizontal Finite Difference Model

C
C PROGRAM NAME -- SIMPLE.FORT
C
C PROGRAM CALCULATES DEGRADATION OF CONTAMINANT AND REMOVAL
C OF OXYGEN IN AN N BY M FINITE DIFFERENCE GRID
C
C PROGRAM ASSUMES REMOVAL OF HYDROCARBON AND OXYGEN IS
C INSTANTANEOUS.
C
C PROGRAM USES A BACKWARD FINITE DIFFERENCE FORMULATION FOR
C THE ADOPTION TERM TO ELIMINATE OVERSHOOT. THE DISPERSION
C TERMS ARE CALCULATED USING CENTRAL DIFFERENCE FORMS.
C EXCESS NUMERICAL DISPERSION IS ELIMINATED BY USING THE
C CORRECTION FACTOR GENERATED BY LANTZ.
C THE LONGITUDINAL DISPERSIVITY IS REDUCED BY (DELTA X - DELTA T)/2.
C
C
C***************************************************************************** PARAMETERS***************************************************************************** C
C
C S = SUBSTRATE (MG/L)
C O = OXYGEN(MG/L)
C CL = TRACER CONCENTRATION(MG/L CHLORIDE)
C T = TIME (D)
C V = VELOCITY(FT/D)
C ALFAL = LONGITUDINAL DISPERSIVITY(FT)
C ALFAT = TRANSVERSE DISPERSIVITY (FT)
C DAIR = SOIL GAS DIFFUSION COEFFICIENT(FT=FT/D)
C DX = DELTA X (FT)
C DY = DELTA Y (FT)
C THICK = AQUIFER THICKNESS (FT)
C UNSAT = THICKNESS OF UNSATURATED ZONE(FT)
C DT = DELTA T (D)
C RHO = DENSITY (LBS/FT**3)
C PORO = POROSITY
C KD = PARTITION COEFFICIENT(FT**3/LBS)
C F = RATIO OF OXYGEN REMOVED TO SUBSTRATE CONSUMED
C N = NUMBER OF CELLS IN X DIRECTION
C M = NUMBER OF CELLS IN Y DIRECTION
C TF = NUMBER OF TIME STEPS
C TOUT = NUMBER OF TIME STEPS BETWEEN OUTPUT
C NSRC = NUMBER OF SOURCE NODES
C NX = CONTAMINANT SOURCE LOCATION(X)
C NY = CONTAMINANT SOURCE LOCATION(Y)
C SSS = S CONC. IN CONSTANT CONCENTRATION NODE -- NOT IN USE
C ODD = O CONC. IN CONSTANT CONCENTRATION NODE -- NOT IN USE
C CLCL = CHLORIDE CONC. IN CONSTANT CONCENTRATION NODE -- NOT IN USE
C WS(I,J) = SUBSTRATE LOADING IN SOURCE NODE(MG/D)
C WO(I,J) = OXYGEN LOADING IN SOURCE NODE (MG/D)
C WCl (I,J) = CHLORIDE LOADING IN SOURCE NODE (MG/D)
C
C*****************************************************************************
REAL S0(250,20), S1(250,20), 00(250,20), 01(250,20)
REAL CL0(250,20), CL1(250,20)
REAL WS(250,20), WD(250,20), WCL(250,20)
REAL WSS(10), WOO(10), WCLCL(10)
REAL REAIR(250,20)
REAL KD,F,FS,0IN,SIN,CLIN
REAL SSS, 000, CLCL
INTEGER TF,TT,TDUT,NX(10),NY(10)

C******************************************************************************
C
C READ PARAMETERS
C
READ(5,2000) V,ALFAL,ALFAT,DAIR,DX,DY,DT
READ(5,2000) THICK,UNSAT
READ(5,2010) RH0,PORO,KD,F
READ(5,2020) N,M,TF,TDUT,NSRCE
READ(5,2040) SIN,OIN,CLIN
IF(NSRCE.EQ.0) GOTO 8
DO 5 K=1,NSRCE
READ(5,2030) NX(K),NY(K),WSS(K),WOO(K),WCLCL(K)
5 CONTINUE
6 CONTINUE
2000 FORMAT(7F10.5)
2010 FORMAT(7F10.5)
2020 FORMAT(5I10)
2030 FORMAT(2I10,3F10.5)
2040 FORMAT(3F10.5)
C
C******************************************************************************
C
C PRINT COEFFICIENTS
C
WRITE(6,1000) V,ALFAL,ALFAT
WRITE(6,1010) RH0,PORO,KD
WRITE(6,1020) DX,DY,DT
WRITE(6,1025) THICK,UNSAT,DAIR
WRITE(6,1030) N,M,TF,NSRCE
WRITE(6,1040) F
1000 FORMAT(7H VEL = ,F8.4,8H ALFAL = ,F8.4,8H ALFAT = ,F8.4)
1010 FORMAT(7H RH0 = ,F8.4,8H PORO = ,F8.4,8H KD = ,F8.4)
1020 FORMAT(8H DX = ,F8.2,8H DY = ,F8.2,8H DT = ,F10.2)
1025 FORMAT(8H THICK = ,F5.1, 8H UNSAT = ,F5.1, 7H DAIR = ,F8.5)
1030 FORMAT(5H N = ,I5,5H M = ,I5,6H TF = ,I10, 8H NSRCE = ,I5)
1040 FORMAT(5H F = ,F8.5)
C
C******************************************************************************
C
C LOAD INITIAL AND BOUNDARY CONDITIONS
C
DO 20 I=1,N
DO 10 J=1,M
S0(I,J) = SIN
00(I,J) = OIN
CL0(I,J) = CLIN
20 CONTINUE
WD(I,J) = 0.0
WS(I,J) = 0.0
WCL(I,J) = 0.0
10 CONTINUE
20 CONTINUE
   SO(2, 9) = 33.3333
   DO(2, 9) = 0.
   CLO(2, 9) = 100.
   SO(2,10) = 33.3333
   DO(2,10) = 0.
   CLO(2,10) = 100.
   SO(2,11) = 33.3333
   DO(2,11) = 0.
   CLO(2,11) = 100.
   DO 25 K=1,NSRCE
      NXX = NX(K)
      NYY = NY(K)
      WD(NXX,NYY) = WOO(K)/(DX+THICK*PORD+28.32)
      WS(NXX,NYY) = WSS(K)/(DX+THICK*PORD+28.32)
      WCL(NXX,NYY) = WCLL(K)/(DX+THICK*PORD+28.32)
25 CONTINUE

C******************************************************************************

C CALCULATE COEFFICIENTS

C

   R = 1 + (RMD*KD)/PORD
   DLOM = V=(ALFAL+DX*2.+V=DT/2.)
   DTRANS = V= ALFAT
   A = (1./DT^2.*DLOM/(DX*DX) - 2.*DTRANS/(DX*DY) - V/DX)
   AA = (R/DT^2.*DLOM/(DX*DX) - 2.*DTRANS/(DX*DY) - V/DX)
   B = DLOM/(DX*DX) + V/DX
   C = DTRANS/(DY*DY)
   D = DLOM/(DX*DX)
   CT = DT*(4.*DLOM +V=DX)/(DX*DX)
   WRITE(6,1050) DLOM,DTRANS
   WRITE(6,1060) A,B,C,D
   WRITE(6,1070) CT
1050 FORMAT(8H DLOM = ,F8.6,10H DTRANS = ,F8.6)
1060 FORMAT(8H A = ,F8.6,5H B = ,F8.6,5H C = ,F8.6,5H D = ,F8.6)
1070 FORMAT(8H CT = ,F8.5)

NM1 = N-1
NM1 = N-1

C******************************************************************************

C SOLVE FOR PLUME

C

   T = 0.0
   CALL DUMP(SO,DO,CLO,T,N,W)
   TT = TF/TOUT
   DO 125 K = 1,TT
   DO 120 KX = 1,TOUT
   DO 60 I = 2,NM1
DO 50 J = 2, NM1
REAIR(I,J) = DAIR=(QIN - DD(I,J))/(UNSAT=UNSAT=THICK)
S1(I,J) = AA=SO(I,J) + B=SO(I-1,J) + C=SO(I,J-1) +
1 D=SO(I+1,J) + C=SO(I,J+1) + WS(I,J)
S1(I,J) = S1(I,J)=DT/R
O1(I,J) = A=OO(I,J) + B=OO(I-1,J) + C=OO(I,J-1) +
1 D=OO(I+1,J) + C=OO(I,J+1) + WD(I,J) + REAIR(I,J)
O1(I,J) = O1(I,J)=DT
CLO(I,J) = A=CLO(I,J) + B=CLO(I-1,J) + C=CLO(I,J-1) +
1 D=CLO(I+1,J) + C=CLO(I,J+1) + WCL(I,J)
CLO(I,J) = CLO(I,J)=DT
FS = F=S1(I,J)
IF(FS.GT.O1(I,J)) GOTO 40
O1(I,J) = O1(I,J) - FS
S1(I,J) = 0.0
GOTO 50
40 CONTINUE
S1(I,J) = S1(I,J) - O1(I,J)/F
O1(I,J) = 0.0
50 CONTINUE
60 CONTINUE
C RESET SO,OO,CLO
DO 100 I = 2, NM1
DO 80 J = 2, NM1
SO(I,J) = S1(I,J)
OO(I,J) = O1(I,J)
CLO(I,J) = CLO(I,J)
IF(SO(I,J).LT.0.0) SO(I,J)=0.0
IF(DD(I,J).LT.0.0) DD(I,J)=0.0
80 CONTINUE
100 CONTINUE
T=DT + T
120 CONTINUE
CALL DUMP(SO,OO,CLO,T,N,N)
125 CONTINUE
STOP
END
C
C*****************************************************************************
C
C SUBROUTINE DUMP(SO,OO,CLO,T,N,N)
REAL SO(250,10),OO(250,10),CLO(250,10)
C
C PRINT PLUME
C
WRITE(6,1170)
WRITE(6,1140): T
WRITE(6,1170)
DO 140 I =1,N
WRITE(6,1150)(SO(I,J),J=1,N)
140 CONTINUE
WRITE(6,1170)
DO 180 I = 1,N
WRITE(6,1150)(DD(I,J),J=1,N)
160 CONTINUE
   WRITE(*,1170)
   DO 180 I = 1,N
   WRITE(*,1160)(CLO(I,J),J=1,M)
180 CONTINUE
   WRITE(*,1170)
   WRITE(*,1170)
120 CONTINUE
1140 FORMAT(8H TIME = , F8.2)
1150 FORMAT(1H0,20(1H,F4.2))
1160 FORMAT(1H0,20(1H,F4.0))
1170 FORMAT(1H   )
   RETURN
END
APPENDIX B3: 2-D Vertical Finite Difference Model

C
C PROGRAM NAME -- VERTICAL.FORT
C
C PROGRAM CALCULATES VERTICAL PROFILE OF OXYGEN AND CONTAMINANT
C IN AN N BY M FINITE DIFFERENCE GRID
C OXYGEN AND NAPHTHALENE CONCENTRATIONS IN THE UNSATURATED ZONE
C ARE IN ATMOSPHERES. PARTITIONING AT THE WATER TABLE IS BY
C HENRY'S LAW COEFFICIENT. CONSUMPTION OF OXYGEN IN THE TOP
C FOOT IS BY SOIL RESPIRATION.
C
C PROGRAM USES A BACKWARD FINITE DIFFERENCE FORMULATION FOR
C THE ADVECTION TERM TO ELIMINATE OVERTURE. THE DISPERSION
C TERMS ARE CALCULATED USING CENTRAL DIFFERENCE FORMS.
C EXCESS NUMERICAL DISPERSION IS ELIMINATED BY USING THE
C CORRECTION FACTOR GENERATED BY LANTZ.
C THE LONGITUDINAL DISPERSIVITY IS REDUCED BY (DELTA X - DELTA T)/2.
C
C
C **************************** PARAMETERS ***************************
C
C S = SUBSTRATE (MG/L)
C O = OXYGEN(MG/L)
C CL = TRACER CONCENTRATION(MG/L CHLORIDE)
C T = TIME (D)
C V = VELOCITY(FT/D)
C ALFAL = LONGITUDINAL DISPERSIVITY(FT)
C ALFAT = TRANSVERSE DISPERSIVITY (FT)
C DX = DELTA X (FT)
C DY = DELTA Y (FT)
C DT = DELTA T (D)
C F = RATIO OF OXYGEN REMOVED TO SUBSTRATE CONSUMED
C N = NUMBER OF CELLS IN X DIRECTION
C M = NUMBER OF CELLS IN Y DIRECTION
C TF = NUMBER OF TIME STEPS
C TOUT = NUMBER OF TIME STEPS BETWEEN OUTPUT
C DIFFO = MOLECULAR OXYGEN DIFFUSION COEFFICIENT(FT/FT/D)
C DIFFS = MOLECULAR SUBSTRATE DIFFUSION COEFFICIENT(FT/FT/D)
C DIFFC = MOLECULAR CHLORIDE DIFFUSION COEFFICIENT(FT/FT/D)
C HO = OXYGEN HENRY'S LAW COEFFICIENT(0.0226 ATM=L/MG)
C HS = SUBSTRATE HENRY'S LAW COEFFICIENT(0.00833 ATM=L/MG)
C HCL = CHLORIDE HENRY'S LAW COEFFICIENT(0.0 ATM=L/MG)
C SRR = SOIL RESPIRATION RATE(1/D)
C
C*************************************************************************
C
C REAL S0( 20,40),S1( 20,40),00( 20,40),01( 20,40)
C REAL CLO( 20,40),CL1( 20,40)
C REAL DLON(40),DTRANS(40),AS(40),BS(40),CS(40),DS(40)
C REAL DLON(40),DTRANS(40),AC(40),BD(40),CD(40),DD(40)
C REAL DLONC(40),DTRANC(40),ACL(40),BCL(40),CCL(40),DCL(40)
C REAL DIFFO(40),DIFFS(40),DIFFC(40),SRR(40)
C REAL F,FS,OIN,SIN,CLIN
INTEGER TF, TT, TOUT

C******************************************************************************
C
C READ PARAMETERS
C
READ(5,2000) V, ALFAL, ALFAT, DX, DY, DT
READ(5,2010) SSS, OOD, CLCL, SRRR
READ(5,2020) N, M, TF, TOUT
2000 FORMAT(8F10.5)
2010 FORMAT(4F10.5)
2020 FORMAT(4I10)
C
C******************************************************************************
C
C LOAD INITIAL AND BOUNDARY CONDITIONS
C
NM1 = N-1
NM1 = M-1
F = 3.0
HS = 0.00533
HD = 0.0228
HCL = 0.0
DO 10 J=1,15
DIFFD(J) = 5.0 E-5
DIFFS(J) = 5.0 E-5
DIFFC(J) = 5.0 E-5
SRR(J) = 0.0
10 CONTINUE

DO 20 J=16,N
DIFFD(J) = .0015
DIFFS(J) = .00075
DIFFC(J) = .0014
SRR(J) = 0.0
20 CONTINUE
SRR(30) = SRRR
SRR(31) = SRRR
SRR(32) = SRRR

C
DO 50 I=1,N
DO 30 J=1,15
SO(I,J) = SSS
OO(I,J) = OOD
CLO(I,J) = CLCL
30 CONTINUE

DO 40 J=16, NM1
SO(I,J) = 0.0
OO(I,J) = 0.0555
CLO(I,J) = 0.0
40 CONTINUE

SO(I,40) = 0.0
OO(I,40) = 0.209
CLO(I,40) = 0.0

50 CONTINUE
DO 55 J=1,40
S0(N,J) = 0.0
G0(N,J) = 0.0
CLO(N,J) = 0.0

55 CONTINUE
C
C******************************************************************************
C
C CALCULATE COEFFICIENTS
C
C
DDLOM = V=(ALFAL - DX/2.+V * DT/2.)
CT = DT=(4.*DDLOM +V*DX)/(DX*DX)
DO 80 J=1,15
DLONS(J) = V=(ALFAL - DX/2.+V * DT/2.) + DIFFS(J)
DTRANS(J) = V= ALFAT + DIFFS(J)
AS(J) = (1./DT-2.*DLONS(J)/(DX*DX)-2.*DTRANS(J)/(DY*DY)- V/DX)
BS(J) = DLONS(J)/(DX*DX) + V/DX
CS(J) = DTRANS(J)/(DY*DY)
DS(J) = DLONS(J)/(DX*DX)

DLONO(J) = V=(ALFAL - DX/2.+V * DT/2.) + DIFFO(J)
DTRANO(J) = V= ALFAT + DIFFO(J)
AO(J) = (1./DT-2.*DLONO(J)/(DX*DX)-2.*DTRANO(J)/(DY*DY)- V/DX)
BO(J) = DLONO(J)/(DX*DX) + V/DX
CO(J) = DTRANO(J)/(DY*DY)
DO(J) = DLONO(J)/(DX*DX)

DLONC(J) = V=(ALFAL - DX/2.+V * DT/2.) + DIFFC(J)
DTRANC(J) = V= ALFAT + DIFFC(J)
ACL(J) = (1./DT-2.*DLONC(J)/(DX*DX)-2.*DTRANC(J)/(DY*DY)-V/DX)
BCL(J) = DLONC(J)/(DX*DX) + V/DX
CCL(J) = DTRANC(J)/(DY*DY)
DCL(J) = DLONC(J)/(DX*DX)

80 CONTINUE
DO 70 J=16,N
DLONS(J) = DIFFS(J)
DTRANS(J) = DIFFS(J)
AS(J) = (1./DT-2.*DLONS(J)/(DX*DX)-2.*DTRANS(J)/(DY*DY))
BS(J) = DLONS(J)/(DX*DX)
CS(J) = DTRANS(J)/(DY*DY)
DS(J) = DLONS(J)/(DX*DX)
DLONO(J) = DIFFO(J)
DTRANO(J) = DIFFO(J)
AO(J) = (1./DT-2.*DLONO(J)/(DX*DX)-2.*DTRANO(J)/(DY*DY))
BO(J) = DLONO(J)/(DX*DX)
CO(J) = DTRANO(J)/(DY*DY)
DO(J) = DLONO(J)/(DX*DX)
DLONC(J) = DIFFC(J)
DTRANC(J) = DIFFC(J)
ACL(J) = (1./DT-2.*DLONC(J)/(DX*DX)-2.*DTRANC(J)/(DY*DY))
BCL(J) = DLONC(J)/(DX*DX)
CCL(J) = DTRANC(J)/(DY*DY)
DCL(J) = DLONC(J)/(DX*DX)

70 CONTINUE
C
C******************************************************************************
C
C PRINT COEFFICIENTS
C
WRITE(B,1010) V,ALFAL,ALFAT
WRITE(B,1020) DX,DY,DT
WRITE(B,1030) N,M,TF
WRITE(B,1040) F,CT
WRITE(B,1070) HS,HO,HCL
WRITE(B,1000)
WRITE(B,1050)
WRITE(B,1000)
DO 80 J=1,N
WRITE(B,1060) J,DLONS(J),DTRANS(J),AS(J),BS(J),CS(J),DS(J),SRR(J)
80 CONTINUE
WRITE(B,1000)
WRITE(B,1050)
WRITE(B,1000)
DO 90 J=1,N
WRITE(B,1060) J,DLONG(J),DTRANS(J),AO(J),BO(J),CO(J),DO(J),SRR(J)
90 CONTINUE
WRITE(B,1000)
WRITE(B,1050)
WRITE(B,1000)
DO 100 J=1,N
WRITE(B,1060) J,DLONC(J),DTRANC(J),ACL(J),BCL(J),CCL(J),DCL(J),
1 SRR(J)
100 CONTINUE
WRITE(B,1000)
1000 FORMAT(1H )
1010 FORMAT(7H VEL = ,F8.4,9H ALFAL = ,F8.4,9H ALFAT = ,F8.4)
1020 FORMAT(9H RX = ,F8.2,9H DRY = ,F8.2,9H DT = ,F10.2)
1030 FORMAT(5H N = ,I5,5H M = ,I5,6H TF = ,I10)
1040 FORMAT(5H F = ,F8.5,9H CT = ,F8.5)
1050 FORMAT(5H J DLON DTRANS A(J) B(J) C(J) D(J) SRR(J) )
1060 FORMAT(2H ,I2,7(1H ,F8.3))
1070 FORMAT(6H HS = ,F8.6,6H HO = ,F8.6,7H HCL = ,F8.6)
C
C===============================================================
C
C SOLVE FOR PLUME
C
T = 0.0
CALL DUMP(SO,OO,CL0,T,N,M)
TT = TF/TOUT
DO 310 K = 1,TT
DO 300 KK = 1,TOUT
DO 250 I = 2,NM1
SO(I,15) = (SO(I,15) + SO(I,16)/HS)/2.
SO(I,16) = SO(I,15)+HS
DD(I,15) = (DD(I,15) + DD(I,18)/HO)/2.
DD(I,18) = DD(I,15)+HO
DO 200 J = 2,14
S1(I,J) = AS(J)*SO(I,J) + BS(J)*SO(I-1,J) + CS(J)*SO(I,J-1) +
1 DS(J)*SO(I+1,J) + CS(J)*SO(I,J+1)
S1(I,J) = S1(I,J)*DT
O1(I,J) = AO(J)+DO(I,J) + BO(J)+DO(I-1,J) + CO(J)+DO(I,J-1) +
1 DO(J)+DO(I+1,J) + CO(J)+DO(I,J+1) + SRR(J)+DO(I,J)
O1(I,J) = O1(I,J)+DT
CL1(I,J) = ACL(J)+CL0(I,J) + BCL(J)=CL0(I-1,J) + CCL(J)=CL0(I,J-1)
1 + DCL(J)=CL0(I+1,J) + CCL(J)=CL0(I,J)
CL1(I,J) = CL1(I,J)+DT

200 CONTINUE
DO 210 J = 17,NM1
S1(I,J) = AS(J)+SO(I,J) + BS(J)+SO(I-1,J) + CS(J)+SO(I,J-1) +
1 DS(J)+SO(I+1,J) + CS(J)+SO(I,J+1)
S1(I,J) = S1(I,J)+DT
O1(I,J) = AO(J)+DO(I,J) + BO(J)+DO(I-1,J) + CO(J)+DO(I,J-1) +
1 DO(J)+DO(I+1,J) + CO(J)+DO(I,J+1) + SRR(J)+DO(I,J)
O1(I,J) = O1(I,J)+DT
CL1(I,J) = ACL(J)+CL0(I,J) + BCL(J)=CL0(I-1,J) + CCL(J)=CL0(I,J-1)
1 + DCL(J)=CL0(I+1,J) + CCL(J)=CL0(I,J)
CL1(I,J) = CL1(I,J)+DT

210 CONTINUE
S1(I,15) = SO(I,15)
O1(I,15) = DO(I,15)
CL1(I,15) = CL0(I,15)
S1(I,18) = SO(I,18)
O1(I,18) = DO(I,18)
CL1(I,18) = CL0(I,18)
DO 230 J = 2,NM1
FS = F=S1(I,J)
IF(FS.GT.O1(I,J)) GOTO 220
O1(I,J) = O1(I,J) - FS
S1(I,J) = 0.0
GOTO 230

220 CONTINUE
S1(I,J) = S1(I,J) - O1(I,J)/F
O1(I,J) = 0.0

230 CONTINUE

250 CONTINUE
C RESET SO,DO,CL0
DO 270 I = 2,NM1
DO 260 J = 2,NM1
SO(I,J) = S1(I,J)
DO(I,J) = O1(I,J)
CL0(I,J) = CL1(I,J)
IF(SO(I,J).LT.0.0) SO(I,J) = 0.0
IF(00(I,J).LT.0.0) O0(I,J) = 0.0

260 CONTINUE
SO(I,1) = SO(I,2)
OO(I,1) = DO(I,2)
CL0(I,1) = CL0(I,2)

270 CONTINUE
T=DT + T

300 CONTINUE
CALL DUMP(SO,DO,CL0,T,N,M)

310 CONTINUE
STOP
END
SUBROUTINE DUMP(SO,OO,CLO,T,N,M)
REAL SO( 20,40),OO( 20,40),CLO( 20,40)

C
C PRINT PLUME
C
WRITE(8,1120)
WRITE(8,1100) T
WRITE(8,1120)
DO 140 J =1,N
WRITE(8,1110)(SO(I,J),I=1,N)
140 CONTINUE
WRITE(8,1120)
DO 180 J = 1,N
WRITE(8,1110)(OO(I,J),I=1,N)
180 CONTINUE
WRITE(8,1120)
DO 180 J = 1,N
WRITE(8,1110)(CLO(I,J),I=1,N)
180 CONTINUE
WRITE(8,1120)
WRITE(8,1120)
120 CONTINUE
RETURN
1100 FORMAT(8H TIME = , F8.2)
1110 FORMAT(1H ,20(1H ,F5.3))
1120 FORMAT(1H )
END
APPENDIX B4: 1-D Radial Solution of Push-Pull Test

TITLE PUSHPULL - 1-D RADIAL SIMULATION OF OXYGENATED TEST

* PROGRAM CALCULATES DEGRADATION OF CONTAMINANT, REMOVAL
* OF OXYGEN AND GROWTH OF BACTERIA IN A SERIES OF CSTR.
* THIS IS EQUIVALENT TO AN UPWINDED FINITE DIFFERENCE
* SOLUTION IN WHICH THE NUMERICAL DISPERSION IS
* CORRECTED FOR BY DECREASING BY DELTA X/2.
*
* *************** PARAMETERS *********************
*
* S = SUBSTRATE (MG/L)
* O = OXYGEN(MG/L)
* M = MICROBES(MG/L)
* V = VELOCITY(FT/D)
* Q = FLOW RATE(FT**3/D)
* THICK = SATURATED THICKNESS = 5.00 FT
* PORO = POROSITY = 0.305
* ALFA = DISPERSIVITY(FT)
* X = DISTANCE TRAVELED(FT)
* T = TIME(DAYS)
* K1 = MAXIMUM SUBSTRATE UTILIZATION RATE(1/D)
* F = RATIO OF OXYGEN TO SUBSTRATE CONSUMED
* Y = MICROBE YIELD COEFFICIENT(MG/MG)
* KS = SUBSTRATE HALF SATURATION CONSTANT(MG/L)
* KD = OXYGEN HALF SATURATION CONSTANT(MG/L)
* K0 = MICROBE DECAY COEFFICIENT(1/D)
* OMIN = MINIMUM OXYGEN CONCENTRATION(MG/L)
*
MACRO T,O,S,M =CSTR(SIN,SOUT,OIN,OOUT,TIN,TOUT,V,D,K,FA,FB)
  A = D/(DR*DR) + V*FB/DR
  B = -2.*D/(DR*DR) - V*DR
  C = D/(DR*DR) + V*FA/DR
  MONOD = (O*S)/(((KD+O)*(KS+S))
  DSDT = A*SOUT + B*S + C*SIN -K*M*MONOD*(O-OMIN)/O
  S = INTEGR(SO,DSDT)
  DODT = A*OOUT + B*O + C*OIN -F*K*M*MONOD*(O-OMIN)/O
  O = INTEGR(00,DODT)
  DTDT = A*TOUT + B*T + C*TIN
  T = INTEGR(T0,DTDT)
  DMOT = -(K*Y*M*MONOD-KD*M)*(O-OMIN)/O
  M = INTEGR(M0,DMOT)
ENDMAC
*
* FLOW PARAMETERS
PARAM Q=2.473, ALFA=0.1, THICK = 5.0, PORO = 0.305
PARAM PI = 3.14159
*
* INITIAL CONDITIONS
PARAM OO=0.7,TO=75.,MO=1.80, START = 1.80
PARAM CONST = 1.25, HN = 0.936
*
* KINETIC PARAMETERS
PARAM F =3.00, KS=0.13, KD=0.10, Y=.50, KD = 0.01
PARAM DMIN=0.700

BOUNDARY CONDITIONS
PARAM D15 = 0.7, T15 = 75.0

INITIAL

SO = 0.114*CONST
S15 = 0.114*CONST
DR = 2.*ALFA
POROB = POROB*THICK
V1 = Q/(2.*PI*POROB*(0.0 + DR/2.))
V2 = Q/(2.*PI*POROB*(0.0 + DR/2. + DR))
V3 = Q/(2.*PI*POROB*(0.0 + DR/2. + 2.*DR))
V4 = Q/(2.*PI*POROB*(0.0 + DR/2. + 3.*DR))
V5 = Q/(2.*PI*POROB*(0.0 + DR/2. + 4.*DR))
V6 = Q/(2.*PI*POROB*(0.0 + DR/2. + 5.*DR))
V7 = Q/(2.*PI*POROB*(0.0 + DR/2. + 6.*DR))
V8 = Q/(2.*PI*POROB*(0.0 + DR/2. + 7.*DR))
V9 = Q/(2.*PI*POROB*(0.0 + DR/2. + 8.*DR))
V10 = Q/(2.*PI*POROB*(0.0 + DR/2. + 9.*DR))
V11 = Q/(2.*PI*POROB*(0.0 + DR/2. + 10.*DR))
V12 = Q/(2.*PI*POROB*(0.0 + DR/2. + 11.*DR))
V13 = Q/(2.*PI*POROB*(0.0 + DR/2. + 12.*DR))
V14 = Q/(2.*PI*POROB*(0.0 + DR/2. + 13.*DR))
D1 = V1*(ALFA - DR*0.5)
D2 = V2*(ALFA - DR*0.5)
D3 = V3*(ALFA - DR*0.5)
D4 = V4*(ALFA - DR*0.5)
D5 = V5*(ALFA - DR*0.5)
D6 = V6*(ALFA - DR*0.5)
D7 = V7*(ALFA - DR*0.5)
D8 = V8*(ALFA - DR*0.5)
D9 = V9*(ALFA - DR*0.5)
D10 = V10*(ALFA - DR*0.5)
D11 = V11*(ALFA - DR*0.5)
D12 = V12*(ALFA - DR*0.5)
D13 = V13*(ALFA - DR*0.5)
D14 = V14*(ALFA - DR*0.5)

DYNAMIC
SIN = CONST*HIN = (1.0 - STEP(START))
TIN = 290. - 215.*STEP(START)
DIN = 4.00 - 3.30*STEP(START)
FA = 1.0*STEP(START)
FB = STEP(START)
K = 1.70*STEP(START)
T1,01,S1,M1 = CSTR(SIN,S2,DIN,02,TIN,T2,V1,D1,K,FA,FB)
T2,02,S2,M2 = CSTR(S1,S3,01,03,T1,T3,V2,D2,K,FA,FB)
T3,03,S3,M3 = CSTR(S2,S4,02,04,T2,T4,V3,D3,K,FA,FB)
T4,04,S4,M4 = CSTR(S3,S5,03,05,T3,T5,V4,D4,K,FA,FB)
T5,05,S5,M5 = CSTR(S4,S6,04,08,T4,T6,V5,D5,K,FA,FB)
T6,06,S6,M6 = CSTR(S5,S7,05,07,T5,T7,V6,D6,K,FA,FB)
T7,07,S7,M7 = CSTR(S6,S8,06,08,T6,T8,V7,D7,K,FA,FB)
T8,08,S8,M8 = CSTR(S7,S9,07,09,T7,T9,V8,D8,K,FA,FB)
T9,09,S9,M9 =CSTR(S8,S10,08,010,T8,T10,V8,D8,K,FA,FB)
T10,010,S10,M10 =CSTR(S9,S11,09,011,T9,T11,V10,D10,K,FA,FB)
T11,011,S11,M11 =CSTR(S10,S12,010,012,T10,T12,V11,D11,K,FA,FB)
T12,012,S12,M12 =CSTR(S11,S13,011,013,T11,T13,V12,D12,K,FA,FB)
T13,013,S13,M13 =CSTR(S12,S14,012,014,T12,T14,V13,D13,K,FA,FB)
T14,014,S14,M14 =CSTR(S13,S15,013,015,T13,T15,V14,D14,K,FA,FB)
HYDRO = S1/CONST

TERMINAL
TIMER FINTIM= 6.0, PRDEL=0.10, OUTDEL=0.100, DELT=0.100
METHOD STIFF
PRINT HYDRO,S1,01,T1,M1,V1
OUTPUT HYDRO,S1,T1,M1,01
END
STOP
ENDJOB
APPENDIX B5

Flow Chart - Biodegradation Calculation

Start Hydrocarbon simulation

Generate 1st order decay coefficient $K'$ where $K' = f(v, D_v, B)$

Generate hydrocarbon distribution including first order decay ($H'$)

Combine Oxygen and Hydrocarbon distributions
where $H' \geq O'/F$
$H = H' - O'/F$, $O = 0$

where $O' \geq H' \cdot F$
$O = O' - H' \cdot F$, $H = 0$

Final Oxygen ($O$) and Hydrocarbon ($H$) distributions including biodegradation due to respiration and horizontal mixing

Start Oxygen simulation

No Decay

Generate Oxygen distribution in absence of Biodegradation ($O'$)