Natural Attenuation of BTEX Compounds: Model Development and Field-Scale Application

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Abstract

Benzene, toluene, ethyl benzene and xylene (BTEX) dissolved into groundwater and migrated from a light nonaqueous phase liquid (LNAPL) source into a sandy aquifer near a petroleum, oil, and lubricants (POL) facility at Hill Air Force Base (AFB), Utah. Field observations indicated that microbiologically mediated BTEX degradation using multiple terminal electron-accepting processes including aerobic respiration, denitrification, Fe(III) reduction, sulfate reduction, and methanogenesis has occurred in the aquifer. To study the transport and transformation of dissolved BTEX compounds under natural conditions, a reactive flow and transport model incorporating biochemical multispecies interactions and BTEX was developed. The BTEX, oxygen, nitrate, Fe(III), sulfate, and methane plumes calculated by the model agree reasonably well with field observations. The first-order biodegradation rate constants, estimated based on model calibration are 0.051, 0.031, 0.005, 0.004, and 0.002 day\textsuperscript{-1} for aerobic respiration, denitrification, Fe(III), sulfate reduction, and methanogenesis, respectively. The results of a sensitivity analysis show that the saturated aquifer thickness, hydraulic conductivity, and reaction rate constants are the most critical parameters controlling the natural attenuation of BTEX at this site. The hydraulic conductivity and aquifer thickness were found to be the key factors affecting the restoration of oxygen, nitrate, and sulfate after their interaction with the BTEX plume. The multispecies reactive transport modeling effort, describing BTEX degradation mediated by multiple electron-accepting processes, represents one of the few attempts to date to quantify a complete sequence of natural attenuation processes with a detailed field data set. Because the case study is representative of many petroleum-product contaminated sites, the results and insights obtained from this study are of general interest and relevance to other fuel-hydrocarbon natural attenuation sites.

Introduction

Organic chemicals, discharged from various waste sources, have contaminated ground water in many regions of the United States. During the past decade, a number of engineered accelerated bioremediation technologies have been developed to treat the contaminated ground water at these sites. Recently, there is increased interest in understanding the mechanisms of natural attenuation, particularly intrinsic bioremediation, a method that relies on the naturally occurring biodegradation removal processes that occur at a field site (Wiedemeier et al. 1996). In fact, natural attenuation is quickly becoming an acceptable treatment technology for managing organic solute plumes (U.S. EPA 1997). The United States Air Force Center for Environmental Excellence developed a detailed protocol for evaluating natural attenuation at fuel-hydrocarbon contaminated sites (Wiedemeier et al. 1995). This protocol was used to evaluate a dissolved BTEX plume originating from a petroleum, oil, and lubricant facility operations site at Hill Air Force Base, Utah (Wiedemeier et al. 1995). This study focuses on developing a multispecies reactive modeling framework to model the natural attenuation data set collected at the POL site at Hill AFB.

Due to the complex nature of the subsurface system undergoing natural attenuation, multispecies reactive transport simulation is generally needed both to accurately reflect existing site conditions and to quantify the effectiveness of the biodegradation processes. Multispecies transport of biodegradable contaminants in one-dimensional soil columns has been numerically modeled by several researchers (Molz et al. 1986; Kindred and Celia 1989; Zysset et al. 1994; Clement et al. 1997). Models incorporating simultaneous transport of dissolved organic carbon and dissolved oxygen were presented by Borden and Bedient (1986) and MacQuarrie and Sudicky (1990). Other subsurface biochemical processes such as denitrification and fermentation reactions have also been considered in the literature (Widdowson et al. 1988; Kinzelbach et al. 1991; Kindred and Celia 1989).

Early studies (GTC Ltd. 1982; Diersch and Kaden 1984; Kinzelbach 1985) did not consider reactive transport and made use of simplified zero- or first-order source/sink terms to represent a single species, dissolved organic carbon.

Using a two-dimensional horizontal transport model linked to an improved reaction model, which combined first-order decay and simplified multispecies reactions, Borden et al. (1986) studied the reactive transport of hydrocarbons in the ground water below a creosote site in Texas. They matched their model results to measured concentrations by varying the dispersivity values. Application of a

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more sophisticated model for simulating microbially mediated organic carbon degradation at the same site was presented by Borden et al. (1989). The measured and simulated concentrations were compared to investigate the degradation potential of site contaminants via in situ aerobic reactions. Rifai et al. (1988) used the BIOPLUME-II code to model biodegradation at a U.S. Coast Guard site in Traverse City, Michigan. Chiang et al. (1989) simulated the aerobic degradation of benzene, toluene, and xylene with a two-dimensional flow and transport model, which was coupled to the reaction model of Borden et al. (1986), by matching concentration distributions measured in a contaminated aquifer in Michigan. The study identified that the initial distribution of the organic compounds and the longitudinal dispersivity were crucial model parameters.

MacQuarrie and Sudicky (1990) simulated benzene transport in a vertical cross section of the Borden Aquifer in Ontario, Canada, with a two-dimensional flow and transport model incorporating a kinetic model for aerobic biodegradation. The effect of aquifer heterogeneity on benzene degradation under natural flow conditions was considered using a heterogeneous hydraulic conductivity distribution.

Aerobic and denitrifying microbial processes coupled to substrate consumption were considered by Kinzelbach et al. (1991) to simulate in situ bioremediation of a ground water aquifer contaminated by benzene and toluene in the Upper Rhine Valley in Germany. In another study, a one-dimensional flow and transport model coupled with rate-limited sorption and a two-domain mass transfer approach was used by Brusseau (1992) to successfully simulate measured organic contaminant behavior for selected field-scale experiments described in the literature.

A more complex biodegradation model was used by Sempirni and McCarty (1991, 1992) to investigate in situ biorestorations of a TCE plume present beneath the Moffet Naval Air Station in California. The coupled reactive model considered microbial growth, subsequent methane and oxygen consumption, cometabolic degradation of chlorinated aliphatic compounds and rate-limited sorption. However, the advective transport was simplified by using a one-dimensional modeling approach. The presence of uniform flow field was used to justify the use of one-dimensional approach.

The methanogenic degradation of phenolic compounds in an aquifer below a wood treatment plant in Florida was simulated by Bekins et al. (1993). Schafer and Therrien (1995) simulated transport incorporating biochemical multispecies interactions and removal of xylene during remediation of a sandy aquifer, in which microbially mediated xylene degradation and oxygen and nitrate reduction occurred in the aquifer. Biodegradation of volatile and non-volatile fractions of dissolved organic carbon by aerobic processes, manganese and iron reduction, and methanogenesis at a crude oil spill site at the Bemidji, Minnesota crude oil spill site were simulated by Essaid et al. (1995). Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer, under mixed aerobic-denitrifying conditions, was studied by Borden et al. (1997).

The objectives of this study are to (1) simulate the fate and transport of BTEX and associated electron-acceptors observed at the POL facility site at Hill AFB, Utah; (2) present a comprehensive modeling framework for simulating the natural attenuation of fuel-hydrocarbons using the RT3D computer code; and (3) assess the relative sensitivity of model parameters with respect to BTEX removal via natural attenuation. The manuscript is organized into three sections. An overview of the study site and available data are discussed in the first section, the modeling approach is discussed in the second section, and the results of model calibration and sensitivity analysis are discussed in the last section.

**Site Description**

Hill AFB is located on a bench of the Wasatch Mountains that was formed by fluvial-deltaic basin fill deposits of the ancient Weber River on the edge of the Great Salt Lake Basin. The POL facility is located in the southwestern corner of Hill AFB, Utah. Figure 1 is a detailed map of the POL Facility. This figure includes underground storage tank site 870 (UST 870, the believed source of the release) and various surface features in the vicinity. The surface topography at the site slopes to the southwest.

The unconfined aquifer beneath this site consists of poorly to moderately sorted, yellowish-brown to reddish-brown, silty fine-grained sands that coarsen downward into moderately sorted medium- to coarse-grained sands. These sands range in thickness from approximately 3 to 22 feet (0.91 to 6.71 m) and the shallow saturated zone occurs within these sands. The shallow saturated zone typically is less than 3 feet (0.91 m) thick. Abruptly overlying the sands is a clayey silt to silty clay interval, ranging in thickness from approximately 4 to 15 feet (1.22 to 4.57 m). Underlying the sandy
Table 1
Values for Selected Model Parameters for the POL Facility Site at Hill AFB

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average hydraulic conductivity</td>
<td>19 ft/day (5.79 m/day)</td>
</tr>
<tr>
<td>Porosity, ( \theta )</td>
<td>0.25</td>
</tr>
<tr>
<td>Longitudinal dispersivity, ( \alpha )</td>
<td>27 feet (8.23 m)</td>
</tr>
<tr>
<td>Ratio of transverse to longitudinal dispersivity</td>
<td>0.01</td>
</tr>
<tr>
<td>Discretization in:</td>
<td></td>
</tr>
<tr>
<td>( \Delta x )</td>
<td>110 feet (33.53 m)</td>
</tr>
<tr>
<td>( \Delta y )</td>
<td>85 feet (25.91 m)</td>
</tr>
<tr>
<td>Extent of model in:</td>
<td></td>
</tr>
<tr>
<td>( x )-direction</td>
<td>3300 feet (1005.84 m)</td>
</tr>
<tr>
<td>( y )-direction</td>
<td>1700 feet (518.16 m)</td>
</tr>
<tr>
<td>Background concentration (in mg/L)</td>
<td>0</td>
</tr>
<tr>
<td>BTEX</td>
<td>6.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>17.0</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.001</td>
</tr>
<tr>
<td>Ferrous iron (Fe(^{2+}))</td>
<td>100</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.0001</td>
</tr>
<tr>
<td>Methane</td>
<td>20.5</td>
</tr>
<tr>
<td>Maximum Fe(II) concentration</td>
<td>0.0001</td>
</tr>
<tr>
<td>Maximum methane concentration</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Hydraulic conductivity in the medium- to coarse-grained sands of the shallow saturated zones was estimated using rising head slug tests conducted in five different boreholes (Wiedemeier et al. 1995; Figure 1). The measured hydraulic conductivity ranges from 0.43 to 53 ft/day (0.13 to 16.15 m/day) with an average value of 19 ft/day (5.79 m/day). The longitudinal dispersivity for the plume was estimated to be about 27 feet (8.2 m). This value is based on preliminary model calibration runs and is consistent with the value used by Wiedemeier et al. (1995) for modeling the site and with those for other sites with similar plume scales (Gelhar et al. 1992). The ratio of transverse to longitudinal dispersivity is set at 0.01 (Gelhar et al. 1992). Values of other model parameters used are summarized in Table 1.

At the POL facility, a 1000 gallon underground storage tank (UST 870) was used to store condensed and off-specification JP-4. The tank was excavated and removed in May 1991 and upgraded with a new double-walled steel UST serving the same purpose. The soil and ground water at the site were found to be contaminated during removal of UST 870. The actual source of contamination at the POL facility is not known with any degree of certainty, nor is the total amount of fuel that leaked into the subsurface. Potential sources of contamination include direct leaks from the former UST, leaky piping associated with the UST, surface spills and release from operations since the 1940s, and a faulty 6 inch diameter pipe located behind the pump facility Building 870 (Wiedemeier et al. 1995).

Mobile LNAPL was present in several monitoring wells and piezometers at the site. Figure 3a is an isopach map showing the distribution and measured thickness of mobile LNAPL at the site on December 28, 1993, suggesting that the mobile LNAPL plume extended approximately 750 feet downgradient from the source area. The areal extent of suspected mobile LNAPL contamination was approximately 225,000 square feet (20,903.2 m\(^2\)). From July through December 1993, the distribution of LNAPL was similar. However, only 23 days after the December observation, the shape of LNAPL plume seems to have changed dramatically. Figure 3b is an isopach map of LNAPL observed on January 20, 1994. As shown in the figure, the LNAPL seems to have migrated downgradient within a relatively short time. Review of available monitoring data for 20 field monitoring events, between August 1992 to April 1994 (Wiedemeier et al. 1995), revealed that LNAPL at this site seems to follow a distinct cyclic pattern: From May to December it seems to occupy a smaller areal extent and from January to April a larger areal extent. This changing pattern may be the result of LNAPL interaction between clayey silt and silty clay lenses at the site and other seasonal recharge events. Several clay lenses have been commonly detected in the area around borehole EPA-82-C (Figure 3b). Although water table data for the unconfined aquifer indicate an overall steady-state pattern, a local area around borehole CPT-19 (Figure 3b), located upstream of both CPT-20 and CPT-37, experiences a head rise of 5.67 feet (1.73 m). This is probably due to the flow resistance created by the extremely thin aquifer around borehole EPA-82-A, which might have restricted ground water movement when the water level is high; thus creating large local surges. The unusual local changes in ground water level might redistribute the perched LNAPL, thus creating a more extended shape. In addition, when the water table rises, it also picks up

Figure 3. Approximate LNAPL plume map (feet). (a) Approximate LNAPL plume from August 1, 1993 to January 9, 1994 (data shown were measured on December 28, 1993). (b) Approximate LNAPL plume from January 10 to April 25, 1994 (data shown were measured on January 20, 1994). (Data from Wiedemeier et al. 1995).
LAPL in the unsaturated soil pores, causing the residual LAPL to float on the water table. Residual-phase LAPL resulting from vertically and laterally migrating LAPL was found over a wide area at the POL site. The highest observed concentration of residual-phase BTEX is 554 mg of BTEX per kg of soil in a soil core sample taken from approximately 18 feet (5.49 m) below ground surface in the soil boring EPA-82-I (Figure 3a).

Twenty-two monitoring wells were installed to monitor the extent of dissolved ground water contamination in the area (Figure 1). For each well the entire thickness of the sand interval of the shallow aquifer was screened so that seasonal fluctuations of the water table can be measured. The measured concentrations and distribution of different geochemical species support the hypothesis that natural attenuation reactions, using multiple terminal electron accepting processes, occur at this site (Wiedemeier et al. 1995; also Figure 4). The upstream portion of the aquifer is characterized by elevated BTEX concentrations, low concentrations of dissolved oxygen (DO), nitrate, and sulfate, and high concentrations of Fe(II) and methane. In contrast the contaminated area, DO, nitrate, and sulfate concentrations are high (Figures 4a, 4b, 4c, and 4e), and Fe(II) and methane concentrations are low (Figures 4d and 4f). These observations indicate that bacteria are actively using oxygen, nitrate, Fe(III), and sulfate as electron acceptors and producing methane via methanogenesis. The in situ microbes seem to be using fuel hydrocarbons as their carbon and energy sources, thereby contributing to the natural removal process.

Mathematical Model

Governing Equations

Over the past two decades, numerous laboratory and field studies have shown that microorganisms indigenous to subsurface environment can degrade fuel hydrocarbons under both aerobic and anaerobic conditions (Wiedemeier et al. 1995, 1999). During biodegradation, microorganisms transform available carbon into forms useful for energy and cell production. This results in oxidation of the electron donor (ED) and reduction of electron acceptor (EA). The EDs would include natural organic matter and anthropogenically introduced carbon, such as fuel hydrocarbons. The EAs include elements or compounds that occur in relatively oxidized states. The common EAs present in ground water aquifers (in ground water or in oxide form) are dissolved oxygen, nitrate, iron(III) or Mn(III), sulfate, and carbon dioxide (Wiedemeier et al. 1995; Essaid et al. 1995). The EAs are listed here in the expected sequence of use which is established based on the Gibb’s free energy of the redox reactions. In addition to these direct electron acceptor processes, methanogenesis would also contribute to hydrocarbon removal.

The fate and transport of BTEX and various EAs (or degradation products) observed at Hill AFB are modeled using the following set of reactive transport equations:

\[
R_{\text{BTEX}} \frac{\partial [\text{BTEX}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [\text{BTEX}]}{\partial x_j} \right) - \frac{\partial (v_i [\text{BTEX}])}{\partial x_i} + q_i [\text{BTEX}]_k + r_{\text{BTEX}} \tag{1}
\]

\[
R_{O_2} \frac{\partial [O_2]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [O_2]}{\partial x_j} \right) - \frac{\partial (v_i [O_2])}{\partial x_i} + q_i [O_2]_k + r_{\text{BTEX,O}_2} \tag{2}
\]

\[
R_{\text{NO}_3} \frac{\partial [\text{NO}_3^-]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [\text{NO}_3^-]}{\partial x_j} \right) - \frac{\partial (v_i [\text{NO}_3^-])}{\partial x_i} + q_i [\text{NO}_3^-]_k + r_{\text{BTEX,NO}_3} \tag{3}
\]

\[
R_{\text{Fe}^{2+}} \frac{\partial [\text{Fe}^{2+}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [\text{Fe}^{2+}]}{\partial x_j} \right) - \frac{\partial (v_i [\text{Fe}^{2+}])}{\partial x_i} + q_i [\text{Fe}^{2+}]_k + r_{\text{BTEX,Fe}^{2+}} \tag{4}
\]

\[
R_{\text{SO}_4^{2-}} \frac{\partial [\text{SO}_4^{2-}]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [\text{SO}_4^{2-}]}{\partial x_j} \right) - \frac{\partial (v_i [\text{SO}_4^{2-}])}{\partial x_i} + q_i [\text{SO}_4^{2-}]_k + r_{\text{BTEX,SO}_4^{2-}} \tag{5}
\]

\[
R_{\text{CH}_4} \frac{\partial [\text{CH}_4]}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial [\text{CH}_4]}{\partial x_j} \right) - \frac{\partial (v_i [\text{CH}_4])}{\partial x_i} + q_i [\text{CH}_4]_k + r_{\text{BTEX,CH}_4} \tag{6}
\]

where \( R \) is used to represent the retardation coefficient for various transported species, \( r \) represents various biodegradation reaction terms.
(these terms are described explicitly in the following sections). \(D_{ij}\) is the dispersion tensor, \(v_i\) is the transport velocity, \(u_i\) is the fluid sink/source term, and \(\varphi\) is porosity. The concentrations of different species are represented by a square bracket around an appropriate notation to represent the species.

In this study, total BTEX concentration levels are assumed to represent the overall hydrocarbon contamination at the POL facility at Hill AFB. Others have shown that the BTEX compounds, which are the most soluble contaminants, correlate well with the overall hydrocarbon contamination at field sites (Happel et al. 1998). Moreover, concentrations of individual BTEX species (i.e., concentration of benzene, toluene, ethyl benzene, and xylene) seem to correlate well with each other at several fuel-spill sites (Mace et al. 1997).

BTEX biodegradation is essentially an oxidation-reduction process where the BTEX compounds are oxidized and an EA (e.g., \(O_2\), \(NO_3^-\), \(Fe^{3+}\), \(SO_4^{2-}\), or \(CO_2\)) is reduced. The following conceptual biochemical model can be used to represent various degradation reactions that occur at Hill AFB site:

\[
\text{BTEX (ED) + EA + microorganisms + nutrients} \rightarrow \text{carbon dioxide + water + microorganisms + "respiration" products}
\]

Field observations at Hill AFB have shown that a complete sequence of microbially mediated BTEX biodegradation processes are actively using the electron acceptors \(O_2\), \(NO_3^-\), \(Fe^{3+}\), \(SO_4^{2-}\), or \(CO_2\) and producing \(Fe^{2+}\) and methane. Using benzene as an example reactant, the stoichiometry of different degradation processes can be described by the following set of biochemical reactions (Wiedemeier et al. 1995, 1999):

\[
C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \quad (7)
\]

\[
6NO_3^- + 6H^+ + C_6H_6 \rightarrow 6CO_2 + 6H_2O + 3N_2 \quad (8)
\]

\[
30Fe(OH)_3 + 60H^+ + C_6H_6 \rightarrow 6CO_2 + 78H_2O + 30Fe^{2+} \quad (9)
\]

\[
3.75SO_4^{2-} + 7.5H^+ + C_6H_6 \rightarrow 6CO_2 + 3H_2O + 3.75H_2S \quad (10)
\]

\[
C_6H_6 + 4.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4 \quad (11)
\]

The reactions are listed in the order in which they are expected to occur.

A kinetic model was developed to describe the aforementioned BTEX biodegradation reactions. The model describes the degradation pattern of BTEX under aerobic, denitrifying, \(Fe(III)\)-reducing, sulfate-reducing, and methanogenic conditions. The BTEX decay rates using five different EAs are approximated by five first-order decay terms. A Monod term is used to account for the presence (or the absence) of various EAs, and an inhibition model is used to simulate inhibition due to the presence of any one of the earlier EAs (i.e., an EA with higher free energy) in the reaction chain. The kinetic model is written as

\[
r_{\text{BTEX,O}_2} = -k_{O_2}[\text{BTEX}] \frac{[O_2]}{K_{O_2} + [O_2]} \quad (12)
\]

\[
r_{\text{BTEX,NO}_3^-} = -k_{NO_3^-}[\text{BTEX}] \frac{[NO_3^-]}{K_{NO_3^-} + [NO_3^-]} \frac{K_{O_2}}{K_{O_2} + [O_2]} \quad (13)
\]

\[
r_{\text{BTEX,Fe}^{3+}} = -k_{Fe^{3+}}[\text{BTEX}] \frac{[Fe^{3+}]}{K_{Fe^{3+}} + [Fe^{3+}]} \frac{K_{O_2}}{K_{O_2} + [O_2]} \frac{K_{NO_3^-}}{K_{NO_3^-} + [NO_3^-]} \quad (14)
\]

\[
r_{\text{BTEX,SO}_4^{2-}} = -k_{SO_4^{2-}}[\text{BTEX}] \frac{[SO_4^{2-}]}{K_{SO_4^{2-}} + [SO_4^{2-}]} \frac{K_{O_2}}{K_{O_2} + [O_2]} \frac{K_{NO_3^-}}{K_{NO_3^-} + [NO_3^-]} \frac{K_{Fe^{3+}}}{K_{Fe^{3+}} + [Fe^{3+}]} \quad (15)
\]

\[
r_{\text{BTEX,Me}} = -k_{Me}[\text{BTEX}] \frac{[CO_2]}{K_{CO_2} + [CO_2]} \frac{K_{O_2}}{K_{O_2} + [O_2]} \frac{K_{NO_3^-}}{K_{NO_3^-} + [NO_3^-]} \frac{K_{Fe^{3+}}}{K_{Fe^{3+}} + [Fe^{3+}]} \frac{K_{SO_4^{2-}}}{K_{SO_4^{2-}} + [SO_4^{2-}]} \quad (16)
\]

where \(r_{\text{BTEX,O}_2}\) is the BTEX destruction rate using oxygen as EA, \(r_{\text{BTEX,NO}_3^-}\) is the destruction rate using nitrate, \(r_{\text{BTEX,Fe}^{3+}}\) is the destruction rate using \(Fe^{3+}\) (or producing \(Fe^{2+}\)), \(r_{\text{BTEX,SO}_4^{2-}}\) is the destruction rate using sulfate, \(r_{\text{BTEX,Me}}\) is the destruction rate via methanogenesis, \([O_2]\) is oxygen concentration \([}\text{ML}^{-3}]\), \(K_{O_2}\) is the first-order biodegradation rate constant for BTEX using oxygen as EA \([}\text{T}^{-1}]\), \(K_{NO_3^-}\) is the saturation constant for oxygen \([}\text{ML}^{-3}]\), and \(K_{Fe^{3+}}\) is the oxygen inhibition constant \([}\text{ML}^{-3}]\); similar nomenclature is used for subsequent reactions. Note that by setting the half-saturation constants to small values, we can simulate zero-order dependency with respect to the electron donor and thus a first-order degradation model with respect to BTEX. The values of all the saturation constants were set at 0.01 mg/L.

Similarly, the inhibition constants can be set to small values to simulate pure sequential EA process. The inhibition function is used to represent the concept that the availability of any one of the EAs may inhibit the use of other EAs that provide less Gibbs free energy to the system. However, if \(K_i\) is assigned a very large value (much larger than the maximum value of the EA species), then the inhibition function becomes one and the simultaneous use of EAs can be simulated. In our model all \(K_i\) values, except \(K_{Fe^{2+}}\) and \(K_{Fe^{3+}}\), were set at 1.0 mg/L. The value of \(K_{Fe^{2+}}\) was set at 10 mg/L to allow simultaneous iron- and sulfate-use reactions that are expected to occur at Hill AFB site.

Since the concentrations of biologically available electron acceptors \(Fe(III)\) and \(CO_2\) cannot be measured under field conditions and because they can change over time (Wiedemeier et al. 1995), these terms were replaced in the model to predict the products of these EA reactions. The concentration levels of the products at every node were limited by using two "expressed capacity" terms for iron reduction and methanogenesis defined by the equations

\[
[Fe^{3+}] = [Fe^{2+}]_{\text{max}} - [Fe^{3+}]\quad (17)
\]

\[
[CO_2] = [CH_4]_{\text{max}} - [CH_4]\quad (18)
\]
where \([\text{Fe}^{2+}_{\text{max}}]\) and \([\text{CH}_4]_{\text{max}}\) are maximum measured concentrations of these species, which represent the aquifer’s “expressed” capacity for iron reduction and methanogenesis, respectively. Equations 17 and 18 are used to indirectly quantify the iron reducing and methanogenic capacity of the node at a given time. The concentration term for CO\(_2\) used in Equation 18, should be considered as a hypothetical term that simply indicates the expressed local methanogenic capacity of the node at a given time. Similarly, the concentration term for Fe(III) should also be considered as a hypothetical term that simply indicates the expressed local iron reduction capacity (biologically available Fe(III)) of the node.

The total rate of BTEX destruction via all five aerobic and anaerobic degradation pathways can be represented as

\[ r_{\text{BTEX}} = r_{\text{BTEX}, \text{O}_3} + r_{\text{BTEX}, \text{NO}_3} + r_{\text{BTEX}, \text{Fe}^{2+}} + r_{\text{BTEX}, \text{SO}_4^{2-}} + r_{\text{BTEX}, \text{CH}_4} \]  

(19)

Rates of EA use or degradation product formation are given by the corresponding rate of BTEX destruction term multiplied by an appropriate stoichiometric yield coefficient \((Y)\):

\[ r_{\text{O}_3} = Y_{\text{O}_3/\text{BTEX}} r_{\text{BTEX}, \text{O}_3} \]  

(20)

\[ r_{\text{NO}_3} = Y_{\text{NO}_3/\text{BTEX}} r_{\text{BTEX}, \text{NO}_3} \]  

(21)

\[ r_{\text{Fe}^{2+}} = -Y_{\text{Fe}^{2+/\text{BTEX}}} r_{\text{BTEX}, \text{Fe}^{2+}} \]  

(22)

\[ r_{\text{SO}_4^{2-}} = Y_{\text{SO}_4^{2-/\text{BTEX}}} r_{\text{BTEX}, \text{SO}_4^{2-}} \]  

(23)

\[ r_{\text{CH}_4} = -Y_{\text{CH}_4/\text{BTEX}} r_{\text{BTEX}, \text{Me}} \]  

(24)

By making the assumption that BTEX makes up the majority of the compounds found in the aqueous phase, the stoichiometric yield values are: \(Y_{\text{O}_3/\text{BTEX}} = 3.14, Y_{\text{NO}_3/\text{BTEX}} = 4.9, Y_{\text{Fe}^{2+/\text{BTEX}}} = 21.8, Y_{\text{SO}_4^{2-/\text{BTEX}}} = 4.7, \) and \(Y_{\text{CH}_4/\text{BTEX}} = 0.78\) (Wiedemeier et al. 1995, 1999).

It is important to note the presented model is based on several important assumptions. The model should be used with caution only at sites where these assumptions are valid. The key assumptions used in the model are (1) the fuel chemical species benzene, toluene, ethyl benzene, and xylene species are assumed to degrade at similar rates, and hence are combined and modeled as a single electron donor species BTEX; (2) production of Fe\(^{2+}\) and methane are restricted at a node at a “maximum-observed level”; however, the model assumes that an infinite supply of electron acceptors will be available for iron-reduction and methanogenic reactions; (3) more complex processes such as the rate-limited interaction of biologically available, solid-phase Fe(III) and aqueous-phase Fe\(^{2+}\), interaction of oxygen and Fe\(^{2+}\), and/or variations in the spatial pattern of methanogenic activity and CO\(_2\) availability are not considered; (4) growth and decay of various microbial populations and their interactions with contaminants and aquifer solids are assumed to be negligible; and (5) all BTEX decay reactions are approximated as first-order reactions and hence the model ignores Monod limitations due to the availability of electron donors (BTEX). These assumptions are expected to be reasonable approximations for most BTEX field sites; however, there will always be some exceptions.

**Simulation Code**

The RT3D (reactive transport in three-dimensions) computer code was used to numerically solve the reactive transport model (Clement 1997; Clement and Jones 1998). The code was benchmarked against other analytical and numerical solutions (Clement et al. 1998; Sun and Clement 1999; Clement 1997). The RT3D code is a general-purpose reactive transport simulator that solves any number of coupled partial differential equations that describe reactive flow and transport of multiple mobile and/or immobile species in a three-dimensional saturated ground water system. RT3D is a generalized multispecies reactive package coupled with the modular transport code, MT3D (Zheng 1990). As with MT3D, RT3D also uses the U.S. Geological Survey (USGS) groundwater flow code MODFLOW for computing spatial and temporal variations in groundwater head distribution.

The current version of RT3D (version 1.0) has a set of built-in reaction packages for simulating biodegradation of common environmental contaminants, such as fuel hydrocarbons and chlorinated solvents. In addition, it provides an interface for defining any other user-specified reaction module (Clement 1997). The kinetic model previously described was programmed as one of the built-in reaction modules. Therefore, the code can be used directly to simulate the bioreactive transport scenarios that occur at the POL facility at Hill AFB.

**Conceptual Site Model**

Field observations at the study site determined the choice of an appropriate conceptual model. The POL facility site is modeled as a shallow unconfined aquifer comprised of medium-grained, moderately sorted sands. The saturated thickness is generally less than 3 feet (0.91 m), with a relatively impermeable clayey-silt layer directly underlying the saturated zone.

The transport and fate of BTEX at the POL facility site was simulated from August 1993 until July 1994. Measured ground water levels indicate that the average ground water flow direction and gradient at the site remained fairly constant during the study period (Wiedemeier et al. 1995). Therefore, the flow was assumed to be at steady state. The aquifer was modeled using MODFLOW as a single saturated layer. Measured total organic carbon (TOC) for the shallow saturated zone ranged from 0.069% to 0.094%, resulting in low sorption estimates that would lie within the range of uncertainty in the velocity estimates (Wiedemeier et al. 1995). For this reason, no sorption was included in the model. Also, seasonal changes in aquifer saturated thickness were neglected.

**Discretization and Boundary Conditions**

Figure 5 shows a horizontal view of the model grid along with the location of the NAPL as measured in soil. All input data
for the modeling study are based on the information presented in Wiedemeier et al. (1995). A finite-difference grid of 20 rows and 30 columns was used to model the site. Each model cell is 110 feet (33.53 m) long by 85 feet (25.91 m) wide. The grid was oriented so that the longest cell dimension was parallel to the direction of ground water flow. Constant head boundaries were used along the left-hand and right-hand borders of the model grid to simulate the ground water flow pattern observed at the site. The constant-head boundaries were placed sufficiently far away from the plume to avoid potential boundary interferences. The upper and lower boundaries of the model grid were approximately parallel to the regional flow direction and hence were treated as no-flow boundaries.

The boundary conditions for the transport model are (1) no mass flux at the upper and lower boundaries, (2) specified concentration at the left boundary, and (3) specified mass flux at the right boundary (Figure 5). The concentrations of BTEX, oxygen, nitrate, Fe(II), sulfate, and methane are assumed to have no seasonal variation and were set at the upstream boundary (on the left) at the measured background concentrations. At the downstream boundary (on the right) the solutes are allowed to move freely out of the domain. The assumed values for the site are given in Table 1. The recharge flux has a constant and uniform concentration. The recharge is assumed to be free of BTEX (or LNAPL), Fe(II), and methane. DO, nitrate, and sulfate concentrations of the recharge water are identical to the background concentration levels.

**Initial Conditions and Definition of Sources**

No data are available concerning the volume of fuel hydrocarbons spilled at this site. All source details were inferred from the distributions of LNAPL in July-August 1993, December 1993, and January 1994. Plumes of BTEX and other species were based on the field measurements made in July-August 1993 and July 1994. The July-August 1993 data set was used for defining the initial condition for our model. Natural attenuation simulations were completed to simulate the plume fate after 365 days of transport, until July 1994.

The distribution of LNAPL was used to characterize the BTEX source. The LNAPL source was characterized by a variable shrink-and-spread pattern. Therefore, the total simulation time of 365 days was divided into three stress periods: 162, 106, and 97 days. The first stress period lasted from August 1, 1993, to January 9, 1994, and was characterized by the narrow distribution of LNAPL (Figure 3a); the second period was from January 10 to April 25, 1994, and characterized by a widespread distribution (Figure 3b); and the third period covered the time period from April 26 to July 30, 1994, and was assumed to have a pattern similar to the first period. There were no 1994 field data available for characterizing the LNAPL pattern for the third period; therefore, the pattern was inferred by reviewing the LNAPL seasonal variation and LNAPL thickness data collected during the same time period in the years 1992 and 1993 (Wiedemeier et al. 1995). Constant concentration cells were used to simulate the continuous sources of BTEX contamination caused by the mobile LNAPL. The cells in which LNAPL was present were the sources of BTEX and assigned constant concentration of the corresponding measured values of BTEX plumes. The constant concentration for the first stress period was inferred from July-August 1993 measured values. The third stress period was referred from the measured values of July 1994. The concentration for the second stress period was referred from the first and third stress periods and some data from the same period in the years 1992 and 1993.

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**Figure 6.** Calibrated flow field observed head in feet as measured in August 1993 for POL facility site at Hill AFB.

**Table 2**

<table>
<thead>
<tr>
<th>Well No.</th>
<th>Measured Head (h_m)</th>
<th>Simulated Head (h_s)</th>
<th>(h_m - h_s)</th>
<th>(\frac{(h_m - h_s)^2}{n})</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA-82-B</td>
<td>608.28</td>
<td>608.35</td>
<td>-0.07</td>
<td>0.0049</td>
</tr>
<tr>
<td>EPA-82-C</td>
<td>603.37</td>
<td>604.10</td>
<td>-0.73</td>
<td>0.5329</td>
</tr>
<tr>
<td>EPA-82-D</td>
<td>631.70</td>
<td>632.69</td>
<td>-0.99</td>
<td>0.7921</td>
</tr>
<tr>
<td>EPA-82-E</td>
<td>595.21</td>
<td>594.92</td>
<td>0.29</td>
<td>0.0841</td>
</tr>
<tr>
<td>EPA-82-F</td>
<td>600.06</td>
<td>599.70</td>
<td>0.36</td>
<td>0.1296</td>
</tr>
<tr>
<td>EPA-82-H</td>
<td>599.66</td>
<td>599.27</td>
<td>0.14</td>
<td>0.0196</td>
</tr>
<tr>
<td>CPT-2</td>
<td>659.34</td>
<td>659.20</td>
<td>-0.14</td>
<td>0.1023</td>
</tr>
<tr>
<td>CPT-11</td>
<td>666.70</td>
<td>666.79</td>
<td>-0.09</td>
<td>0.0081</td>
</tr>
<tr>
<td>CPT-12</td>
<td>643.21</td>
<td>643.51</td>
<td>-0.30</td>
<td>0.0900</td>
</tr>
<tr>
<td>CPT-13</td>
<td>630.56</td>
<td>630.76</td>
<td>-0.20</td>
<td>0.0400</td>
</tr>
<tr>
<td>CPT-15</td>
<td>607.29</td>
<td>607.62</td>
<td>-0.33</td>
<td>0.1089</td>
</tr>
<tr>
<td>CPT-17</td>
<td>623.61</td>
<td>623.72</td>
<td>-0.11</td>
<td>0.0121</td>
</tr>
<tr>
<td>CPT-18</td>
<td>629.10</td>
<td>628.96</td>
<td>0.14</td>
<td>0.0196</td>
</tr>
<tr>
<td>CPT-21</td>
<td>624.80</td>
<td>624.32</td>
<td>0.48</td>
<td>0.2304</td>
</tr>
<tr>
<td>CPT-23</td>
<td>617.65</td>
<td>617.82</td>
<td>-0.17</td>
<td>0.0289</td>
</tr>
<tr>
<td>CPT-26</td>
<td>579.59</td>
<td>579.65</td>
<td>-0.06</td>
<td>0.0036</td>
</tr>
<tr>
<td>CPT-27</td>
<td>596.35</td>
<td>596.20</td>
<td>0.15</td>
<td>0.0225</td>
</tr>
<tr>
<td>CPT-31</td>
<td>604.83</td>
<td>604.75</td>
<td>0.08</td>
<td>0.0064</td>
</tr>
<tr>
<td>CPT-41</td>
<td>635.89</td>
<td>635.91</td>
<td>-0.02</td>
<td>0.0004</td>
</tr>
<tr>
<td>MW-10</td>
<td>634.15</td>
<td>634.14</td>
<td>0.01</td>
<td>0.0001</td>
</tr>
<tr>
<td>MW-12</td>
<td>653.76</td>
<td>653.65</td>
<td>0.11</td>
<td>0.0121</td>
</tr>
<tr>
<td>MW-14</td>
<td>668.16</td>
<td>668.30</td>
<td>-0.14</td>
<td>0.0196</td>
</tr>
</tbody>
</table>

\(n = 22, \text{RMS} = 0.319, \text{RMS} = \frac{(\sum (h_m - h_s)^2)^{1/2} (h_m - h_s)^2}{n}\).

---

**Table 3**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic degradation rate constant ((k_{O_2}))</td>
<td>0.051 day(^{-1})</td>
</tr>
<tr>
<td>Denitrification rate constant ((k_{NO_2}))</td>
<td>0.031 day(^{-1})</td>
</tr>
<tr>
<td>Iron reduction rate constant ((k_{Fer}^{-}))</td>
<td>0.005 day(^{-1})</td>
</tr>
<tr>
<td>Sulfate reduction rate constant ((k_{SO_4}))</td>
<td>0.004 day(^{-1})</td>
</tr>
<tr>
<td>Methanogenic degradation rate constant ((k_{M_e}))</td>
<td>0.002 day(^{-1})</td>
</tr>
</tbody>
</table>
Table 2 shows a comparison between the measured (August 1993) and simulated piezometric head distribution. The root-mean-square (rms) error between observed and calibrated values at these points was 0.319 feet or about 0.22% of the maximum head difference of 145 feet from northeast (left boundary) to southwest (right boundary) across the model grid.

The initial values of all the first-order, biodegradation rate constants were selected based on the literature data (Rifai et al. 1995). During transport calibration step, reaction rate constants were perturbed to understand their effects on plume development. Later, the calibration process was started from the most sensitive to the less sensitive rate parameter. The estimated (via model calibration) biodegradation rate constants for the site are reported in Table 3.

**Discussion of Results**

The observed distribution of BTEX, DO, nitrate, Fe(II), sulfate, and methane in August 1993 are shown in Figure 4. These plumes were used as the initial condition in the simulation model. Simulations were completed for 365 days and the model results are compared against the plume distribution observed in July 1994 (Figures 7 and 8). The figures show that the model predicted the overall plume pattern reasonably well. In addition, the model results also reasonably matched the front shape of the plumes.

An estimate of the total mass of BTEX in the aquifer was used during the calibration process. To estimate BTEX mass, the concentration data from all the wells were used for interpretation to get the estimated concentration for each cell in the model domain. Then the volume of the saturated pore water for each cell was acquired by multiplying the x-, y-, and z-spacing (saturated thickness) data with porosity. Porosity for the types of sediments

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**Figure 7.** Observed (July 1994) and calculated plumes (concentration in mg/L): (a) BTEX, (b) dissolved oxygen (DO), (c) nitrate. (Observed plumes modified from Wiedemeier et al. 1995).

**Figure 8.** Observed (July 1994) and calculated plumes (concentration in mg/L): (a) ferrous iron (Fe^{2+}), (b) sulfate, (c) methane. (Observed plumes modified from Wiedemeier et al. 1995).
observed in the saturated zone ranges from 0.15 to 0.35 (Domenico and Schwartz 1990). A porosity of 0.25 was assumed for this modeling effort. Mass-balance results show that the discrepancy of the total mass of BTEX in the aquifer at the end of one-year simulation period, as calculated by the model, is within 8.5% of the total mass estimated from field observations of the BTEX plume in July 1994. In general, the agreement between the calculated and observed plumes is reasonably good, considering the uncertainties in the source conditions.

Several difficulties were encountered during the calibration phase of this work. Most of the difficulties encountered were due to the nature of the flow field at this site. The flow field is characterized by an extremely thin saturated layer (averaging 2.75 feet [0.84 m]) with highly irregular aquifer bottom elevations. The MODFLOW code had difficulty in representing this flow field because the unconfined aquifer frequently became artificially “dry” due to the lowering of head below the bottom elevation during the nonlinear iteration process. We circumvented this problem by running the flow model in confined mode with variable transmissivity values adjusted manually according to the observed hydraulic conductivity and saturated thickness. The values of degradation rate constants estimated by the model are summarized in Table 3. The dominant electron accepting process in terms of BTEX degradation is the anaerobic degradation. Anaerobic processes account for 70% of degradation of BTEX: 22% by denitrification, 18% by Fe(III) reduction, 25% by sulfate reduction, and 4% by methanogenesis. Sulfate reduction contributes the most to the BTEX degradation, followed by denitrification and Fe(III) reduction. Methanogenesis results in the least amount of BTEX degradation. Aerobic respiration accounts for the remaining 30% of the degraded BTEX mass.

**Sensitivity Analysis**

In order to evaluate how the key model parameters affect the BTEX mass in the aquifer and the BTEX front, a detailed, systematic sensitivity analysis was conducted. The sensitivity coefficient with respect to a particular parameter can be approximated by making a small perturbation in the parameter value while keeping all other parameters constant, and dividing the change in the dependent variable BTEX mass or BTEX front (represented by 0.05 mg/L contour line) by the change in the parameter. This can be expressed by the formula (Zheng and Bennett 1995):

\[
X_k = \frac{\partial y}{\partial a_k} \times \frac{y(a_k + \Delta a_k) - y(a_k)}{\Delta a_k/a_k}
\]

(25)

where \(X_k\) is the sensitivity coefficient of the model dependent variable \(y\) with respect to the \(k\)th parameter; and \(y(a_k)\) and \(y(a_k + \Delta a_k)\) are the values of the dependent variable obtained for the base case and for the perturbed-parameter case, respectively. In this study, the calibrated model was used as the base case, and the parameters were perturbed to 5% over its base case.

Table 4 summarizes the results of the sensitivity analysis study. As shown in the table, the total mass is least sensitive to changes in dispersivity, suggesting that hydrodynamic dispersion is not sensitive in the multispecies reactive transport system simulated in this study. The simulation results were more sensitive to changes in the hydraulic conductivity, overall reaction rate constant, and recharge, respectively, listed in decreasing order of sensitivity.

In general, biodegradation was more sensitive to anaerobic degradation rate constant than aerobic. This is consistent with the dominance of anaerobic degradation at the POL site. The thin nature of the aquifer, the overlying silts and clays upgradient, and the degree of surface cover by roads and houses that would reduce infiltration would make anaerobic conditions more likely than aerobic conditions.

Anaerobic processes were sensitive to changes in reaction rate constants, with sulfate, Fe(III) reductions, methanogenesis, and denitrification in the decreasing order. The study also showed that small changes in the value of one of the anaerobic parameter values could result in large changes in the order of importance among all the anaerobic processes. This is because of the relatively low kinetic rate constants for all the anaerobic degradations, and relatively high background concentrations of nitrate and sulfate.

In addition to the sensitivity to BTEX mass, quantifying the sensitivity of the predicted plume configurations to variations in model parameters is also of interest. Questions related to the sensitivity of the model to predicted extent of BTEX plume, and to the predicted oxygen, nitrate and sulfate depletion zones, are also important to consider. The BTEX contour line of 0.05 mg/L was chosen as the front position and the scale of plume was set to correspond to the longitudinal length of the calibrated BTEX plume. The sensitivity results are summarized in Table 4. The results show that the front locations of BTEX, oxygen, nitrate, and sulfate plumes are strongly influenced by aquifer saturated thickness, hydraulic conductivity, and longitudinal dispersivity. Findings from model calibration showed that the saturated thickness to the right of the BTEX plume is a key factor in the control of plume migration: Large thickness ahead of the front helps to slow down the migration of the plume. The plume front is the most sensitive to the reaction rate constants of oxygen, nitrate, sulfate, and Fe(II), and the least to methane.

<table>
<thead>
<tr>
<th>Sensitivity Coefficient</th>
<th>Hydraulic Conductivity</th>
<th>Recharge</th>
<th>Longitudinal Dispersivity</th>
<th>Retardation Factor</th>
<th>DO</th>
<th>Degradation Rate Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Nitrate</td>
</tr>
<tr>
<td>Total BTEX mass</td>
<td>-0.202</td>
<td>-0.047</td>
<td>-0.036</td>
<td>-0.058</td>
<td>-0.031</td>
<td>-0.047</td>
</tr>
<tr>
<td>Front of BTEX plume</td>
<td>+0.563</td>
<td>-0.088</td>
<td>-0.419</td>
<td>-0.077</td>
<td>-0.331</td>
<td>-0.287</td>
</tr>
</tbody>
</table>

*Sensitivity analysis performed on 0.05 mg/L contour line of BTEX plume.
Dispersion plays two interesting roles for plume development. The BTEX plume shape is much more sensitive to dispersivity compared to the BTEX total mass. The increase in dispersivity will shrink the BTEX plume front. This is because although BTEX in the plume perimeter is much lower, stronger dispersion leads to more active BTEX-electron-acceptor interaction, resulting in a shrunken BTEX plume shape. However, the dispersivity change did not noticeably affect the BTEX total mass since most of the mass is in the central area of the BTEX plume.

Conclusion

A reactive transport model, incorporating a multispecies biochemical model, has been developed for modeling the natural attenuation of a fuel-hydrocarbon plume present at Hill AFB. The model describes sequential degradation pathways for BTEX using multiple terminal electron accepting processes including aerobic respiration, denitrification, Fe(III) reduction, sulfate reduction, and methanogenesis. Model calibration consisted of fitting the flow model to the observed hydraulic head distribution and simulating the distribution of various chemical species as observed in July 1994 using the August 1993 data set as the initial condition. The hydraulic conductivity distribution and reaction rate constants were estimated based on this calibration process. The calibration results suggest that the location of LNAPL distribution coincides with the low hydraulic conductivity zone. This perhaps explains why the LNAPL has persisted for a long time in this area.

Comparison of the calibrated model results to observed data show that the natural attenuation model developed in this work predicted various plume patterns reasonably well. In addition, the model also reasonably predicted the plume front locations. Mass balance analyses show that the total mass of BTEX in the aquifer at the end of one-year simulation period, as calculated by the model, is within a difference of 8.5% from the total mass estimated from field observations.

The calibrated first-order decay rate constants for BTEX biodegradation using different electron acceptor processes, as calculated from the model, are 0.051, 0.031, 0.005, 0.004, and 0.002 day\(^{-1}\) for aerobic respiration, denitrification, Fe(III) reduction, sulfate reduction, and methanogenic degradation, respectively. The anaerobic degradation accounts for 70% of the total BTEX degradation. Sulfate reduction, denitrification, and Fe(III) reduction are the most important contributors for BTEX degradation, with methanogenesis the least significant process. Aerobic respiration results in the remaining 30% of BTEX degradation.

Sensitivity analysis shows that the hydraulic conductivity, first-order degradation rate constants, and recharge, listed in the order of decreasing sensitivity, are the most critical parameters that control the total amount of BTEX mass present in the aquifer. Aquifer thickness, especially in the area immediately ahead of the plume front, and hydraulic conductivity are also found to be key parameters for controlling the shape of the BTEX plume. Dispersivity was found to be the next most sensitive parameter with respect to plume shape, but changes in dispersivity values had virtually no effect on the total mass.

As for biodegradation, the model is more sensitive to the anaerobic degradation rate constant than the aerobic. Anaerobic processes were sensitive to changes in the biodegradation rate constants with sulfate, Fe(II) iron, methane, and nitrate, listed in decreasing order of sensitivity.

The simulation modeling effort to describe fuel-hydrocarbon degradation, along with an entire set of field data, represents a novel attempt to quantify the complete sequence of BTEX natural attenuation processes with a detailed modeling framework. Because this case study is representative of a typical petroleum product contaminated site, the results and insights obtained from this study are of general interest and relevance to other fuel-hydrocarbon natural attenuation sites.

Acknowledgments

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References


