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BIOPHUME II MODELING OF THE MADE-2 SITE IN COLUMBUS, MISSISSIPPI

by

KEVIN C. APPLING

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE

APPROVED, THESIS COMMITTEE

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ABSTRACT

Bioplume II Modeling of the MADE-2 Site in Columbus Mississippi

by

Kevin Appling

In 1993, a tracer solution containing benzene, p-xylene, napthalene, o-dichlorobenzene, and tritium was pulse injected into the subsurface at the Macrodispersion Experiment (MADE) site at Columbus Air Force Base in Mississippi. The hydraulic head, hydraulic conductivity, and contaminant concentration data from this experiment are documented in Boggs et al., 1993a. The Bioplume II biodegradation model was used to simulate this data. All organic tracers were considered as a lumped contaminant requiring 2.731 grams of oxygen to degrade 1.000 gram of total organic contaminants. Natural attenuation was modeled as both first-order decay and instantaneous degradation with first-order decay. The simulations matched the observed tritium data, but did not closely match the organic tracer data.
Acknowledgments

Without the patience and assistance of the following people this thesis could not have been completed:

Thanks to my advisor, Dr. Hanadi S. Rifai, for her guidance throughout the project, along with thanks to Joseph B. Hughes and Katherine B. Ensor for serving on my committee. Thanks to all of the other graduate students in the department, with special thanks to Anthony Holder, Tom Jagiella, and Lauren Hopkins for providing support and listening to my ramblings. Thanks to Paul LaWare for all his help and technical expertise. Finally, thanks to my family for their constant support and love, especially my fiancé Tamra Thweatt, without whom I could not have finished this work.
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1.0 Introduction

"Groundwater at many... DoD ... sites is contaminated by organic compounds such as JP-4, gasoline, diesel... as well as chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE)." (Beach et al., 1996.) The fate and transport of contaminated groundwater is of concern to the United States Air Force (USAF) and the Department of Defense (DoD). To facilitate research in this area, the USAF has conducted several field scale studies at the MADE site, located at the Columbus Air Force Base in Mississippi.

On June 26, 1990, a tracer solution containing benzene, naphthalene, \( p \)-xylene, \( o \)-dichlorobenzene, and tritium was injected at the MADE site. Over a period of 48.5 hours, 9.7 cubic meters of solution were injected through five wells. This experiment is known as MADE-2. The progress and concentration of the tracers was monitored for 440 days using a network of 328 multilevel samplers. Data for time-series analyses were collected by sampling two rows of wells oriented perpendicular to the direction of groundwater flow. Hydraulic conductivity, hydraulic head, and tracer concentration data from this experiment are available in electronic form in Boggs et al. (1993a).

This thesis details the use of this data to: 1) perform a preliminary analysis of the three-dimensional database with respect to suitability of biodegradation modeling, 2) investigate the use of a two-dimensional model (Bioplane II) to simulate observed data, 3) identify gaps and issues in using
models for predictive analysis at sites, and 4) provide guidance for data
collection and modeling for the MADE-3 experiment.

Bioplume II (developed by Rifai et al., 1987) was used to model the fate
and transport of the contaminants injected during the MADE-2 experiment.
Bioplume II is based on the Method of Characteristics (MOC) solute transport
model developed by Konikow and Bredehoeft (1978) of the United States
Geological Survey (USGS) to describe contaminant transport in groundwater.
Biodegradation of the contaminants is simulated in Bioplume II by first-order
decay or instantaneous degradation based upon the mass of oxygen required
to degrade one unit mass of hydrocarbon. Hydrocarbon and oxygen
replenishment/removal are described in Bioplume II through a variety of
sources, sinks, and model boundary conditions.

Modeling the MADE-2 experiment was completed in collaboration with
Intera, Inc. of Austin Texas (Beach et al., 1996). Intera modeled the hydraulics
of the site using the MODFLOW model (McDonald and Harbaugh, 1988).
Intera’s efforts resulted in the estimated transmissivity field used in the Bioplume
fate and transport simulations.

Two plumes were modeled, using three sampling events for each. The
first plume, consisting of the injected tritium, was used to estimate the base
transport parameters. The second, consisting of the sum of all injected organic
contaminants, was used to simulate natural attenuation at the site. Two different
source configurations, pulse and continuous injection, were considered in
simulating the tritium and organic plumes. The three sampling events for each plume; snapshots two, three, and four, were used for calibration, validation, and prediction; respectively.
2.0 Literature Review

This literature review consists of three basic sections. These are: natural attenuation, contaminant transport, and the Bioplume II model. The natural attenuation section focuses on possible reasons for contaminant removal in the subsurface and protocols for determining that natural attenuation is occurring. The transport section mentions the major transport mechanisms and gives the governing equation in two dimensions. Finally, the section on Bioplume II describes the model and gives several examples of sites where the Bioplume II model has been previously applied.

2.1 Natural Attenuation

Natural attenuation is the reduction of contaminant mass and concentrations in the environment due to naturally occurring physical, chemical and biological processes. A major source of contamination is fuel-hydrocarbon releases from storage tanks at service stations, DoD sites, and industrial facilities. It has been estimated that upwards of a million releases have occurred nationwide from underground fuel storage tanks alone (Evans, 1994). Natural attenuation of fuel-hydrocarbon contamination has thus emerged as a potentially important plume remediation and management strategy.

Hydrocarbons can be attenuated through both abiotic and biotic means. The abiotic processes include dilution, volatilization, and abiotic oxidation. Dilution in groundwater is caused by two processes: dispersion and diffusion.
Dispersion is mixing due to velocity variations in the flow field. Diffusion is contaminant migration from areas of high concentration to areas of lower concentration. Volatilization is the phase change of contaminant from the aqueous phase to the gaseous phase, usually occurring relatively close to the ground surface. In the cases of dilution and volatilization, the original contaminant is not destroyed. In contrast, abiotic oxidation results in a change in the chemical structure of the contaminant.

Like abiotic oxidation, biological processes chemically alter the contaminant. These processes typically consist of either aerobic microbial respiration or anaerobic hydrocarbon utilization. Specific types of anaerobic degradation include denitrification, ferric iron reduction, sulfate reduction, and methanogenesis. Other types of biotic attenuation exist, including cometabolism and plant uptake, however, they are not discussed in this thesis.

In general, aerobic degradation occurs before anaerobic degradation. Oxygen is toxic to most anaerobic microbes, so prior to anaerobic activity beginning, the amount of oxygen within a system must be reduced. After the dissolved oxygen levels drop below toxicity limits, anaerobic degradation may occur. The redox-based preferential order of anaerobic electron acceptor use, is: 1) $\text{NO}_3^-$, 2) $\text{Fe}^{3+}$, 3) $\text{SO}_4^{2-}$, and 4) $\text{CO}_2$ (Rifai et al., 1995a). However, the groundwater chemistry (pH, temperature, alkalinity, etc.) at any specific site may inhibit some of the degradation reactions utilizing these acceptors (Godsy, 1994). This can result in differing preferential orders from site to site.
As previously mentioned, aerobic microorganisms use dissolved oxygen as the electron acceptor. The fuel-hydrocarbon, called the primary substrate, provides the bulk of the raw material for cell growth and reproduction. In addition, the primary substrate is the electron donor and provides the energy needed by the cell. Using benzene as the primary substrate and neglecting cell production, complete aerobic biodegradation is represented by the reaction:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$  \hspace{1cm} (2.1)

In equation (2.1), 3.1 grams of oxygen are required to degrade one gram of benzene. (Wiedemeier et al., 1995a).

Denitrification involves the conversion of nitrogen containing compounds to nitrogen gas. Typically, nitrate (NO$_3^-$) in the ground water is the source of nitrogen. The denitrification reaction for benzene is:

$$C_6H_6 + 6H^+ + 6NO_3^- \rightarrow 6CO_2 + 3N_2 \text{ (g)} + 6H_2O$$  \hspace{1cm} (2.2)

The stoichiometric mass ratio of nitrate to benzene is 4.8 : 1 (Wiedemeier et al., 1995a). This ratio assumes complete conversion of the nitrate to nitrogen gas. In some instances, nitrite (NO$_2^-$) may be found at a site. In this case, it is possible that a similar reaction to the one above may occur, or that the reaction described in equation 2.2 did not progress to completion.

Following denitrification, ferric iron reduction becomes the most likely biodegradation mechanism. Ferric iron (Fe$^{3+}$) is typically insoluble and is often present as ferric hydroxide Fe(OH)$_3$. During iron reduction, the ferric iron is reduced to soluble ferrous iron (Fe$^{2+}$). This reaction is usually monitored by
analyzing the amount of ferrous iron present in the contaminated ground water. The corresponding reaction is:

$$C_6H_6 + 30Fe(OH)_3 + 60H^+ \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$$ \hspace{1cm} (2.3)

The stoichiometric mass ratio of ferric hydroxide to benzene is 41.1 : 1 (Wiedemeier et al., 1995a).

During sulfate reduction, sulfate is reduced to hydrogen sulfide. The sulfate is usually present as a background concentration in the ground water. The stoichiometric mass ratio of sulfate to benzene is 4.6 : 1 (Wiedemeier et al., 1995a) in this reaction, and the equation describing this process is:

$$C_6H_6 + 7.5H^+ + 3.75SO_4^{2-} \Rightarrow 6CO_2 + 3.75H_2S (g) + 3H_2O$$ \hspace{1cm} (2.4)

The least preferred of the electron acceptors is typically carbon dioxide used in a process referred to as methanogenesis. Equation 2.5 shows that an excess of carbon dioxide is produced. However, carbon dioxide is both consumed and produced in the reaction. The stoichiometric relationship describing methanogenesis is calculated a little differently than for the other electron acceptors. In this case, the reported mass ratio is that of methane produced to benzene degraded, which is 0.77 : 1 in the following reaction.

$$C_6H_6 + 4.5H_2O \Rightarrow 2.25CO_2 + 3.75CH_4$$ \hspace{1cm} (2.5)

(Wiedemeier et al., 1995a.)

For any biologically controlled attenuation of contaminants to occur, certain requirements must be met. Godsy (1994) listed some of the conditions that must be met for contaminants to be removed from ground water by bacteria.
1. The bacteria must be in the immediate vicinity of the contaminant.
2. The contaminant must be available to the bacteria.
3. The bacteria must have the capacity to participate in some part of the degradation or transformation process.

In addition to the electron acceptor and hydrocarbon, microbial growth requires other trace nutrients. These nutrients include sulfur, nitrogen, and phosphorous. Sufficient sulfur is usually available; however, the lack of nitrogen and phosphorous can be growth limiting. Godsy (1994) states that an ideal carbon/nitrogen/phosphorous ratio is usually around 300-100 : 10 : 1-0.05 depending on the contaminant of interest. Godsy also mentions that biodegradation proceeds best at near-neutral pH and that the rate of degradation approximately doubles for every 10° C increase in ambient temperature until “inhibitory” temperatures are reached (usually around 40 to 50° C).

Due to the complexity of quantifying natural attenuation at the field scale, a number of researchers have developed technical protocols for measuring and identifying indicator parameters. Wiedemeier et al. (1994) presented an overview of a "technical protocol...for data collection, ground water modeling, and exposure assessment in support of intrinsic remediation (natural attenuation) with long term monitoring for restoration of fuel-hydrocarbon contaminated ground water." In this protocol, Wiedemeier et al. (1994) outline the following eight steps to determine the viability of intrinsic remediation at a site.
"1. Review existing site data.
2. Develop a preliminary conceptual model for the site, and assess the potential significance of intrinsic remediation.
3. Perform site characterization in support of intrinsic remediation.
4. Refine the conceptual model based on site characterization data, complete premodeling calculations, and document indicators of intrinsic remediation.
5. Model intrinsic remediation using numerical data and transport models that allow incorporation of a biodegradation term.
7. Prepare a long-term monitoring plan, long-term monitoring wells at the site, and point of compliance wells.
8. Present findings to regulatory agencies, and obtain approval for the intrinsic remediation with long-term monitoring option."

Wiedemeier et al. (1994) suggest that the soil and groundwater at the site be analyzed for the following parameters.

**Table 2-1**

**Parameters for Demonstrating Natural Attenuation**

<table>
<thead>
<tr>
<th>Soil</th>
<th>Ground Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>total volatile hydrocarbons</td>
<td>sulfide</td>
</tr>
<tr>
<td>aromatic hydrocarbons</td>
<td>ferrous iron</td>
</tr>
<tr>
<td>total extractable hydrocarbons</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>total organic carbon</td>
<td>methane</td>
</tr>
<tr>
<td></td>
<td>chloride</td>
</tr>
<tr>
<td></td>
<td>total petroleum hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>aromatic hydrocarbons</td>
</tr>
</tbody>
</table>

In general, Wiedemeier et al. (1994) state that by comparing concentration contour plots of the electron acceptors (dissolved oxygen, sulfate, etc.), degradation by-products (methane, carbon dioxide, etc.) and the fuel-hydrocarbon, one can locate areas of probable natural attenuation. In areas
where biodegradation is occurring, there should be a decrease in the available amount of electron acceptors and an increase in the amount of degradation by-products. For example, in areas where aerobic respiration is suspected to be taking place, decreased levels of dissolved oxygen would be seen. Similarly, in areas where methanogenesis is taking place, elevated levels of methane would be observed. Wiedemeier et al. (1994) state that indicators of these types alone are not sufficient to demonstrate that natural attenuation is occurring. These plots should be supported by microcosm studies, tracer studies, and biodegradation modeling showing probable natural attenuation.

Novick et al. (1995) presented a protocol developed by Mobil Oil Corporation. Their approach consists of three tiers, or levels of assessment. A Tier I approach is the easiest to accomplish; if it is accepted, no further work is required. If a Tier I approach is not accepted, the analysis progresses to Tier II, and then continues to Tier III if required. The following summary of the three tiers is taken from Novick et al. (1995).

"The Tier I assessment categorizes the plume as stable, expanding or shrinking, estimates plume migration distance, with and without natural attenuation, and establishes the rate of natural attenuation ..."

Tier II requires collecting monitoring data on indicators specific to intrinsic bioremediation. This may include measurements of dissolved oxygen, sulfate, nitrate, soluble iron (Fe\textsuperscript{ii}) and manganese (Mn\textsuperscript{ii}), methane and inorganic carbon.

A Tier III approach, if necessary, uses microcosm studies and detailed groundwater modeling to further demonstrate the significance of natural attenuation at a given site."
This approach provides several different levels of detail that are not as rigidly defined in the protocol given by Wiedemeier et al. 1994. A similar approach to those given by both Novick et al. (1995) and Wiedemeier et al. (1994), is presented by McAllister and Chiang (1994).

In addition to the development of field protocols, a number of field studies have documented the natural attenuation of existing ground water plumes.

Table 2-2 lists some of the most recent of these studies.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Contaminant</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barker et al., 1995</td>
<td>Benzene, toluene, ethylbenzene, and xylene (BTEX)</td>
<td>Denver Basin, Colorado</td>
</tr>
<tr>
<td>Butler and Bartlett, 1995</td>
<td>Volatile organic compounds (VOCs)</td>
<td>Central New Jersey</td>
</tr>
<tr>
<td>Davis et al. 1994</td>
<td>Benzene</td>
<td>U. S. eastern seaboard</td>
</tr>
<tr>
<td>Eganhouse et al., 1994</td>
<td>Petroleum hydrocarbons</td>
<td>Bemidji, Minnesota</td>
</tr>
<tr>
<td>Ginn et al., 1995</td>
<td>Polycyclic aromatic hydrocarbons (PAHs)</td>
<td>New York</td>
</tr>
<tr>
<td>King, et al., 1995</td>
<td>Coal tar organics</td>
<td>Canadian Force Base Borden</td>
</tr>
<tr>
<td>Nelson, 1994</td>
<td>BTEX</td>
<td>Denver, Colorado</td>
</tr>
<tr>
<td>Toze et al., 1995</td>
<td>BTEX</td>
<td>Perth, Australia</td>
</tr>
<tr>
<td>Wilson et al., 1994a</td>
<td>BTEX</td>
<td>Traverse City, Michigan</td>
</tr>
<tr>
<td>Wilson et al., 1994b</td>
<td>BTEX, JP-4 jet fuel</td>
<td>Eglin Air Force Base (AFB), Hill AFB</td>
</tr>
<tr>
<td>Wilson et al., 1995</td>
<td>BTEX</td>
<td>George AFB</td>
</tr>
<tr>
<td>Wiedemeier et al., 1995a</td>
<td>BTEX</td>
<td>Hill AFB and Patrick AFB</td>
</tr>
<tr>
<td>Wiedemeier et al., 1995b</td>
<td>Petroleum hydrocarbons</td>
<td>Phoenix, Arizona</td>
</tr>
</tbody>
</table>

State and federal governments have begun to develop guidelines for investigating natural attenuation as a viable remediation technique. The Air Force Center for Environmental Excellence (AFCEE, 1994), the Florida Department of Environmental Regulation (1990) and Giesfeldt, (1993) provide
details for several regions. AFCEE (1994) reviewed the regulations for Delaware, Florida, Iowa, Michigan, North Carolina, Ohio, Wisconsin and the District of Columbia. AFCEE concluded that the majority of these states required that both the source of the contamination and the free product be removed prior to the consideration of natural attenuation as a remediation option. All of the states in AFCEE’s review require continual monitoring of natural attenuation to ensure that no future health risks occur due to contaminant migration. The states generally differed in their requirements for demonstrating natural attenuation and permit approvals.

Natural attenuation has also been discussed as a “polishing’ step. After an active remediation system (typically a pump-and-treat system) has been in place and operating for some time, the rate of contaminant extraction starts to fall off and contaminant concentrations decline to low levels. Once such a system is shut off, the monitored levels of contaminants within the aquifer often rebound to some higher level. If the active treatment system is then restarted, the contaminant levels will quickly go down, but will most likely rebound again after the system is switched off for the second time. Continuing remediation through a pump-and-treat system is extremely inefficient at such sites. Natural attenuation monitoring provides a low cost alternative that often allows such sites to be closed. A regulatory approach, a case study, and mathematical modeling of this type of site are discussed by Walker and Weers, 1994; Maresco et al., 1995; and Illangasekare et al., 1994, respectively.
The key to using natural attenuation at sites is analyzing the resulting risk to human health and the environment. Generally, sites with low risk are good candidates for natural attenuation. Sites which pose a significant risk to nearby receptors may be amenable to risk reduction efforts through source control and natural attenuation of the dissolved contaminant plume.

In any case, the ability to determine exposure from these sites from a risk assessment standpoint relies on the use of ground water models. These predictive tools allow environmental scientists and engineers to answer three questions:

1. the extent of ground water contamination, both spatially and temporally;
2. the time required for attenuation of the contaminants to below specified regulatory limits;
3. the anticipated receptor well concentrations as a function of time.

The need for assessing ground water models that can be used to simulate natural attenuation was the motivation behind this work. While the Bioplume II model has been applied to a number of field sites, it had not been applied for simulating a controlled field experiment with the wealth of data available from the MADE-2 site.
2.2 Solute Transport Processes and Mathematical Formulation

Contaminant transport processes include advection, diffusion, and dispersion. For the purposes of this review these will be defined per Bedient et al., 1994:

"Advection is the movement of contaminants along with flowing ground water at the seepage velocity in porous media.

Diffusion is a molecular mass-transport process in which solutes move from areas of higher concentration to areas of lower concentration.

Dispersion is a mixing process caused by velocity variations in the porous media."

Advection causes contaminants to migrate away from the release point. The distance traveled by the contaminants in a given period of time may be estimated from the velocity of the groundwater. Dispersion causes the attenuation of sharp fronts and causes the plume to spread out. The magnitude of the diffusion component of contaminant transport in ground water is small when compared to the magnitude of the transport due to advection and dispersion. With this in mind, solute transport is typically described by the advection-dispersion equation (Fetter, 1993).

\[
D_i \frac{\partial^2 C}{\partial x^2} + D_r \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (2.6)
\]
where
\[ D_L = \text{longitudinal dispersion} \]
\[ D_T = \text{transverse dispersion} \]
\[ C = \text{total microbial concentration} \]
\[ x = \text{axis along direction of ground water flow} \]
\[ y = \text{transverse axis} \]
\[ v_x = \text{ground water velocity} \]
\[ t = \text{time} \]

Adsorption can play an important role in solute transport by “retarding” the transport due to solute sorbing to the aquifer media. The equation used to determine the retardation factor assuming linear sorption is as follows:

\[ R = \left(1 + \frac{p_bK_d}{n}\right) \]  \hspace{1cm} (2.7)

where
\[ R = \text{retardation factor} \]
\[ p_b = \text{oxygen concentration} \]
\[ K_d = \text{total microbial concentration} \]
\[ n = \text{maximum hydrocarbon utilization rate per unit mass organism} \]

This retardation factor is used to calculate the velocity of the contaminant relative to that of the ground water.

Analytical solutions to equation 2.6 exist for simplified initial and boundary conditions. These include both steady-state and pulse source models. However, real-life situations rarely fit the simplified conditions that are used in these analytical solutions. For complicated situations, a numerical model must often be used. One such model is Biopluwe II which solves the two-dimensional form of equation (2.6) as will be seen in the following section.
2.3 The Bioplume Model

2.3.1 History and Background

The Bioplume model was developed by Borden and Bedient (1986, 1987), Borden et al. (1986), and Borden et al. (1989), based on studies performed at the United Creosoting Company, Inc. (UCC) site in Conroe, Texas. Bioplume relies on the concept that hydrocarbon biodegradation in groundwater is often limited by the available dissolved oxygen. Borden and Bedient (1986) combined Monod kinetics with the advection-dispersion equation to create an aerobic degradation simulator. This simulator was later modified by replacing the Monod kinetics with a simplifying assumption of an instantaneous reaction between oxygen and the hydrocarbon that relies on the stoichiometry of the reaction to determine oxygen utilization and hydrocarbon consumption.

Rifai et al. (1987) integrated the Bioplume concepts developed by Borden and Bedient (1986) into the two-dimensional USGS solute transport model, better known as the method of characteristics (MOC) model (Konikow and Bredehoeft, 1978). The resulting model, Bioplume II, tracks two plumes: contaminant and oxygen. These plumes are superimposed and the instantaneous reaction assumption is applied at each time step to determine the new hydrocarbon and oxygen concentrations. The development of Bioplume II is documented in more detail in Rifai (1989), Rifai and Bedient (1987), and Rifai et al. (1988, 1989).
Bioplume II provides all of the functionality of the USGS model as related to sources, sinks, and boundary conditions. It also allows the simulation of in-situ bioremediation so that bioreclamation schemes can be examined prior to implementation. Bioplume II is limited, in its application as only oxygen is considered as a terminal electron acceptor.

The biodegradation equations used in all versions of Bioplume are those developed by Borden and Bedient (1986). Hydrocarbon and oxygen removal and microorganism growth were originally described by modified Monod functions as follows:

\[
\frac{dH}{dt} = -M_i \cdot k \cdot \frac{H}{(K_h + H)(K_s + O)} \cdot O \tag{2.8}
\]

\[
\frac{dO}{dt} = -M_i \cdot k \cdot F \cdot \frac{H}{(K_s + H)(K_o + O)} \cdot O \tag{2.9}
\]

\[
\frac{dM}{dt} = M_i \cdot k \cdot Y \cdot \frac{H}{(K_s + H)(K_o + O)} \cdot O + K_c \cdot Y \cdot OC - b \cdot M_i \tag{2.10}
\]
where
\[ H = \text{hydrocarbon concentration} \]
\[ O = \text{oxygen concentration} \]
\[ M_t = \text{total microbial concentration} \]
\[ K = \text{maximum hydrocarbon utilization rate per unit mass organism} \]
\[ Y = \text{microbial yield coefficient (g cells/g hydrocarbon)} \]
\[ K_h = \text{hydrocarbon half saturation constant} \]
\[ K_o = \text{oxygen half saturation constant} \]
\[ K_c = \text{first order decay rate of natural organic carbon} \]
\[ OC = \text{natural organic carbon concentration} \]
\[ b = \text{microbial decay rate} \]
\[ F = \frac{\text{ratio of oxygen to hydrocarbon consumed}}{} \]

After combining equations (2.8) and (2.9) with the advection-dispersion
equation, Borden and Bedient (1986) obtained the following system of
equations:

\[ \frac{\partial H}{\partial t} = \frac{\nabla(D \nabla H - vH)}{R_H} - \frac{M_t \cdot k}{R_H} \frac{H}{(K_h + H)(K_o + O)} \]  
(2.11)

\[ \frac{\partial O}{\partial t} = \nabla(D \nabla O - vH) - M_t \cdot k \cdot F \frac{H}{(K_h + H)(K_o + O)} \]  
(2.12)

where
\[ D = \text{dispersion tensor} \]
\[ v = \text{ground water velocity vector} \]
\[ R_h = \text{retardation factor for hydrocarbon} \]

The transfer of organisms between the soil surface and the ground water
was assumed to be related to total microorganism concentration and also to
follow a linear relationship. This transfer was simulated using a retardation
factor approach given in Freeze and Cherry (1979):

\[ \frac{\partial M_t}{\partial t} = \frac{\nabla(D \nabla M_t - vM_t)}{R_m} + M_t \cdot k \cdot Y \frac{H}{(K_h + H)(K_o + O)} + \frac{K_c \cdot Y \cdot OC}{R_m} \cdot b \cdot M_t \]  
(2.13)
where

\[ M_s = \text{concentration of microbes in solution} \]
\[ M_a = \text{concentration of microbes attached to solids} \]
\[ K_m = \text{ratio of microbes attached to microbes in solution} \]
\[ M_a = K_m M_s \]
\[ M_t = M_s + M_a \]
\[ = (1 + K_m) M_s \]
\[ = R_m M_s \]

Using the assumption that the removal of hydrocarbon and oxygen is instantaneous and independent of the microbial parameters, the loss of oxygen and hydrocarbon in explicit finite difference form is written as follows:

\[ H(t+1) = H(t) - \frac{O(t)}{F} \]
\[ O(t+1) = 0 \]

where \( H(t) > \frac{O(t)}{F} \)

\[ O(t+1) = O(t) - H(t) \cdot F \]
\[ H(t+1) = 0 \]

where \( O(t) > H(t) \cdot F \)

where

\[ H(t) = \text{hydrocarbon concentration at time } t \]
\[ O(t) = \text{oxygen concentration at time } t \]
\[ H(t+1) = \text{hydrocarbon concentration at time } t+1 \]
\[ O(t+1) = \text{oxygen concentration at time } t+1 \]

Equations (2.14) and (2.15) were used to replace the Monod kinetics in equations (2.11) and (2.12) yielding the following:

\[
\frac{\partial H}{\partial t} = \frac{1}{R_s} \left( D_x \frac{\partial^2 H}{\partial x^2} + D_y \frac{\partial^2 H}{\partial y^2} - \nu \frac{\partial H}{\partial x} \right) - \frac{\delta}{R_s} \pm W_s \tag{2.16}
\]
\[ \frac{\partial O}{\partial t} = \left( D_x \frac{\partial^2 O}{\partial x^2} + D_y \frac{\partial^2 O}{\partial y^2} - \nu \frac{\partial O}{\partial x} \right) - \delta F \pm W \] (2.17)

where

- \( R_h \) = retardation factor for hydrocarbon
- \( F \) = ratio of oxygen to hydrocarbon consumed
- \( \delta \) = \( \min(R_h, H, O/F) \)
- \( D_t \) = transverse dispersion coefficient
- \( \alpha_t \) = transverse dispersivity
- \( D_l \) = \( \alpha_t \nu \)
- \( W_h \) = hydrocarbon source or sink
- \( W_o \) = oxygen source or sink

Equations (2.16) and (2.17) are solved in Bioplume II. Since the reactions are assumed to be instantaneous, microbial growth is no longer a factor and equation 2.13 can be neglected.

The parameters required for the Bioplume II model can be divided into three major categories as shown in Table 2-3.

**Table 2-3**

**Required Bioplume Parameters**

**Basic Problem Set-Up**
- Simulation time (years)
- Grid Size (unitless)
- Cell Size (feet)
- Location of all injection/extraction wells (unitless)
- Injection/extraction rate at all wells (cubic feet/second)
- Half life of the hydrocarbon (seconds)
- Anaerobic decay coefficient for the hydrocarbon (1/day)
- Node values
  - Leakance (unitless)
  - contaminant concentration (mass/volume)
  - oxygen concentration (mass/volume)
  - diffuse recharge/discharge (cubic feet/second)
- Initial water table (feet)
### Table 2-3 (cont.)
**Required Bioplume Parameters**

<table>
<thead>
<tr>
<th>Hydrogeologic Parameters</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>(unitless)</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>(feet)</td>
</tr>
<tr>
<td>Horizontal dispersivity</td>
<td>(feet)</td>
</tr>
<tr>
<td>Transmissivity in the x direction</td>
<td>(square feet/second)</td>
</tr>
<tr>
<td>Transmissivity in the y direction</td>
<td>(square feet/second)</td>
</tr>
<tr>
<td>Aquifer thickness</td>
<td>(feet)</td>
</tr>
<tr>
<td>Hydraulic gradient</td>
<td>(unitless)</td>
</tr>
<tr>
<td>Bulk density of the soil</td>
<td>(mass/volume)</td>
</tr>
<tr>
<td>Distribution coefficient of the contaminant</td>
<td>(volume/mass)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biodegradation Parameters</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of oxygen in injected water</td>
<td>(mass/volume)</td>
</tr>
<tr>
<td>Concentration of hydrocarbon in injected water</td>
<td>(mass/volume)</td>
</tr>
<tr>
<td>Initial oxygen plume concentrations</td>
<td>(mass/volume)</td>
</tr>
<tr>
<td>Initial hydrocarbon plume concentrations</td>
<td>(mass/volume)</td>
</tr>
<tr>
<td>Recharge concentration of oxygen</td>
<td>(mass/volume)</td>
</tr>
<tr>
<td>Reaeration coefficient</td>
<td>(1/day)</td>
</tr>
</tbody>
</table>

(Rifai *et al.* 1987, Appendix A)

#### 2.3.2 Model Applications

Bioplume has been applied to a variety of sites by industry, academic institutions, consultants, and governmental agencies. At all of the sites, aerobic biodegradation was considered to be the primary degradation mechanism.

These applications of the Bioplume model have led to the development of new modeling techniques and to the improvement of existing methods of biodegradation modeling. The first case study, the UCC Site in Conroe, Texas, is the only study described here that used the Bioplume I model. All other
studies used Bioplume II. The UCC site is included for completeness as the
governing biodegradation equations are the same in all versions of Bioplume.

**UCC Site - Conroe, Texas.** Borden and Bedient (1986, 1987) and
Borden *et al.* (1986) applied the Bioplume I model to the United Creosoting
Company Inc. (UCC) site. The site is located in Conroe, Texas, where UCC
operated a wood preserving facility from 1946 to 1972 and placed the wastes
from this treatment process into two on-site, unlined ponds. The wastes were
composed primarily of polycyclic aromatic hydrocarbons and
pentachlorophenol. Elevated levels of these compounds and chloride were
discovered in the ground water beneath the site.

Borden and Bedient (1986) injected known amounts of chloride,
naphthalene, and p-dichlorobenzene in order to study the probable fate and
transport of the original contaminants at this site. Based on this field work,
laboratory studies carried out at Rice University, and a review of the applicable
literature, Borden and Bedient (1986) selected the following parameters for use
in the model.

Sensitivity analyses using a one dimensional model indicated that the
microbial parameters \( K_m, K_o, k, Y, \) and \( F \) had little to do with the distribution of
hydrocarbon within the plume or with the time until hydrocarbon breakthrough.
This led Borden and Bedient (1986) to the instantaneous reaction assumption
mentioned in Section 2.3.1. Using this assumption, along with the established
biodegradation and transport parameters, Borden and Bedient (1986)
performed a series of two-dimensional simulations. The background
concentrations were used to establish boundary and initial conditions, while the influent concentrations were considered to describe the contaminant source.

Table 2-4
Bioplume Parameters for the UCC Site - Conroe, Texas

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity</td>
<td>( \nu )</td>
<td>0.015 m/d</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>( \alpha_i )</td>
<td>9.1 m</td>
</tr>
<tr>
<td>Transverse dispersivity</td>
<td>( \alpha_t )</td>
<td>1.8 m</td>
</tr>
<tr>
<td>Maximum hydrocarbon utilization rate</td>
<td>( k )</td>
<td>1.7 day</td>
</tr>
<tr>
<td>Ratio of oxygen to hydrocarbon consumed</td>
<td>( F )</td>
<td>3.0</td>
</tr>
<tr>
<td>Microbial yield coefficient</td>
<td>( Y )</td>
<td>0.5 g cell/g H</td>
</tr>
<tr>
<td>Hydrocarbon half saturation constant</td>
<td>( K_h )</td>
<td>0.13 mg/L</td>
</tr>
<tr>
<td>Oxygen half saturation constant</td>
<td>( K_o )</td>
<td>0.10 mg/L</td>
</tr>
<tr>
<td>Microbial decay coefficient</td>
<td>( b )</td>
<td>0.01 day</td>
</tr>
<tr>
<td>Background hydrocarbon concentration</td>
<td>( H_b )</td>
<td>0.0 mg/L</td>
</tr>
<tr>
<td>Background oxygen coefficient</td>
<td>( O_b )</td>
<td>3.0 mg/L</td>
</tr>
<tr>
<td>Background microbial biomass</td>
<td>( M_b )</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Background organic carbon</td>
<td>( C )</td>
<td>750 mg/L</td>
</tr>
<tr>
<td>Influent hydrocarbon concentration</td>
<td>( H_i )</td>
<td>4.5 mg/L</td>
</tr>
<tr>
<td>Influent oxygen concentration</td>
<td>( O_i )</td>
<td>3.0 mg/L</td>
</tr>
<tr>
<td>Influent microbe concentration</td>
<td>( M_i )</td>
<td>0.001 mg/L</td>
</tr>
<tr>
<td>Organic carbon utilization rate</td>
<td>( k_c )</td>
<td>2.7 x 10^5 day</td>
</tr>
<tr>
<td>Hydrocarbon retardation factor</td>
<td>( R_h )</td>
<td>1.0</td>
</tr>
<tr>
<td>Microbial retardation factor</td>
<td>( R_m )</td>
<td>100</td>
</tr>
</tbody>
</table>

Based on their simulations, Borden and Bedient (1986) drew several conclusions. Three of their conclusions which pertain to simulating natural attenuation with the Bioplume model were:

1. “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 in situations where the native microbial population has not yet adapted to the foreign hydrocarbon.”
2. "Transverse mixing will be the dominant source of oxygen for most hydrocarbon plumes when adsorption is not significant. Longitudinal mixing appears to have little effect on hydrocarbon biodegradation."

3. "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."

**Traverse City, Michigan.** In 1969, a substantial quantity of aviation fuel leaked from a flange on an underground storage tank at the U.S. Coast Guard Air Station in Traverse City, Michigan. Several researchers have applied the Bioplume II model to this site. These include: Alder-Schaller 1989; Miller 1989; Rifai and Bedient 1987, 1989, and 1992; Rifai et al. 1988; and Ward et al. 1989. Between 37,850 and 75,700 liters of fuel were released, most likely forming a pool of non-aqueous phase liquid (NAPL) within the aquifer. This caused the formation of a long BTEX contaminant plume in the underlying drinking water aquifer.

Rifai et al. (1988) applied Bioplume II to the Traverse City and used the parameters given in Table 2-5 for their simulations.
Table 2-5
Bioplane Parameters for the Traverse City, Michigan Site

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid size</td>
<td>16 x 38</td>
</tr>
<tr>
<td>Cell size</td>
<td>30 m. x 20 m.</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.3</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>3 m.</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>50 m/day</td>
</tr>
<tr>
<td>Dissolved oxygen concentration</td>
<td>8.0 mg/L</td>
</tr>
<tr>
<td>Reaeration decay coefficient</td>
<td>0.003 day^{-1}</td>
</tr>
<tr>
<td>Recharge</td>
<td>1.14 x 10^{-3} m/day</td>
</tr>
</tbody>
</table>

The contaminant source was represented by seven injection wells with a total flow rate of 6.85 m³/day. The average injection concentration was approximately 1,380 mg/L. Constant head cells were used to establish the boundary conditions. Natural recharge of oxygen across the boundaries was set at 8.0 mg/L.

Rifai et al. (1988) determined that more investigation was necessary at the Traverse City site to define the source area. However, based upon the sensitivity analyses performed during this study, they concluded that the coefficient of reaeration, the coefficient of anaerobic decay, and the hydraulic conductivity had the most influence on the amount of mass lost due to biodegradation at this site. Rifai et al. (1988) also concluded that more research was necessary in order to understand anaerobic biodegradation and to provide a better definition of the vertical exchange of oxygen from the unsaturated zone to the saturated zone. Finally, they stated that more advanced numerical techniques for simulating biodegradation were needed.
**Amoco Sites, Florida.** Caldwell *et al.* (1992) used Bioplume II to model the fate and transport of BTEX (as a group) and benzene (individually) at a service station. Amoco performed field studies using both shallow and deep wells to determine the amount of BTEX, methyl tert-butyl ether (MTBE) and total recoverable petroleum hydrocarbons present in the soil and ground water at three service stations in Broward County, Florida. Caldwell *et al.* modeled one of these sites using the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid size</td>
<td>12 x 12</td>
</tr>
<tr>
<td>Cell size</td>
<td>15 ft x 30 ft</td>
</tr>
<tr>
<td>Flow velocity</td>
<td>0.34 ft/day</td>
</tr>
<tr>
<td>Infiltration oxygen concentration</td>
<td>4.0 mg/L</td>
</tr>
<tr>
<td>Infiltration rate</td>
<td>30 in/yr</td>
</tr>
<tr>
<td>F ratio</td>
<td>3.0</td>
</tr>
<tr>
<td>Benzene retardation factor</td>
<td>1.7</td>
</tr>
<tr>
<td>BTEX retardation factor</td>
<td>2.7</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>7.5 ft</td>
</tr>
<tr>
<td>Transverse dispersivity</td>
<td>2.5 ft</td>
</tr>
<tr>
<td>Anaerobic degradation coefficient</td>
<td>0.00012 day(^{-1})</td>
</tr>
<tr>
<td>Reaeration coefficient</td>
<td>0.005 day(^{-1})</td>
</tr>
</tbody>
</table>

The source of the contamination was unknown. Caldwell *et al.* (1992) assumed that the contaminant source had been a continual release over several years that had gradually tapered off. Four injection wells were used to simulate the source, with the maximum initial injection rate being slightly over three gallons of gasoline per year. The gasoline was assumed to contain 2.0% benzene and 8.6% total BTEX.
The model output matched the monitoring well data for both benzene and BTEX. Next, the biodegradation and oxygen coefficients were set to zero and the model was run again. The output from these runs showed the possible extent of the hydrocarbon plume assuming no biodegradation. This plume extended up to one hundred feet beyond the boundaries of the biodegraded plume. By comparing these plumes, Caldwell *et al.* concluded that biodegradation processes were probably limiting the extent of the plume migration.

**Michigan Gas Plant.** Chiang *et al.* (1990) modeled a plume consisting of benzene, toluene, and xylene (BTEX) that was contained in a sandy aquifer beneath a gas plant facility in Michigan. The sources of contamination were an on-site flare pit and a slop oil tank area. Examination of field data revealed that a decrease in the amount of BTEX in the ground water corresponded to a decrease in the amount of available dissolved oxygen. Two models, a MOC code (modified to include first-order decay) and Bioplume II, were used to model natural attenuation at the site.

The field data from February, 1987, were used to set the initial conditions for both dissolved oxygen and BTEX. The following parameters were also used in modeling the site.
Table 2-7
Biopluce Parameters for the Michigan Gas Plant

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid size</td>
<td>10 x 17</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>$1.1 \times 10^{-1}$ cm/s</td>
</tr>
<tr>
<td>F ratio</td>
<td>3.0</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>80 cm</td>
</tr>
<tr>
<td>Transverse dispersivity</td>
<td>30 cm</td>
</tr>
</tbody>
</table>

Chiang *et al.* (1990) noted that the Biopluce II simulation was highly sensitive to variations in the transverse and longitudinal dispersivities. However, they were able to calibrate Biopluce II and obtain similar results for the observed and predicted BTX plumes. Unfortunately, they were unable to model the dissolved oxygen plume accurately.

Chiang *et al.* (1990) suggested two possibilities for this discrepancy. The first was their difficulty in accurately determining the oxygen recharge through the flare pit and the unsaturated zone. The second was that the F ratio in Biopluce II did not account for the hydrocarbon utilized in cell growth. If cell growth is taken into account, less oxygen is needed to degrade the same amount of hydrocarbon.

Denver Fuel Spill. Wiedemeier *et al.* (1993) modeled a plume at a jet fueling facility near Denver, Colorado. The plume source was Jet-A aviation fuel leaking from on-site underground storage tanks. Both dissolved and non-aqueous phase liquid (NAPL) contamination was observed at this site. The NAPLs were present in the vadose zone and provided a continuous source of dissolved phase BTEX.
Of the BTEX components, only benzene exceeded Colorado regulatory limits. Analysis of the free product showed that benzene was not present in the NAPL. (Wiedemeier et al. suggest that this is most likely due to "subsurface weathering" of the NAPL.) BTEX partitioning calculations showed that the maximum dissolved phase contamination, resulting from future partitioning of the NAPL into the ground water, was below regulatory limits for the other BTEX components (toluene, ethyl-benzene, and the xylenes). The collected field data showed that the current dissolved phase contaminants actually exceeded these possible future values.

Based on these calculations, the collected field data were used as model input for the initial BTEX plume. Wiedemeier et al. (1993) used additional parameters in modeling the site as shown in Table 2-8.

**Table 2-8**  
Bioplume Parameters for the Denver Fuel Spill

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid size</td>
<td>20 x 24</td>
</tr>
<tr>
<td>Cell size</td>
<td>75 ft x 75 ft</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>1.0 x 10^{-3} cm/s</td>
</tr>
<tr>
<td>F ratio</td>
<td>3.1</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>10 ft</td>
</tr>
<tr>
<td>Transverse dispersivity</td>
<td>1 ft</td>
</tr>
<tr>
<td>Reaeration coefficient</td>
<td>0.0 day^{-1}</td>
</tr>
<tr>
<td>Anaerobic degradation coefficient</td>
<td>0.0 day^{-1}</td>
</tr>
</tbody>
</table>

The initial oxygen plume was also determined from site data. To ensure a conservative simulation, Wiedemeier et al. (1993) allowed no oxygen transfer across the constant head boundaries.
The Biopluime II results indicated that the maximum travel for the center of mass of the plume was less than 0.5 mile. The endangered receptors were located approximately 2.5 miles downgradient. Using this worst case scenario, Wiedemeier et al. (1993) showed that no active remediation was required. However, a bioventing system was later installed to remove the remaining NAPL trapped in the vadose zone.

**Houston / Florida Underground Storage Tanks.** Evans (1995) used Biopluime II to develop a risk-based approach to remediation. Evans considered two sites in Texas (identified only as sites A and B) and one site in Florida (site C) that were contaminated by leaking underground storage tanks. These tanks had been used to store gasoline and had released an unknown amount of BTEX into the surrounding ground water.

Evans used the following parameters to model the three sites:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Site A</th>
<th>Site B</th>
<th>Site C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid size</td>
<td>20 x 75</td>
<td>40 x 75</td>
<td>40 x 75</td>
</tr>
<tr>
<td>Cell size</td>
<td>20 ft x 20 ft</td>
<td>20 ft x 20 ft</td>
<td>20 ft x 30 ft</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>$1.4 \times 10^3$ cm/s</td>
<td>$2.4 \times 10^4$ cm/s</td>
<td>$1.0 \times 10^3$ cm/s</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.45</td>
<td>0.40</td>
<td>0.30</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>5 ft</td>
<td>5 ft</td>
<td>5 ft</td>
</tr>
<tr>
<td>Transverse dispersivity</td>
<td>0.5 ft</td>
<td>0.5 ft</td>
<td>0.5 ft</td>
</tr>
<tr>
<td>Source concentration</td>
<td>25, 35, 70, 85 mg/L</td>
<td>30, 50, 100 mg/L</td>
<td>4-150 mg/L</td>
</tr>
<tr>
<td>Source recharge rate</td>
<td>$2.0 \times 10^7$ ft/s</td>
<td>$5.0 \times 10^9$ ft/s</td>
<td>$5.0 \times 10^9$ ft/s</td>
</tr>
<tr>
<td>Background dissolved oxygen</td>
<td>0.0 mg/L</td>
<td>0.0 mg/L</td>
<td>0.0 mg/L</td>
</tr>
</tbody>
</table>
A steady state approach was used to evaluate the following remediation techniques:

1. No action.
2. Source removal only.
3. Oxygen injection with source removal.
4. Pump and treat with source removal.
5. Pump and treat combined with oxygen injection and source removal.

Evans also used the results of these simulations to evaluate the current clean-up standards with respect to exposure of possible receptors at the three sites. The study demonstrated that immediately removing the source of the contamination gave the most significant risk reduction. Based on this work, Evans concluded that, in certain specific cases, "the wisest course of action may be to implement an initial corrective action ... and then pursue a risk-based assessment to determine an appropriate endpoint for remediation."

**USAF - Risk-based Studies.** Parsons Environmental Services (Parsons ES) used Bioplume II in the development of a risk-based approach to remediation. The United States Air Force contracted Parsons ES to "perform intrinsic remediation demonstrations at thirty-one United States Air Force (USAF) bases and conduct risk-based approach remediation at eight USAF bases nationwide" (Moutox, 1995). The overall purpose of these studies was to "develop a systematic process for scientifically investigating and documenting naturally occurring attenuation processes that can be factored into overall site remediation plans." (Moutox, 1995) Two specific goals of this program were to:
1. "... provide defensible evidence that intrinsic remediation of dissolved phase hydrocarbons can be used to develop an effective groundwater remediation strategy."

2. "... provide a series of regional case studies demonstrating that natural degradation often reduces contaminant concentrations in groundwater to below acceptable cleanup standards before completion of possible exposure pathways."

The contaminants of interest at these sites were benzene, toluene, ethylbenzene and xylene (BTEX). This risk-based approach regarded reducing the concentrations of these contaminants as being more important than reducing the total concentration of petroleum hydrocarbons, due to the relative toxicities of the two groups. By taking into account the benefit from intrinsic remediation, a significant cost savings can be obtained. Details of the Biopluume II modeling are available from Parsons ES in Denver.
3.0  The MADE-2 Site

This chapter describes the site, the experiments conducted at the site, and the data available from these experiments as compiled in the database documented in Boggs et al., 1993a. The site description consists of the location, basic hydrogeologic information, and climatic information. Next, the two major experiments, MADE-1 and MADE-2 are described, including experimental set-up and results. The database description gives information on what data are contained within the database, along with the experiments that produced the data.

3.1  Site Description

The MADE site is located on Columbus Air Force Base in Columbus, Mississippi. (See Figure 3-1.) The site consists of approximately 25 hectares of undeveloped land in the northeastern corner of the base. The site is outside of the 100 year floodplain of the two nearby rivers - the Tombigee, 6 km to the west, and the Buttahatchee, 2.5 km to the north. Site elevation is between 66.5 m above mean sea level (MSL) in the southeast corner and 64.6 m above MSL at the northern edge (Boggs et al., 1990).

The site sits upon the uppermost terrace in a series of deposits from the Pleistocene Age. These terraces have been deposited over time by the Buttahatchee River, and consist of irregular lenses of sand, gravel, silt and clay.
Figure 3-1, Site Location Map  
(Adapted from Boggs et al., 1990)
Underlying these terrace deposits is the Cretaceous Age Eutaw Formation. This formation is composed of marine clay, silt and sand (Boggs et al., 1990).

The area has a temperate climate, with a mean annual air temperature of 17° C. The mean maximum daily temperature in July is 33° C, while the mean minimum daily temperature in January is 3° C. The site receives 144 cm of rain annually. The month with the least rainfall is July, with 7.5 cm, while March receives the most, 17.8 cm (Boggs et al., 1990).
3.2 On-Site Experiments

The MADE site has a well-characterized heterogeneous aquifer that is well-suited for field scale studies. The characterization of the site was accomplished during two major controlled field experiments, MADE-1 and MADE-2, completed by Boggs et al. (1990, 1993b). The majority of the site characterization was performed during MADE-1, while MADE-2 focused on fate and transport of pollutants in the subsurface. However, during MADE-2 the existing site characterization was refined by information taken from new wells added for MADE-2.

3.2.1 MADE-1

The first of the two MADE experiments was performed in late October 1986. At this time, 10.07 cubic meters of tracer solution were injected through five injection wells spaced approximately one meter apart. The screened depth of the injection wells ranged from approximately 7.4 to 8.0 meters below grade. Four conservative tracers were used - calcium dibromide, pentafluorobenzoic acid, trifluoromethylbenzoic acid, and orthodifluorobenzoic acid. This solution was injected over a 48.5 hour period.

The goal of the MADE-1 study was to characterize the physical transport occurring at the site. In order to monitor the transport of the tracers through the aquifer, a network of 258 multilevel samplers was installed. The first 70 samplers were installed before the tracer solution was injected, with the
remainder being installed throughout the test period as the direction and speed of the contaminant transport were determined. Eight complete sampling events were conducted during the study, with one sampling event occurring every five to nineteen weeks. To monitor contaminant breakthrough, selected samplers were sampled more frequently than others, once every three to six weeks.

As previously mentioned, the primary hydrogeologic characterization of the MADE site was performed during this time (Boggs et al., 1990). Five different techniques were used to assess the hydraulic conductivity of the site. These included pump tests, borehole flowmeter logging, double packer tests, slug tests, and laboratory permeameter tests. Two pump tests, AT-1 and AT-2, were performed at the site. During the pump tests, one well was pumped while head observations were made at twelve wells located in radial lines extending directly away from the pumping well.

Borehole flowmeter tests were performed at fifty-eight wells. In these tests, the flow entering the wells at different levels is measured by impellers suspended within the well. The measured flow can be converted to a measure of the hydraulic conductivity at that elevation. Boggs et al. (1990) state that this is the most reliable of the methods used to evaluate the hydraulic conductivity at the site.

Double-packer tests involve using two inflatable bladders to seal off a section of the well. Then, either water is injected between the two bladders at a known rate, and the pressure is monitored; or the pressure is kept constant, and the flow rate is monitored. This technique allows individual values to be
determined for different depths within the same well and is well suited for a heterogeneous site such as the MADE site. The values obtained from this analysis were higher than those obtained from the borehole flowmeter test, possibly due to water movement within the well annulus (Boggs et al. 1990).

Slug tests were performed at twenty-two wells at the site. These tests consist of adding a measured volume of water into a well and monitoring the response over time. The rate at which the added water dissipates into the surrounding formation can be correlated to the hydraulic conductivity of the aquifer. The results from these tests were expected to be inaccurate, as the site was known to be heterogeneous (Boggs et al., 1990).

The final tests performed were laboratory permeameter tests. These tests were performed on undisturbed cores taken from the site. A steady flow was established through the core and the pressure drop along the core was monitored. These data were then used to calculate the hydraulic conductivity from Darcy’s equation.

The MADE site proved to be extremely heterogeneous with reported hydraulic conductivities ranging over two orders of magnitude, from $10^{-2}$ cm/s to $10^{-4}$ cm/s. The areas of lowest conductivity were located immediately around the injection wells. This area of low conductivity held the bulk of the injected tracers within twenty meters of the injection site. Once the plume passed beyond the low conductivity zone, the ground water flow carried the
contaminants quickly downgradient. The resulting plume was non-Gaussian, with much lower concentrations in the outermost edges of the plume than in the center of the plume.
3.2.2 MADE-2

The second MADE experiment began in June, 1990. The purpose of MADE-2 was to determine the fate and transport of four organic contaminants. Approximately 9.7 cubic meters of tracer solution were injected over 48.5 hours at the same location as the injected tracer solution of MADE-1. The solution contained known amounts of benzene, napthalene, $^{14}$C labeled $p$-xylene, and $o$-dichlorobenzene. Tritium was also injected to provide a conservative tracer to estimate the various transport properties.

Numerous samples were collected in the 16 months after injection. Two strategies were implemented in an attempt to characterize the fate and transport of the tracers. The first strategy was to sample "fencelines" that were oriented perpendicular to ground water flow. The second was to sample each multi-level sampler in the area where the plume was thought to have moved. These data sets are known as "snapshots."

The fenceline data were taken from 56 BarCad samplers that were sampled at 13, 48, 83, 111, 160, 195, and 281 days after injection. BarCad samplers are closed pressure driven samplers that were selected based upon their ability to be sampled often without suffering the volatile losses associated with the multi-level samplers (Boggs et al., 1993b). These samplers were arranged in two parallel rows aligned orthogonal to the direction of groundwater flow, approximately 6 meters and 16 meters downgradient from the injection
points. The data from these events are useful in time series analysis of the contaminant transport.

The network of multilevel samplers installed for MADE-1 was expanded from 258 to 328 samplers. Five “snapshots” consisting of measurements from the fenceline samplers plus the multi-level samplers were taken at days 27, 132, 224, 328 and 440. These events give the most complete three-dimensional representation of the contaminant plume and as such are the events used to calibrate and validate the Bioplume II model.

As in MADE-1, the bulk of the contaminants remained in the areas immediately around the injection point. The tritium plume did progress throughout the site and eventually extended beyond the edges of the sampling network (the fifth multilevel sampling event is incomplete for this reason). The organic tracers did not spread throughout the site. In fact, the furthest significant extent of the organics was approximately twenty meters downgradient.

In the near field, the groundwater velocities were relatively low; five meters per year. In the far field, the ground water velocities were approximately four hundred meters per year (Boggs et al., 1993b). The tritium plume was used to estimate longitudinal dispersivity and transverse dispersivity at approximately 10 and 2.2 meters, respectively. Retardation values of 1.20, 1.45, 1.16, and 1.33 were determined for benzene, naphthalene, p-xylene, and o-dichlorobenzene, respectively; by fitting the data with an analytical model that incorporated first-order decay (Boggs et al., 1993b).
In general, the maximum downgradient extent of the organic plumes was about twenty meters from the injection point. The organic tracers disappeared throughout the study in a manner that was approximately first-order. Half-lives of 69, 53, 43, and 139 days for benzene, napthalene, p-xylene, and o-dichlorobenzene were determined by fitting the time series contamination data. As expected, o-dichlorobenzene was the most recalcitrant. This is shown in the fractions of mass remaining after 440 days: benzene, 6 percent; napthalene, six percent; p-xylene, one percent, and o-dichlorobenzene, thirteen percent (estimated through using spatial moments by Boggs et al., 1993b).

The $^{14}$C labeled p-xylene was used to determine the fate of the organics. Between eighty and ninety percent of the radio labeled carbon was eventually found in dissolved carbon dioxide and intermediate products. Boggs et al. (1993b) suggested that this indicates aerobic biodegradation.
3.3 Database Description

An extensive database was compiled by Boggs et al. (1993a) from the two field-scale macrodispersion experiments (MADE-1 and MADE-2). The information is available on diskette in text format files for PC compatible computers. The data are divided into three broad categories: hydraulic conductivity data, head data, and tracer concentration data. Other necessary information, such as dissolved oxygen levels and aquifer porosity, is available in a series of reports and papers from the Electric Power Research Institute.

The majority of the hydraulic conductivity data included in the database were measured during the MADE-1 experiment (Boggs et al., 1990). In addition to the hydraulic conductivity data from MADE-1, hydraulic conductivity profiles at eleven fully-penetrating wells were derived from borehole flowmeter tests as part of MADE-2 (Boggs et al., 1993b).

Additional information contained in the database includes hydraulic head measurements recorded at the site from June 1990 through September 1991 (during MADE-2). The head data were monitored by piezometers scattered throughout the site. The majority of the piezometers were monitored monthly, but 16 were equipped as continuous groundwater level recorders. The groundwater level fluctuated widely during the test period, with a difference between the high and low values of approximately 3.5 meters (Boggs et al., 1993b).

The final element of the database is the tracer concentration data recorded during the MADE-2 experiment. As mentioned in section 3.2,
benzene, napthalene, p-xylene, o-DCB, tritium, and $^{14}\text{C}$ labeled p-Xylene concentrations were monitored throughout the experiment (440 days). Both the fenceline and snapshot data are available in the database. The detection limits for the compounds (as stated in Boggs et al., 1993a) are given in Table 3-1.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Detection Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>50 µg/L</td>
</tr>
<tr>
<td>Napthalene</td>
<td>4 µg/L</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>4 µg/L</td>
</tr>
<tr>
<td>o-DCB</td>
<td>4 µg/L</td>
</tr>
<tr>
<td>Tritium</td>
<td>1 pCi/ml</td>
</tr>
</tbody>
</table>
4.0 Data Visualization

This section describes the corrections applied to the concentration data, the reduction of the data from three- to two-dimensions, and the selection of the snapshots used in modeling the site. The data corrections are used to disregard suspect data prior to modeling, while reducing the data and snapshot selection is necessary before Bioplume II modeling.

4.1 Data Corrections

After correcting for background contaminant concentrations, two adjustments were applied to the field data as suggested in Boggs et al. (1993b). The adjustments were based on the idea that the relative concentration of degrading organic contaminant (benzene, naphthalene, p-xylene, o-dichlorobenzene) cannot be higher than the relative concentration of non-degrading contaminant (tritium):

\[ \begin{align*}
\text{I. } & \quad C_i^{(\text{org})} = 0 \quad \text{then} \quad C_i^{(\text{org})} = 0 \\
\text{II. } & \quad C_i^{(\text{org})} = C_0^{(\text{org})} C_i^{(\text{H})} / C_0^{(\text{H})}
\end{align*} \quad (4.1) \quad (4.2)
\]

where

- \( C^* \) = adjusted concentration
- \( C_0 \) = injection concentration
- \( i \) = 1 to # of samples

Assuming reversible sorption, it is possible that the relative concentration of organic contaminant in the heart of the plume could possibly be greater than the relative concentration of tritium at that point. Comparison of the concentration values for the organic tracers before and after adjustment per
equations 4.1 and 4.2 showed that the impact of these corrections on samples from the center of the plume was very small. The limited effects in the center of plume are most likely due to the low transmissivity zone near the injection point restricting the transport of the tritium, thus allowing most of the high organic concentration values in the center of the plume to be unaffected by these corrections. By applying the corrections in equations (4.1) and (4.2), suspect values downgradient from the main body of the plume were eliminated.
4.2 Data Reduction

During the initial data examination, it became clear that simple vertical averaging of all of the data points within a snapshot gave inconsistent results between locations that were near to each other. Closer examination showed that vertical averaging of the samples taken from the BarCad samplers did not match the averaging from the multilevel samplers. This was mainly due to the differences in the number of samples collected from each type of device. In particular, the multilevel samplers provided greater definition with regard to depth than the BarCad samplers did. In general, only two vertical samples were collected from the BarCad samplers. This resulted in more points being averaged for a multi-level sampler location than for a BarCad location. Because of the preferential flow paths in the aquifer caused by the extreme heterogeneity of the porous media, there was a lower probability of finding tracer in a BarCad sample. To achieve consistency across this site, all data from the BarCad samplers were disregarded. In order to facilitate data analyses, two dimensional plots were developed from the remaining concentration data from MADE-2. A number of steps were taken to prepare these plots:
1. All zero organic values were set to the detection limit for the specific contaminant.
2. All samples that shared the same x,y coordinates were averaged.
3. If all measurements in the multilevel sampler were at or below the detection limit, a zero value was assigned at that location.
4. The four organic tracer vertical averages were summed at each x,y coordinate (referred to as the combined organic concentration).
5. The vertically averaged concentrations for the tritium and the combined organics were then contoured using the SURFER software package for comparison with the Bioplume II model output. The concentrations were interpolated in SURFER onto a regular Cartesian grid using kriging using the default values for the kriging parameters. (See Figures 4-1 and 4-2).

Step 1 was an attempt to compensate for the high detection limit of benzene and to be consistent, step 1 was applied to all four organic tracers. If any of the values being averaged is greater than the detection limit, step 2 will produce a value that is above the detection limit. However, if all of the values are at or below the detection limit, step 3 will place a zero at that location. Since Bioplume II can only simulate the fate and transport of a single or lumped organics, Step 4 takes the four organic values and combines them into a single value. By determining the proper F ratio for the combined organics, this single value can be used to represent the total organic contamination at the site. Step 5 combines the values estimated in steps 1 though 4 and produces a value for every point in the model. (Figures 4-3 and 4-4 show the standard deviations of the averaged values.)

Step 1 most likely skewed the concentration values upwards at some locations. Similarly, step 3 most likely skewed concentration data at other locations downwards. Simply omitting the locations with non-detects for all
Figure 4-1. Vertically Averaged Observed Tritium Concentrations for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection)
Figure 4-2. Vertically Averaged Observed Combined Organic Concentrations for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection)
Figure 4-3. Standard Deviations from Tritium Averaging for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection)
Figure 4-4. Standard Deviations from Combined Organic Averaging for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection)
organic contaminants would result in a dataset with no zero values. To contour the data, some zero values are required. If, in step 3, all values below the detection limit are set to the detection limit, the zero values would have to be determined by some arbitrary method.

One possibility was to arbitrarily assign zero values at some set distance beyond the last value above the detection limit. This was rejected as being too susceptible to modeling error, as this would allow the shape of the plume to be determined by the modeler, not the data. A second possibility was to use the data exactly as the data appears after the two data corrections are applied. However this possibility (and the first) lacked a method to deal with non-detects and reported concentration values that shared the same x,y location.

Figure 4-1 illustrates the non-Gaussian shape of the tritium plume, especially at snapshots 3 and 4. In an ideal system, the plume would expand symmetrically as it progressed downgradient. The movement of the majority of the injected mass away from the injection zone is very slow, as noted by the relatively high percentage of mass surrounding the injection zone at snapshots 3 and 4. The low conductivity zone near the injection location restricts the movement of a large percentage of the pulse injection. The portion of the plume that does move downgradient moves to a higher conductivity zone and is quickly moved downgradient by the relatively fast groundwater velocity that occurs in the far-field. The apparent separation of the plume may be caused by a lack of sampling points, or it may be a real feature of the plume caused by the extreme velocity increases that occur in the area of separation. The velocity
increases could be amplified by rainfall events, which may result in even larger velocity variations throughout the aquifer.

It is important to note that all values below 62 µg/L (this is the sum of the organic detection limits, see Table 3-1) on Figure 4-2 are suspect. As previously mentioned, steps 1 and 3 most likely skewed the concentration data prior to kriging. Since data were not available below these limits, the kriging results below 62 µg/L are extrapolated estimates. The true combined organic concentration value at any point showing a concentration at or below 62 µg/L may fall anywhere between 0 and 62 µg/L.
4.3 Sub-Set Selection

As mentioned in Section 3.2, five snapshots were available for calibration, validation, and prediction. These snapshots occurred 27, 132, 224, 328, and 442 days after injection. Snapshot 5 (442 days after injection) was inconsistent with the previous snapshots as only the multi-level samplers near the injection zone were sampled during this event. Snapshot 1 took place 27 days after injection and did not provide sufficient data for modeling purposes. Therefore snapshots 2, 3, and 4 were used for calibration, validation, and prediction, respectively.
5.0 MODEL SET-UP

This chapter covers the development of the hydraulic parameters and initial parameter estimates for the Bioplume model of the MADE-2 site. In the initial stages of modeling this site, a 33 by 59 model grid was used with 20 ft by 20 ft cells. This grid worked relatively well for modeling the tritium plume. However, subsequent simulations indicated that this coarse grid would not provide sufficient detail for modeling the organic plume.

A more refined model grid was then established which consisted of 92 by 205 cells which had dimensions of 5 ft by 5 ft each. The refined grid incorporated a smaller portion of the MADE site. Coordinates of the rectangular grid domain were -230.0 ft (-70.1 m), -100.0 feet (-30.5 m) for the lower left corner and 230.0 ft (70.1 m), 925.0 ft (281.9 m) for the upper right with 0,0 being located in the center of the injection zone (See Figure 5-1). The new finite-difference grid incorporates most of the sampling network and only excludes three of the sampling points which fall outside the grid (M253, M289, and M279).
Figure 5-1. Sample Collection Locations Used to Monitor Tracers
5.1 Hydraulics

The hydraulics of the MADE-2 site were simulated by Beach et al., 1996. A steady state MODFLOW model was calibrated to provide estimates of hydraulic conductivity, hydraulic head, and recharge. The initial estimate of hydraulic conductivity was based upon borehole flowmeter data. A total of sixty-seven wells were tested at the site, fifty-six during MADE-1 and eleven during MADE-2. Since Bioplume is a two-dimensional model, the conductivities were vertically averaged (by Beach et al., 1996) at each well using the following equation:

\[ K_{av} = \frac{\sum m_i(K_i - K)}{\sum m_i} \]  

(5.1)

where

\( m_i = \) vertical thickness of an individual layer
\( K_i = \) hydraulic conductivity of an individual layer

The resulting conductivity values were then kriged to estimate conductivity values for each cell within the modeling grid.

Initial head values were determined by averaging the water levels recorded throughout the test period for each well. The resulting values were kriged to provide a continuous field across the model domain. A linear drift was implemented in kriging to account for the natural gradient. The initial recharge rate due to precipitation was estimated to be ten inches/year, which corresponds to approximately fifteen percent of the total precipitation during MADE-2.
Particle tracking modeling in conjunction with the MODFLOW model showed that the average velocity of the center of mass of the tritium plume was too low when compared to the field data. To improve the model predictions, the aquifer was divided into even horizontal sections, with the highest conductivity in that section used to calculate the average conductivity for each individual well. Evaluation of section thicknesses of 0.5, 1.0, 2.0, and 3.0 meters, showed that a thickness of 0.5 meters provided the best comparison to field data. (Figures 5-2 and 5-3 show the head and conductivity fields resulting from Intera’s modeling.) The resulting hydraulic conductivity field was “strongly skewed toward the highest observed field measurements” (Beach et al., 1996).

Particle tracking also showed that the simulated direction of flow was significantly different from the direction recorded in the field. Beach et al., (1996), made “several iterations of minor boundary adjustments ... to properly orient the flow direction...”. Additionally, the recharge rate due to precipitation was raised to seventeen inches/year (approximately twenty-five percent of total precipitation.)
Figure 5-2. a. Final Calibrated Steady-State Simulated Heads from MODFLOW simulations
b. Average Water Level Measurements
Figure 5-3. a. Final Calibrated Hydraulic Conductivity (log \( K \)) from MODFLOW simulations
b. Average Hydraulic Conductivity (log \( K \))
5.2 Initial Parameter Estimation

A number of assumptions were used in modeling the MADE-2 experiment. These assumptions include: 1) steady state flow, 2) constant recharge, and 3) uniform aquifer thickness. Bulk density and porosity were assumed to be spatially homogeneous and were assigned values of 1.77 g/cm$^3$ and 0.35, respectively (Boggs et al., 1993b). A weighted average based on the relative percentage of each organic contaminant injected was used to estimate both the F ratio (mass oxygen consumed/ mass hydrocarbon degraded) and the retardation factor for the combined organic. Since Bioplude II simulates a single contaminant, a weighted average allows the values input to the model to reflect the characteristics of the tracers that are the most significant (based on mass of tracer injected).

First, the F ratio for each contaminant was determined from the equations given in Table 5-1. Each individual F ratio was then multiplied by the percent mass for that specific contaminant (determined by dividing the injected mass of the individual contaminant by the total injected mass of all contaminants). Summing the results for all four organics provided an estimate of the F ratio for the lumped organic.

A similar process was used to determine the retardation (R) value for the lumped organic. Instead of using the calculated the F ratios, the R value for each organic contaminant (taken from Boggs et al., 1993b) was multiplied by the percent mass. These values were summed to calculate the overall R value.
The required Biopilume parameter (the distribution coefficient, K_d) was then
calculated as shown in Table 5-1.

Table 5-1
F Ratio and Retardation Calculations

Combined Organic Concentration F Ratio Calculations

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Inj. Mass (g)</th>
<th>% Mass</th>
<th>Mol Wt (g)</th>
<th>F Ratio</th>
<th>% Mass * F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>659.7</td>
<td>45.52</td>
<td>78.113</td>
<td>3.072</td>
<td>1.398</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>402.0</td>
<td>27.74</td>
<td>106.167</td>
<td>3.165</td>
<td>0.878</td>
</tr>
<tr>
<td>Napthalene</td>
<td>70.0</td>
<td>4.83</td>
<td>128.173</td>
<td>2.996</td>
<td>0.145</td>
</tr>
<tr>
<td>o-DCB</td>
<td>317.7</td>
<td>21.92</td>
<td>147.004</td>
<td>1.415</td>
<td>0.310</td>
</tr>
</tbody>
</table>

Total Mass = 1449.4
Mol. Wt. O_2 = 31.999
Total F => 2.731

Contaminant Stoichiometric Equations
Benzene 2 C_6H_6 + 15 O_2 -> 12 CO_2 + 6 H_2O
p-Xylene 2 C_6H_10 + 21 O_2 -> 16 CO_2 + 10 H_2O
Napthalene C_{10}H_8 + 12 O_2 -> 10 CO_2 + 4 H_2O
o-DCB C_{6}H_{5}Cl + 6.5 O_2 -> 6 CO_2 + 1 H_2O + 2 Cl^- + 2 H^+

Combined Organic Concentration Retardation Calculations

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Inj. Mass (g)</th>
<th>% Mass</th>
<th>Retardation</th>
<th>% Mass * R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>659.7</td>
<td>45.52</td>
<td>1.200</td>
<td>0.546</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>402.0</td>
<td>27.74</td>
<td>1.450</td>
<td>0.402</td>
</tr>
<tr>
<td>Napthalene</td>
<td>70.0</td>
<td>4.83</td>
<td>1.160</td>
<td>0.056</td>
</tr>
<tr>
<td>o-DCB</td>
<td>317.7</td>
<td>21.92</td>
<td>1.330</td>
<td>0.292</td>
</tr>
</tbody>
</table>

Total Mass = 1449.4
Total R => 1.296

\[ n \Rightarrow 0.35 \]
\[ pb \Rightarrow 1.77 \text{ g/cm}^3 \]
\[ K_d = (R-1)n/pb \Rightarrow 0.0585 \text{ cm}^3/\text{g} \]
The contaminant source was originally treated as a pulse injection over a 48.5 hour period. This source configuration mimics the actual contaminant injection in the field. After calibration of the pulse source simulations was complete, the decision was made to investigate the possibility of a continuous source model providing greater predictive capability, even though this was not a true representation of the MADE-2 experiment. All transport and biodegradation parameters were held constant in the continuous source runs. This allowed the effects of the source configuration to be considered without interference due to changes in other parameters.

Boggs et al. (1993b) give dissolved oxygen data for 6-18-90, 8-13-90, 10-15-90, 12-4-90, 3-7-91, and 5-22-91. The highest value observed at the site during the MADE-2 experiment was 7.8 mg/L, while the lowest observed value was 2.6 mg/L. The oxygen data were contoured and examined to determine the initial estimate for the dissolved oxygen concentrations across the site. As is common at almost all sites, some dissolved oxygen was always present in the heart of the hydrocarbon plume (Godsy, 1994). During the MADE-2 experiment, the concentration in the heart of the plume ranged from a minimum 2.6 mg/L to a maximum of 6.8 mg/L. By arbitrarily subtracting the approximate average minimum value of 3.6 mg/L from the approximate average maximum value of 6.6 mg/L, an initial dissolved oxygen concentration of 3.0 mg/L was estimated. This value was used as the initial dissolved oxygen concentration in the model.

Boggs et al. (1993b) estimate a longitudinal dispersivity of 10 meters (32.8 feet) at the MADE site. Similarly, transverse dispersivity is given at 2.2
meters (7.22 feet). However, Boggs et al. (1993b) state that 2.2 meters is probably higher than the actual value. Their transport model had a convergent flow field near the injection point, and required a high value to model the transverse spread of the plume. Based on the data from Boggs et al. (1993b), the initial longitudinal dispersivity and ratio of longitudinal to transverse dispersivity in the Bioplume II model were set at 32.8 feet (10 meters) and 0.22, respectively.

The initial estimates of first-order decay rates were determined by taking a weighted average (like that used to calculate the F value and retardation) of the values given in Boggs et al. (1993b). This report gives two values for biodegradation of each tracer; one developed from fenceline data and one developed from snapshot data. Taking a weighted average of these values resulted in estimates of 0.01 day$^{-1}$ from the fenceline values and 0.0075 day$^{-1}$ from the snapshot values. Initially, the 0.01 day$^{-1}$ was used as the first-order decay rate for the combined organic contaminant at the site.
6.0 Model Calibration

All transport and biodegradation parameters were determined using a pulse source configuration. First, the tritium plumes were used to calibrate the injection rate, injection concentration, transmissivity, longitudinal dispersivity, and the ratio of transverse to longitudinal dispersivity. Second, the organic plumes were used to calibrate the initial oxygen concentration and the first-order decay rate. As mentioned in the previous section, the continuous source configuration was used only to improve the predictive ability of the model. Only the source configuration was calibrated; no other parameter calibration was performed using continuous source simulations.

Percent root mean squared error (% RMS error) was selected as the statistical "yardstick" to determine the relative accuracy of the various simulations during calibration. The % RMS error is given by:

\[ RMS = \sqrt{\frac{\sum_{i=1}^{n} (c_o - c_p)^2}{n}} \quad (6.1) \]

\[ \%RMS = \frac{RMS}{(c_{\text{max}} - c_{\text{min}})} \times 100 \quad (6.2) \]

where

- \( c_o \) = observed concentration
- \( c_p \) = predicted concentration

Burgess (1993) suggested a % RMS error of less than 15 is appropriate for calibration purposes. To calculate the % RMS error, base values were
needed to compare with the simulation results. These base values were calculated by averaging all of the observed concentrations in each Bioplume II grid block. If there were no data in a particular grid block, the grid block was not used in calculating the % RMS error. Six sets of observed data were developed; three sets of tritium data and three sets of organic data (snapshots 2, 3, and 4 for each). After each run, the model output was compared with the corresponding snapshot and the percent root mean squared (% RMS) error was calculated.

As mentioned in Section 4.1, combined organic concentration values below 62 µg/L are suspect. In this procedure, if the combined organic concentration value in a grid block was below 62 µg/L in the observed organic data set, the concentration value for that block was considered to be 62 µg/L during the % RMS error calculation. This provided a conservative % RMS error value since it is probable that the concentration within that grid block is below 62 µg/L. The net effect of this transformation is that the calculated % RMS error value will be higher than the true % RMS error.
6.1 Pulse Source Calibration

For the pulse source model, the injection concentration and injection rate were the first parameters to be calibrated. Snapshot 2 (132 days after injection) was used for model calibration. Initially, a total injection rate and tracer concentration identical to the field values in the MADE-2 experiment were used in the Bioplume II simulations. This injection rate caused significant simulated hydraulic mounding at the injection points. The hydraulic mounding is partially caused by the reduction of the number of injection wells from the five used at the site to the two simulated in Bioplume II. The resulting gradient caused the contaminants to spread too quickly during the injection period.

New injection rates and concentrations were established by scaling the injection rates and concentrations such that the total injected mass was constant, but the injection volume and rate decreased. For example, if the injection rate was reduced by a factor of two, the injection concentration was increased by a corresponding factor of two. By trial and error, a factor of nine was determined to give the best estimate. Using the factor of nine resulted in a simulated injection rate of $1.08 \times 10^4$ cfs and a simulated tritium injection concentration of 504,800 pCi/ml (the actual tritium injection concentration was 55,620 pCi/ml).

The hydraulic conductivity determined in the MODFLOW modeling was converted to transmissivity for the Bioplume II simulations. Simulations using the original transmissivity field showed the plume moving in the correct direction
and at a reasonable velocity. However, the field data showed that an area of high concentration remained near the injection points, and that the model was not accurately simulating that area. To improve the model calibration, the transmissivity immediately around the injection zone was reduced from $8.83 \times 10^{-3}$ ft$^2$/s to $1.00 \times 10^{-3}$ ft$^2$/s. Reducing the transmissivity helped to retain the area of high concentration and decrease the transverse spreading of the plume. Per Boggs et al. (1993b) the dispersivity ratio was initially estimated at 0.22. To further reduce the transverse spreading of the tracers, the ratio of longitudinal to transverse dispersivity was decreased to 0.10, resulting in better correlation between the model results and the field data.

Snapshot 3 (224 days after injection) was used to validate the results of the different source scenarios. When the validation simulation results were examined, it was noted that the leading edge of the modeled plume was not traveling to the expected extent. Correspondingly, the estimate of longitudinal dispersivity was increased to 37.0 feet. After the dispersivity was increased, no further changes were made to the transport parameters. The results from the calibrated tritium simulations are shown in Figure 6-1.

Two techniques were used to simulate degradation of the combined organic contaminants. For both of these techniques, the scaling factor of 9 determined during tritium calibration, established the organic injection concentration of 1,358.4 mg/L (the actual organic injection concentration was 159.6 mg/L). The first technique modeled degradation by first-order decay only. Initial calibration simulations (based upon snapshot 2) showed the best
Figure 6-1. Simulated Tritium Concentrations for Snapshots 2, 3, and 4 (132, 224 and 328 Days After Injection) Pulse Source Model
results were obtained when the first-order decay constant was set to 0.0 (no decay). A first-order rate constant of 0.0 was obviously incorrect when the entire time domain is considered, since the combined organic concentrations decrease with time, but was correct for the time period simulated for snapshot 2 (days 1 through 132). The estimated first-order decay rate was arbitrarily left at 0.01 day\(^{-1}\) until the validation simulations (based upon snapshot 3) were completed.

During the validation simulations, the percent RMS error estimates reached a minimum when the first-order decay rate was set to 0.0165 day\(^{-1}\). The calibration simulation was then repeated. The results from the repeated calibration step were not as good as the simulations with no decay, but it was determined that the first-order decay rate of 0.0165 day\(^{-1}\) gave the best overall results when the entire time domain was considered (see Figure 6-2).

The second technique used to simulate the organic decay was a combination of instantaneous degradation and first-order decay. The initial oxygen concentration across the site was set to 3,000 \(\mu g/L\). With the first-order decay rate set to zero, the initial oxygen concentration was varied in numerous simulations to see if a better estimate could be obtained. After testing values from 0 \(\mu g/L\) to 8,000 \(\mu g/L\), it was determined that lowering the initial oxygen concentration to 2,600 \(\mu g/L\) gave the lowest % RMS error when the model results were compared to the field data for snapshot 2. Then the first-order decay rate was set to 0.01 day\(^{-1}\) and increased until the best estimate of the first-order decay rate was found to be between 0.011 day\(^{-1}\) and 0.013 day\(^{-1}\)
Figure 6-2. Simulated Organic Concentrations for Snapshots 2, 3, and 4
(132, 224, and 328 Days After Injection)
Pulse Source, First Order Decay Model
(this first-order decay rate only applies to the simulations which implemented instantaneous degradation with first-order decay).

During the validation simulations for the combined oxygen and first-order decay model, the initial oxygen concentration was again varied. The best overall results were obtained when the initial oxygen concentration estimate was set to 3,000 $\mu$g/L (the original value). The first-order decay rate was varied from $0.011 \text{ day}^{-1}$ to $0.013 \text{ day}^{-1}$ (the range determined in the calibration simulations). The best results were obtained when a value of $0.0125 \text{ day}^{-1}$ was used. Again, the calibration simulations were repeated with these new estimates and found to be acceptable (see Figure 6-3).
Figure 6-3. Simulated Organic Concentrations for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection)
Pulse Source, Aerobic Degradation with First Order decay Model
6.2 Continuous Source Calibration

After examination of the contoured field data, a second conceptual model was considered. It appeared that the source might be better represented by treating a portion of the total mass as a pulse injection during the first 48.5 hours and the remainder of the total mass as a continuous source throughout the remainder of the time experiment. This conceptualization was based on the observation that the measured plumes appeared very non-Gaussian in shape and did not appear to move as an instantaneous injection. The non-Gaussian plume shape is most likely the result of the low conductivity zone that surrounds the injection location.

As previously mentioned, all the transport and biodegradation parameters estimated from the pulse injection model were used in this scenario without alteration. The total injected mass was subdivided into two categories; mass pulse injected and mass continuously injected. The first category, mass pulse injected, represented the percentage of the total mass simulated as being injected in the first 48.5 hours of the experiment. The second category, mass continuously injected, represented mass continuously injected over the remainder of the time domain (slightly under 440 days). The mass in each category was varied by 5-percent increments, ranging from 0 percent pulse, 100 percent continuous to 100 percent pulse, 0 percent continuous. Three configurations (0 percent pulse, 100 percent continuous; 5 percent pulse, 95 percent continuous; and 10 percent pulse, 90 percent continuous) gave
the best overall results with no apparent significant difference in the % RMS error of these three configurations. During the validation step, the best of these scenarios was determined to be 5 percent pulse, 95 percent continuous. It is worthy of note that this injection pattern (5 percent pulse, 95 percent continuous) was determined to give the best results for both the tritium and the combined organic plumes independently, providing confirmation as to the suitability of this injection scenario (see Figures 6-4, 6-5, and 6-6).
Figure 6-4. Simulated Tritium Concentrations for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection)
Continuous Source Model
Figure 6-5. Simulated Organic Concentrations for Snapshots 2, 3, and 4
(132, 224, and 328 Days After Injection)
Continuous Source, First Order Decay Model
Figure 6-6. Simulated Organic Concentrations for Snapshots 2, 3, and 4 (132, 224, and 328 Days After Injection) Continuous Source, Aerobic Degradation with First Order Decay Model
6.3 Parameter Summary and Prediction

A summary of the model parameters determined in the calibration and validation steps is shown in Table 6-1. These parameters remained unchanged for the prediction step.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Observed Value</th>
<th>Modeled</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Simulations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>Time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- calibration (snapshot 2)</td>
<td>132 days (0.3616 years)</td>
<td>0.3616 years</td>
</tr>
<tr>
<td>- validation (snapshot 3)</td>
<td>224 days (0.6137 years)</td>
<td>0.6137 years</td>
</tr>
<tr>
<td>- prediction (snapshot 4)</td>
<td>328 days (0.8986 years)</td>
<td>0.8986 years</td>
</tr>
<tr>
<td>No. injection wells</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

Pulse Injection Only

Injection concentration
- tritium                                      | 55,610 pCi/ml | 504,873 pCi/ml |
- hydrocarbon                                  | 159.63 mg/L   | 1,358.40 mg/L |
Injection rate (per well)                      | 0.67 L/min (3.92E-04 cfs) | 1.08E-04 cfs |
Longitudinal dispersivity                      | 10 m (32.8 ft) | 37.0 ft      |
Transverse dispersivity                        | 2.2 m (7.22 ft) | 3.7 ft       |
Initial oxygen concentration                   | 4.2 mg/L      | 3.0 mg/L     |
1st order decay rate                           |                |              |
- only first-order decay                       | 0.01 day^{-1} | 0.0165 day^{-1} |
- O_2 and first-order decay                    | n/a            | 0.0125 day^{-1} |

Pulse and Continuous Injection

Pulse injection concentration
- tritium                                      | 55,610 pCi/ml | 504,873 pCi/ml |
- hydrocarbon                                  | 159.63 mg/L   | 1,358.40 mg/L |
Continuous injection concentration              |                |              |
- tritium                                      | n/a            | 55,500 pCi/ml |
- hydrocarbon                                  | n/a            | 149.4 mg/L   |
Injection rate (per well)                      |                |              |
- pulse (48.5 hours)                           | 0.67 L/min (3.92E-04 cfs) | 5.40 E-06 cfs |
- continuous (~328 days)                       | n/a            | 5.77 E-06 cfs |
Table 6-2 shows the % RMS error and center of mass location for the calibrated simulations.

<table>
<thead>
<tr>
<th></th>
<th>% RMS</th>
<th>Model COM (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pulse Injection Only</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calibration Results</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Tritium</td>
<td>14.8 %</td>
<td>0.12, 16.75</td>
</tr>
<tr>
<td>- Organic (1st order decay)</td>
<td>14.5 %</td>
<td>0.35, 9.49</td>
</tr>
<tr>
<td>- Organic (1st order + O₂)</td>
<td>15.4 %</td>
<td>0.61, 2.07</td>
</tr>
<tr>
<td>Validation Results</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Tritium</td>
<td>7.5 %</td>
<td>0.04, 33.01</td>
</tr>
<tr>
<td>- Organic (1st order decay)</td>
<td>7.5 %</td>
<td>0.36, 14.14</td>
</tr>
<tr>
<td>- Organic (1st order + O₂)</td>
<td>7.9 %</td>
<td>0.53, 2.01</td>
</tr>
<tr>
<td>Predictive Results</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Tritium</td>
<td>10.5 %</td>
<td>1.12, 52.05</td>
</tr>
<tr>
<td>- Organic (1st order decay)</td>
<td>18.7 %</td>
<td>0.50, 16.57</td>
</tr>
<tr>
<td>- Organic (1st order + O₂)</td>
<td>19.4 %</td>
<td>0.52, 2.06</td>
</tr>
</tbody>
</table>

| **Continuous Injection** |       |               |
| Calibration Results     |       |               |
| - Tritium               | 17.3 %| 0.33, 9.89    |
| - Organic (1st order decay) | 16.6 %| 0.50, 5.53    |
| - Organic (1st order + O₂) | 18.2 %| 0.71, 1.94    |
| Validation Results      |       |               |
| - Tritium               | 7.9 % | 0.79, 20.58   |
| - Organic (1st order decay) | 7.5 % | 0.41, 8.90    |
| - Organic (1st order + O₂) | 7.6 % | 0.51, 2.85    |
| Predictive Results      |       |               |
| - Tritium               | 8.6 % | 0.62, 35.32   |
| - Organic (1st order decay) | 13.1 %| 0.42, 12.02   |
| - Organic (1st order + O₂) | 13.0 %| 0.65, 2.18    |

The most significant trend that can be observed from the data represented in Table 6-2 is that the pulse source simulations more closely mimic the field data in the early stages (snapshot 2) than the continuous source models (based upon the % RMS values). The pulse source and continuous
source models are roughly equivalent in their ability to match the field data for 
snapshot 3. Finally, the continuous source models produce the best results 
when the output of the predictive simulations are compared with the field data 
for snapshot 4..

Similarly, by examining only Table 6-2, it would appear that the first-order 
decay and the aerobic biodegradation with first-order decay simulations are 
roughly equivalent in the accuracy of their ability to simulate the degradation of 
the organic contaminants within consideration of each snapshot. However, 
simply examining the appropriate figures shows that the first-order decay 
simulations more appropriately mimic the extent of the observed plumes. A 
more detailed discussion follows.
7.0 Analysis and Discussion

In this section the following topics are covered: 1) the accuracy of the pulse and continuous models, 2) a statistical analysis of the best simulations, 3) the probable types of degradation, and 4) a sensitivity analysis of the model. This discussion will be used in Section 8.0 to summarize the results in the light of the four original goals of this thesis. These were:

1. to perform a preliminary analysis of the three-dimensional database with respect to suitability of biodegradation modeling,
2. to investigate the use of a two-dimensional model (Bioplume II) to simulate observed data,
3. to identify gaps and issues in using models for predictive analysis at sites,
4. to provide guidance for data collection and modeling for the MADE-3 experiment.

In general, Bioplume II did a good job of simulating the observed field tritium data, but was unable to accurately simulate the organic data due to insufficient data collection.
7.1 Pulse Source

Visual comparison between the tritium contours of the Bioplume II simulations (Figure 6-1) and the tritium contours from field data show that the progress of the leading edge of the simulated plume and the progress of the leading edge of the actual tritium plume are similar. In the near field, the simulated plume is much wider than the actual plume. The increased width of the simulated plume is most likely caused by the high concentration gradient resulting from the simulated pulse injection. The high gradient causes the plume to disperse much faster than is likely to occur in the field. The simulated plumes also show the leading edge of all contours greater than 50 \( \mu \text{g/L} \) of tritium farther downgradient than is evidenced by the field tritium data. The progress of these contours could also be caused by excessive dispersion in the Bioplume II simulation. Most likely, the progress is caused by a combination of dispersion and inexact modeling of the transmissivity in the near field.

The tritium field data also show fingering and plume separation that is not evident in the simulated plumes (see Figure 4-1). The fingering and plume separation could be a result of channelization at the MADE-2 site. Channels of high hydraulic conductivity would allow the contaminants to follow a tortuous path and could cause plume separation.

Figure 4-2 shows vertically averaged combined organic plumes, at times corresponding to snapshots 2, 3, and 4. Upon examination of Figure 4-2, the bulk of the combined organic plumes (neglecting the values below
approximately 62 µg/L) appear to have achieved a steady state, or actually to be decreasing, unlike the tritium field data, where the edge of the contaminated area is continually extending. The steady state appearance of the plume is probably caused by aerobic degradation at the edges of the organic plume. First-order decay simulations do not show this effect. In simulations that only consider first-order decay, the leading edge of the plume progresses slowly, as shown in Figure 6-2. The extent of the simulated organic plumes, like the simulated tritium plumes, is much greater than that shown by the contours of the field data. As with the tritium plume, dispersion and transmissivity are important factors in the transport of the organic contaminants.

When aerobic degradation and first-order decay are considered simultaneously, the organic plumes reach steady-state. However, the area of the plume resulting from this type of simulation is much smaller than observed in the field, based on the implementation of 3.0 mg/L initial oxygen concentration (see Figure 6-3). As time progresses, the oxygen continually degrades the edges of the simulated organic plume. However, the concentrations in the center of the plume remain relatively constant after snapshot 2 because all the oxygen has been depleted. After the initial oxygen is depleted in the heart of the plume, only first-order decay (representing anaerobic degradation or degradation due to oxygen recharge) decreases the combined organic concentrations in the center of the plume, well away from any oxygen carried into the plume by dispersion or advection. The limited
degradation results in organic concentrations above 1,000 μg/L in the heart of
the simulated plumes. The high concentrations in the heart of the simulated
plumes remain relatively constant throughout the simulations for snapshots 2, 3,
and 4. The continued high concentrations do not match the field observations,
which show a reduction in concentration at all points within the plume as time
progresses.
7.2 Continuous Source

As expected, the continuous injection tritium transport simulations do not model the peak concentrations as accurately as the pulse injection simulations (see Figure 6-4, snapshots 2 and 3). However, the difference in peak concentrations due to the source configuration is much smaller in the simulation representing snapshot 4. The inaccuracy in representing the peak concentrations is offset by better representation of plume area.

The continuous source simulations with first-order decay provide the best overall representation of the MADE-2 experiment as evidenced in the percent RMS error (see Figure 6-5). The area of contamination is overpredicted, but the predicted area is closer in size to the contoured field data than the simulations of aerobic degradation with first-order decay (shown in Figure 6-6). Both types of simulations (first-order decay and aerobic degradation with first-order decay) show little change in concentrations in the heart of the plume throughout the time domain. The plume resulting from the first-order decay simulations expands slowly, while the plume resulting from the simulations of aerobic degradation with first-order decay shrinks with time. The simulated results for snapshots 2 and 3 (Figure 6-5) show good correlation with the field data (Figure 4-2). The field data for snapshot 4 show a smaller plume than produced by the model.

The smaller plume may be an indication that aerobic degradation plays a significant role in natural attenuation at the site. However, the simulations
incorporating 3.0 mg/L oxygen (Figure 6-6) probably overestimate the amount of oxygen used in the aerobic degradation processes at the site as evidenced by the smaller plume extent shown in Figure 6-5. In fact, in this respect, the continuous source model gives worse results than the pulse source model. Another model incorporating first-order decay and aerobic degradation might provide better correlation if aerobic degradation was arbitrarily allowed to degrade a smaller amount of organics instantaneously. The reduction in instantaneous degradation would be accomplished by lowering the initial oxygen concentration below the value indicated in the calibration process and adjusting the first-order decay rate to compensate. The aerobic degradation would act to stabilize the growth of the plume without prematurely degrading the entire plume.
7.3 One-Sample t-Test

A statistical analysis based on the one-sample t-test was performed to ascertain the viability of the Bioplume II simulations with respect to the data. The continuous source model was compared to the field tritium data, and the continuous source, first-order decay model was compared to the field combined organic data. Two hypotheses $H_0$ (the null hypothesis) and $H_1$ are formulated as follows:

$H_0$: The model is valid.
$H_1$: The model is invalid.

So by setting:

$Y_{1i} = X_{1i} - \mu_i$
$Y_{2i} = X_{2i} - \mu_i$

where

$\mu_i = \text{model value}$
$X_{1i} = \text{field data - mean of all values sharing the same x,y coordinates}$
$X_{2i} = \text{field data - median of all values sharing the same x,y coordinates}$

Under this scenario the above set of hypotheses can be reformulated as:

$H_0: E[Y] = 0$
$H_1: E[Y] \neq 0$

where $Y$ denotes either $Y_1$ or $Y_2$.

We assume that $Y_1, \ldots, Y_n$ constitute a random sample from a Normal distribution with common mean and variance, where $n = \#$ of data points. Thus the one sample t-test is the appropriate test. In making this assumption, the additional
variation resulting from the summary statistics of the sample mean and median within each grid cell is ignored. This test was performed using the SYSTAT ® software package developed by SYSTAT, Inc. The results of performing this test at each time step (snapshots 2, 3, and 4) for the tritium and organics plumes are summarized in Table 7-1.

<table>
<thead>
<tr>
<th></th>
<th>Based on the Mean</th>
<th>Based on the Median</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Combined Organics</td>
<td>Combined Organics</td>
</tr>
<tr>
<td>Snapshot 2</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>Snapshot 3</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>Snapshot 4</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T value</td>
<td>3.917</td>
<td>1.887</td>
</tr>
<tr>
<td>p value</td>
<td>0.000</td>
<td>0.065</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T value</td>
<td>20.290</td>
<td>15.607</td>
</tr>
<tr>
<td>p value</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T value</td>
<td>17.327</td>
<td>14.726</td>
</tr>
<tr>
<td>p value</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T value</td>
<td>-0.971</td>
<td>-0.396</td>
</tr>
<tr>
<td>p value</td>
<td>0.333</td>
<td>0.692</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T value</td>
<td></td>
<td>1.957</td>
</tr>
<tr>
<td>p value</td>
<td></td>
<td>0.053</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T value</td>
<td></td>
<td>-3.765</td>
</tr>
<tr>
<td>p value</td>
<td></td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 7-1

One-Sample t-Test Results

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>T value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where

n = the number of samples
T = t-distribution identifier
p = the probability value
In general, due to the low probability values, the null hypothesis is rejected for the organics. This indicates that the continuous source model does not adequately represent the contaminant plume. Without better knowledge of the concentrations of benzene at the edges of the plume, the validity of any calibration to the combined organics is tenuous. However due to the higher probability values for the tritium data (greater than .05), the null hypothesis was not rejected for snapshots 3 and 4 when the statistics based on the mean value are considered. This confirms that the continuous source model provides reasonable predictions of the observed tritium plume as stated in section 7-2.
7.4 Consideration of Combined Degradation

One of the considerations that arose during model calibration was the justification of modeling aerobic degradation and first-order decay simultaneously. Examination of the dissolved oxygen data for the near field sampling points (D010, M041, and M066) from Boggs et al. (1993b) shows that the lowest dissolved oxygen measurement taken during the study in the area where degradation is occurring is 2.6 mg/L. (The corresponding maximum in this area is 6.8 mg/L.)

Prior to the start of the study, on June 18, 1990, dissolved oxygen measurements were taken at the site. The next readings were taken on August 13, 1990. During this time, the measured oxygen actually increased by as much as 2.4 mg/L (M041, port 10) during this period. The increase in measured oxygen shows that either significant recharge of dissolved oxygen is occurring at the site, or that the reported data has some inaccuracies.

In the case of significant recharge occurring at the site, the first-order decay can be considered as decay resulting from the oxygen reaeration. It is simply a way of accounting for the introduction of dissolved oxygen into the groundwater from the vadose zone or through infiltrating rainwater.

In addition, since the transmissivity is so low in the area of biodegradation, it is possible that pockets of low dissolved oxygen may be developing. The dissolved oxygen monitoring in the near field was very sparse. Three multi-level samplers were sampled at three ports, approximately every
two or three months. The collected samples may have simply missed finding any of these areas. In this case, the first-order decay term would account for any degradation that is occurring in these pockets.

Unfortunately, these hypotheses were not investigated when the data were being collected. It is possible that a combination of the two explanations given above occurred at the site. There was some influx of oxygen into the ground water through infiltration, which may have resulted in hydrocarbon degradation. Similarly, it is possible that there was some anaerobic degradation. However, since there is no data quantifying the amount of degradation due to these two possibilities, these two types of degradation were collectively represented as first-order decay and the model was fit to the available data.
7.5 Sensitivity Analysis

7.5.1 Transport Parameters

A sensitivity analysis was performed to determine the potential effect of the various parameters on contaminant transport and on mass loss due to biodegradation. The parameters considered were transmissivity, longitudinal dispersivity, the ratio of transverse to longitudinal dispersivity, retardation, first-order decay, and initial oxygen concentration. The base parameters used in the sensitivity analysis are the estimates developed to simulate snapshot two in the calibration and validation process. For consistency, where possible the same parameters were used for both the first-order decay and aerobic degradation with first-order decay models. The base parameters for the sensitivity analysis are shown in Table 7-2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base estimate</th>
<th>Varied</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transport Parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transmissivity scaling factor</td>
<td>1</td>
<td>0.1 to 10</td>
<td></td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>37 ft</td>
<td>15 to 45 ft</td>
<td></td>
</tr>
<tr>
<td>Dispersivity ratio</td>
<td>0.1</td>
<td>0.1 to 0.2</td>
<td></td>
</tr>
<tr>
<td><strong>Biodegradation Parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(First-order decay only)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retardation</td>
<td>1.296</td>
<td>1.144 to 1.447</td>
<td></td>
</tr>
<tr>
<td>First-order decay rate</td>
<td>0.0165 day$^{-1}$</td>
<td>0.0068 to 0.132 day$^{-1}$</td>
<td></td>
</tr>
<tr>
<td><strong>Biodegradation Parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Aerobic degradation with first-order decay)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Retardation</td>
<td>1.296</td>
<td>1.144 to 1.447</td>
<td></td>
</tr>
<tr>
<td>First-order decay rate</td>
<td>0.0125 day$^{-1}$</td>
<td>0.0068 to 0.132 day$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Initial oxygen concentration</td>
<td>3.0 mg/L</td>
<td>0.0 to 8.0 mg/L</td>
<td></td>
</tr>
</tbody>
</table>
Simulated tritium plumes were used to study the sensitivity of model results to transmissivity and dispersivity. The calibrated transmissivity distribution was multiplied by a scaling factor (M) to decrease and increase the transmissivity by an order of magnitude. Figures 7-1(a) and (b) show the tritium concentration along the centerline of the plume for the pulse source and continuous source models. In these figures, peak concentrations and plume extents vary significantly. In general, as the transmissivity increased, the peak concentrations decreased while plume areas increased.

The effects of varying longitudinal dispersivity on the centerline concentrations are shown in Figure 7-2. The longitudinal dispersivity was varied from 15 to 45 feet for both source types. The concentration profiles shown in (a) and (b) are similar for all simulations, regardless of source configuration. As the dispersivity was increased, peak concentration decreased and plume extent increased.

The tritium concentration along the centerline and across a transect of the plume are shown in figures 7-3 and 7-4. Increasing the ratio of transverse to longitudinal dispersivity ratio (RD) has little effect on the shape of the plume. In the center of the plume, the peak concentrations decreased with an increase in the dispersivity ratio. Additionally, the width of the plume increased slightly with an increase in RD.
Figure 7-1.  a. Effect of Transmissivity Scaling Factor (M) on Simulated Centerline Tritium Concentrations for the Pulse Source Model.

b. Effect of Transmissivity Scaling Factor (M) on Simulated Centerline Tritium Concentrations for the Continuous Source Model.

Note that a scaling factor (M) of 1 is used in the calibrated model. Based on response to variance, model is sensitive to transmissivity.
Figure 7-2. a. Effect of Longitudinal Dispersivity (D) on Simulated Centerline Tritium Concentrations for the Pulse Source Model.

b. Effect of Longitudinal Dispersivity (D) on Simulated Centerline Tritium Concentrations for the Continuous Source Model.

Note that a longitudinal dispersivity (D) of 37 is used in the calibrated model. Based on response to variance, model is sensitive to longitudinal dispersivity.
Figure 7-3.  a. Effect of the Ratio of Transverse / Longitudinal Dispersivity (RD) on Simulated Centerline Tritium Concentrations for the Pulse Source Model.
b. Effect of the Ratio of Transverse / Longitudinal Dispersivity (RD) on Simulated Centerline Tritium Concentrations for the Continuous Source Model.

Note that a ratio (RD) of .1 is used in the calibrated model
Based on response to variance, model is slightly sensitive to transverse dispersivity.
Figure 7-4.  a. Effect of the Ratio of Transverse / Longitudinal Dispersivity (RD) on Simulated Transect Tritium Concentrations for the Pulse Source Model.

b. Effect of the Ratio of Transverse / Longitudinal Dispersivity (RD) on Simulated Transect Tritium Concentrations for the Continuous Source Model.

Note that a ratio (RD) of .1 is used in the calibrated model.

Based on response to variance, model is slightly sensitive to transverse dispersivity.
The relative magnitude of the effects resulting from changing the values of transmissivity and dispersivity seem to indicate that advective transport dominates this system. Increasing the transmissivity depleted the contaminant in the heart of the plume, whereas increasing longitudinal dispersivity and dispersivity ratio only slightly lowered the concentration. The minor impact of dispersivity on contaminant transport was also evident during the calibration and validation process. Major plume characteristics were controlled through the transmissivity field, while modifications to the dispersion parameters were used to affect small changes at the edges of the plume.

7.5.2 Biodegradation Parameters

The possible impacts due to retardation and biodegradation parameters were studied by simulating the combined organic plumes. Again, both the pulse source and continuous source models were considered. The type and magnitude of the plume responses were almost identical for both source types.

Combined organic concentration along the centerline of the plume for retardation values ranging from 1.114 to 1.447 are shown in Figures 7-5 (a) and (b), respectively, for pulse and continuous source models. The retardation values are taken from Boggs et al. (1993b) as the limits of the 95% confidence interval for the retardation factor. Because these values are relatively close to unity, no significant impact was expected due to changes in this value. Results indicate that plume extent and peak concentration are almost identical. Figures 7-9 (a) and (b) present the percent mass remaining in the dissolved
Figure 7-5. a. Effect of Retardation (R) on the Simulated Centerline Combined Organic Concentrations for the Pulse Source Model. 
b. Effect of Retardation (R) on the Simulated Centerline Combined Organic Concentrations for the Continuous Source Model.

Note that a retardation value (R) of 1.296 is used in the calibrated model. Based on response to variance, model is not sensitive to retardation.
phase as a function of the retardation factor. As the retardation factor increases, more contaminant adsorbs to the aquifer media, resulting in a decrease in percent mass remaining in the dissolved phase. The relationship between retardation factor and percent mass remaining appears to be approximately linear over the evaluated range.

Figures 7-6 and 7-7 show the combined organic concentration along the plume centerline for first-order decay rates between 0.0068 day$^{-1}$ and 0.0132 day$^{-1}$. Figures 7-6(a) and (b) show the first-order decay only scenario, while Figures 7-7(a) and (b) show the aerobic degradation with first-order decay scenario. From Figures 7-6 and 7-7, it is difficult to assess the impact of first-order decay. Examination of the corresponding figures that illustrate the remaining percent mass (Figures 7-10(a), (b), (c), and (d)) showed that increasing the first-order decay decreased the percent mass remaining for the first-order decay model by approximately 6 and 10 percent (pulse and continuous sources, respectively.) For the aerobic degradation with first-order decay model, an increase in the decay rate from 0.0068 day$^{-1}$ to 0.0132 day$^{-1}$ resulted in a decrease in the percent dissolved mass remaining of approximately 6 percent for the continuous source model, and approximately 5 percent for the pulse source model.

The most significant biodegradation parameter in the Biopluwe II modeling was the initial oxygen concentration. Figures 7-8(a) and (b) show the centerline organic concentration for initial dissolved oxygen rates of
Figure 7-6. a. Effect of First-Order Decay Rate \( (k) \) on the Simulated Centerline Combined Organic Concentrations for the Pulse Source Model.
b. Effect of First-Order Decay Rate \( (k) \) on the Simulated Centerline Combined Organic Concentrations for the Continuous Source Model.

Note that a decay rate \( (k) \) of 0.0165 is used in the calibrated model. Based on response to variance, model is slightly sensitive to first-order decay rate.
Figure 7-7. a. Effect of First-Order Decay Rate (k) on the Simulated Centerline Combined Organic Concentrations for the Pulse Source Model.
   b. Effect of First-Order Decay Rate (k) on the Simulated Centerline Combined Organic Concentrations for the Continuous Source Model.

Note that a decay rate (k) of .0165 is used in the calibrated model. Based on response to variance, model is slightly sensitive to first-order decay rate.
Figure 7-8. a. Effect of Dissolved Oxygen (DO) on the Simulated Centerline Combined Organic Concentrations for the Pulse Source Model.
b. Effect of Dissolved Oxygen (DO) on the Simulated Centerline Combined Organic Concentrations for the Continuous Source Model.

Note that a dissolved oxygen concentration (DO) of 3 is used in the calibrated model. Based on response to variance, model is sensitive to initial oxygen concentration.
Figure 7-9. The Effect of Retardation on the Percent Mass Remaining for (a) the Pulse Source Model and (b) the Continuous Source Model. The Effect of Initial Dissolved Oxygen on the Percent Mass Remaining for (c) the Pulse Source Model and (d) the Continuous Source Model.
Figure 7-10. The Effect of First Order Decay Rate on the Percent Mass Remaining for (a) the Pulse Source Model with First-Order Decay Only; (b) the Continuous Source Model with First-Order Decay Only; (c) the Pulse Source Model with Aerobic Degradation and First-Order Decay; and (d) the Continuous Source Model with Aerobic Degradation and First-Order Decay.
0, 4, and 8 mg/L. Figures 7-9(c) and (d) show the corresponding percent dissolved mass remaining with the addition of the data points for 1 and 2 mg/L initial oxygen concentration. The slope of the percent mass remaining vs. initial oxygen concentration is very steep between values of 0 and 1 mg/L, after which the slope decreases. As the initial oxygen concentration is increased, the edges of the contaminant plume are immediately degraded.

By referring to Figure 7-4(a) and any of the figures showing centerline concentrations, the relatively low concentrations at the edge of the plume can be seen. These low edge concentrations are due to the area of low transmissivity surrounding the injection point which restricts the movement of the contaminant following injection. When the initial concentration of oxygen is increased to a level sufficient to degrade all of the contaminant present in the edges of the plume, the amount of mass degraded per increase in initial concentration decreases significantly. The decrease appears to occur at approximately 2 mg/L. This shows the most appropriate model for the MADE-2 site, assuming that aerobic biodegradation is being simulated, may be one with a lower initial oxygen concentration than indicated in the model calibration. The value might need to be between 0.5 and 2.0 mg/L instead of the 3.0 mg/L estimated by using the % RMS error to compare the model results to the field data.
8.0 Summary, Conclusions, and Recommendations

A Bioplume II model of the natural attenuation occurring during the MADE-2 experiment (described in Boggs et al. 1993a, 1993b) was developed. This model considered two descriptions of biodegradation; first-order decay only and instantaneous aerobic degradation combined with first-order decay. Two source scenarios, pulse injection and continuous injection, were investigated. The simulations with a continuous source and only first-order decay provided the best results based upon % RMS error and visual inspection of the field data and simulation results. The relative accuracies of the simulation types may be attributable to the fact that the majority of the biodegradation of the organic contaminants is occurring in an area of very low transmissivity (approximately $1 \times 10^{-9}$ feet$^2$/second).

During the analysis of the database, the following limitations of the MADE-2 experiment hindered proper conceptualization, visualization, and modeling of the data.

1) The migration of the conservative tracers beyond the sampling network.
2) The need for greater resolution in the near field.
3) The need for more detailed oxygen data in the near field.
4) The relatively high detection limit for benzene, which resulted in the lack of edge data for the benzene plume.

By increasing the extent of the sampling field, conservative tracers can be monitored for greater times during future testing. Most of the hydrocarbon degradation seems to be occurring in the near field, as shown by the almost steady-state plume extent. By increasing the sampling density in the near field,
greater resolution of the plume edge can be obtained as it progresses through
the area immediately downgradient of the injection point. This will present a
clearer picture of the details of the hydrocarbon degradation at the edges of the
plume. Similarly, more oxygen data needs to be collected in the near field.
However, the most important correction would be to lower the detection limit for
benzene, preferably to a maximum of 5 ppb. Approximately 45% of the injected
mass was benzene, thus knowledge of the extent of this plume is critical.

Due to the area of low transmissivity, the instantaneous degradation
assumptions inherent in Bioplume II might not be well-suited for the MADE-2
site. The most basic assumption of the Bioplume model is that the degradation
is oxygen-limited. During the MADE-2 experiment, and given the limited
oxygen sampling, no significant decrease in the amount of dissolved oxygen
present was observed. This observation, plus the low concentrations of organic
contaminants at the plume edges suggest that the biodegradation may be
rate-limited and not transport-limited.

Monod kinetics account for rate-limited degradation based upon
availability of all of the required substrates (Rifai and Bedient, 1990).
Odencrantz et al., (1990) state that "(w)hen the substrate concentration is small
with respect to $K_s$ the kinetics are first-order, when it is high with respect to $K_s$,
they are zero order." $K_s$ is the half-saturation or half-velocity constant. Tabak et
al. (1990) give a $K_s$ value of 22.16 mg/L for benzene based upon their studies.
In the MADE-2 experiment this concentration only ever exceeded in very center
the plume, so according to this theory, the kinetics are first-order in the majority of the affected area.

Biopluume II assumes that the kinetics of the majority of the plume are zero-order. However, based upon the $K_s$ values given above, the kinetics at the edges of a plume where the concentrations are well below the $K_s$ values (such as occurred at the MADE-2 site) may be better represented by first-order decay. A better overall plume representation for the MADE-2 site might be obtained by using a model with the option of describing biodegradation with Monod kinetics, such as the first Biopluume model (Borden and Bedient, 1986) or Biopluume III (Rifai et al., 1995b).

In the modeling process, four issues arose that apply to modeling in general, not only Biopluume II. These are:

1) Using a two-dimensional vertically-integrated model to represent a three-dimensional heterogeneous flow system.
2) Grid definition.
3) Injection well location.
4) Model limits.

Perhaps the most significant assumption in developing the model was assuming that a two-dimensional model represents a three-dimensional flow system. The database describing this system is very large. Simple averaging was used to reduce the three-dimensional dataset to two-dimensions. This may not be the best representation of the data. Further studies should be considered to investigate if another statistical representation provides a better two-dimensional model of the data and if the use of a three-dimensional model may be more appropriate.
The definition of the grid determines the visible resolution of the plume and severely influences the accuracy of the model. The smaller the cell size, the more accurately the shape of the plume can be determined. For the Bioplume modeling, the choice of a 5 ft. by 5 ft. grid represented a trade-off between accuracy and resource allocation. This grid allowed reasonable accuracy while allowing the model to complete a run in a reasonable time. Better accuracy could have been achieved by using a smaller cell size, but the resources required to complete the modeling would have most likely increased greatly.

In the field, the MADE-2 organics were injected through a series of five wells spaced approximately 1 meter apart in a line perpendicular to groundwater flow. In the Bioplume II model as with many numerical models, the location of injection wells is related to grid selection since the injection wells must be located at the center of a cell. Due to Bioplume II's constraints, the best injection scenario was determined to be injection through two wells, approximately 1.5 meters apart. This necessitated a reduction in the injected volume and an increase in the injection concentration to prevent mounding.

The output from the Bioplume model contains values that are below field data detection limits. In this case, this problem was amplified by the high detection limit for benzene. Any strict statistical analysis of the organic data requires that any unreliable information not be used. In this study, any combined organic value of less than 62 mg/L is unreliable. The one-sample t-test showed that the best model of the combined organics cannot be considered
to accurately represent the observed data. This can be generalized to all models in that modeling a site is only valid when the model can be calibrated to reliable data that spans the concentration range that is being studied.

In addition to the database limitations the following issues should be considered with regards to future investigations at the MADE site.

1) Data should be collected on other electron acceptors than oxygen.
2) Microcosm studies should be conducted with material from the site.

The most interesting future study that is possible with this database may be to determine the relative value of the data collected. With the volume of data that is available in the MADE-2 database, further modeling of the contaminant plumes and transmissivity field is possible, using only subsets of the available data. Careful selection of the subsets will allow investigation of the number of data points necessary within a given aquifer volume are necessary to accurately represent the transmissivity and contamination of that volume.


Giesfeldt, M. F. (1993). Natural Biodegradation as a Remedial Action Option. State of Wisconsin, Department of Natural Resources. ERR/GCERA.


