



**MODELING THE FATE OF GROUNDWATER CONTAMINANTS RESULTING
FROM LEAKAGE OF BUTANOL-BLENDED FUEL**

THESIS

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AFIT/GES/ENV/10-M06

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Abstract

Environmental concerns, the rising cost of fossil fuels, and the need to reduce U.S. dependence on foreign oil have sparked the development of alternative fuels, such as synthetic fuels and alcohol-based biofuels. With the projected widespread use of alternative fuels, evaluation of the potential impacts of these alternative fuels on the environment, especially on water supplies, is imperative. Fuel spills and leaks from storage tanks may cause contamination of groundwater. The fuel components of most concern are aromatic hydrocarbons; principally benzene, which is classified as a known carcinogen. These aromatic hydrocarbons are typically attenuated through natural processes in groundwater.

Butanol, derived from biological sources, is a likely replacement for the ethanol that is currently being added to gasoline. It is possible that adding butanol to gasoline will interfere with natural attenuation processes, so that spills and leaks of alternative fuels such as butanol-blended gasoline may result in more persistent hazardous aromatic hydrocarbon plumes. This effect has already been observed with ethanol. In this study, a numerical model was developed to evaluate how adding butanol into gasoline, as is likely in the near future, might adversely impact groundwater quality due to the inevitable spills and leaks that will occur. The model incorporated advection, dispersion, sorption, and biodegradation of contaminants in groundwater. The biodegradation of benzene and butanol was modeled using dual Monod kinetics with degradation occurring under aerobic and anaerobic (sulfate-reducing as well as methanogenic) redox conditions. The

model was implemented as a component of the Department of Defense's Groundwater Modeling System suite of models to simulate the subsurface fate and transport of butanol-blended fuel and evaluate the potential impacts of butanol on the natural attenuation of benzene.

Model simulations indicated that spills of butanol-blended gasoline resulted in benzene plumes that were longer and more persistent than plumes which resulted from leaks of gasoline alone. Electron acceptors (*i.e.*, oxygen and sulfate) are more available for biodegradation of benzene in fuel without butanol. The presence of butanol decreased the availability of electron acceptors—limiting benzene's degradation and resulting in longer plumes from a continuous release of butanol-gasoline mixture.

AFIT/GES/ENV/10-M06

To My family
and
Future modelers

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MODELING THE FATE OF GROUNDWATER CONTAMINANTS RESULTING FROM LEAKAGE OF BUTANOL-BLENDED FUEL

1.0. Introduction

1.1. Overview

A major energy crisis in the 1970s initiated research and development of alternative energy sources. During the 1980s and 1990s, the United States (U.S.) enacted numerous environmental and energy-related laws to address energy security concerns, reduce reliance on foreign petroleum, and improve air quality—decreasing toxic pollutants and greenhouse gases emissions. Laws such as the Clean Air Act (CAA) Amendment of 1990 and Energy Policy Act of 1992 have continued to provide the driving forces to motivate the search for suitable alternative fuels.

In evaluating the potential alternative fuels for implementation, it is critical to consider their environmental impacts. The failure to assess the potential impacts of an alternative fuel or fuel additive on the environment can lead to significant consequences. As an example, consider methyl *tert*-butyl ether (MTBE). MTBE was added to gasoline as a replacement for lead and as a fuel oxygenate in order to reduce air pollution. However, the impact of MTBE on the subsurface environment was not fully understood when the decision was made to add it to gasoline. Subsequently, MTBE has caused widespread contamination of groundwater due to fuel leaks and spills.

This current research examines the potential impacts to groundwater quality of a compound that is being considered for addition to gasoline. The compound under consideration as an alternative fuel is *n*-butanol and will hereby be referred to as butanol.

1.2. Background

The demand for energy resources has significantly increased within the last decade as a result of rapid industrialization and modernization in third world countries. Both developed and developing nations rely on energy to fuel the economy and to maintain a high standard of living. Energy resources are critical to industrialization and modernization. Lack of energy can cause stagnation of economic growth in developing countries and thereby, hinder global economic growth. As energy demand rises, the prices and availabilities of liquefied and gaseous petroleum fuels tend to fluctuate unpredictably. In addition, petroleum fuels have pronounced negative effects on the environment. Petroleum use in transportation has escalated greenhouse gas emissions and caused growing concerns of global warming (Romm, 2006). Security is another important concern. Crude oil reserves are not evenly distributed and the nations with the highest energy demands are not those with the highest oil reserves. For example, in the U.S., 60 percent of the total petroleum that is consumed comes from imports (EIA, 2009). This reliance on other nations for energy supplies is a critical vulnerability to national security. Thus, in terms of the economy, the environment, and perhaps most importantly, national security, U.S. dependence on petroleum-based fuel is extremely costly.

The U.S. established several national policies encouraging the reduction in energy consumption and promoting the use of renewable and alternative energy sources. The Energy Policy Act of 2005 dictates that federal entities to decrease energy usage by 2 percent annually. In 2007, President George W. Bush issued Executive Order (EO) 13432 to reiterate the U.S. policy on reducing energy consumption. The EO states “Federal agencies conduct their environmental, transportation, and energy-related

activities under the law in support of their respective missions in an environmentally, economically and fiscally sound, integrated, continuously improving, efficient, and sustainable manner.” Moreover, EO 13432 sets aggressive energy-related measures including a mandate that requires federal agencies to reduce annual energy expenditure by 3 percent leading to an overall reduction of 30 percent by 2015. The U.S. objective of decreasing the use of petroleum-based fuel as an energy source is further strengthened with the Energy Independence and Security Act of 2007, which “aims to increase U.S. energy security, develop renewable fuel production, and improve vehicle fuel economy.” (USEPA, 2009).

The need to reduce U.S. dependency on foreign energy, environmental concerns, and the rising cost of fossil fuels have sparked significant development toward greener alternative and renewable energy sources such as synthetic fuels (synfuels) and alcohol-based biofuels. In recent years, the Department of Defense (DoD) has moved to reduce its reliance on petroleum to fuel aircraft and ground equipment. The United States Air Force (USAF), in alignment with DoD objectives, initiated several energy reduction goals: (1) reduce the use of petroleum-based fuel by 2 percent annually for the vehicle fleet; (2) increase alternative fuel use in motor vehicles annually by 10 percent; (3) certify all aircraft and weapon systems for a 50/50 alternative fuel blend by 2011; and (4) have USAF aircraft flying on 50 percent alternative fuel blends by 2016 (Donley, 2009). Furthermore, DoD currently is funding extensive research and development of a bio-jet fuel to replace military jet fuel, JP-8, which is now used to power vehicles such as the Boeing B-52 bomber, the Abrams A1 Battle Tank, the Apache Helicopter, and many others (DARPA, 2009). With the projection that alternative fuels will become a

substantial component of our fuel supplies in the upcoming decade, it is clearly prudent to evaluate the potential impacts of these alternative fuels on the environment, especially on water supplies.

Fuel spills and leaks from storage tanks can contaminate groundwater. The fuel components of most concern are aromatic hydrocarbons; particularly benzene, which is classified as a known carcinogen (ACGIH, 2003). Typically in groundwater, aromatic hydrocarbon levels become attenuated through natural processes. Naturally-occurring microorganisms in the subsurface have the ability to biologically transform contaminants such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) into innocuous substances. Microbes utilize these organic contaminants as carbon and energy sources that are essential for their survival and growth. The degradation of these aromatic hydrocarbons can occur under aerobic as well as anaerobic conditions, though BTEX biodegradation via the aerobic pathway is more rapid than anaerobic degradation (Chakraborty and Coates, 2004). Native microbial communities can rapidly oxidize aromatic contaminants with molecular oxygen and systematically catalyze the cleavage of aromatic rings. These native microorganisms prevent contaminant plumes from continuing expansion in the subsurface. When considering implementation of alternative fuels, it is important to consider their impact on the environment. For example, for a number of years ethanol has been blended into gasoline as an oxygenate. Also, as will be discussed below, alcohol-based fuels, such as ethanol, are being considered for use as alternative fuels. However, it is possible that spills and leakages of these alternative fuels may interfere with the natural attenuation processes that currently limit the extent of pollution due to hazardous aromatic hydrocarbons like benzene. In a recent field

experiment and simulation study, it was demonstrated that addition of ethanol to gasoline resulted in slower benzene attenuation and longer benzene groundwater plumes (Mackay et al., 2006; Gomez et al., 2008).

Alternative fuels being considered for blending with petroleum-based fuels are synfuels (produced using the Fischer-Tropsch process) or bioalcohol fuels. The formulation of alternative fuel (bioalcohol or synthetic, and in what percent) depends on the physico-chemical and combustion properties of the fuel as well as the fuels intended application (*e.g.*, aircraft versus ground equipment). The fuel for use in aviation, for example, may contain as high as 50 percent synfuel by volume, while ground transportation fuel may have alcohol as low as 5 percent to as high as 85 percent by volume (Demirbas, 2008; Rahmes et al., 2009).

Synthetic fuel will most likely be the fuel of choice for aircraft application in USAF (Warwick, 2009). The synfuel is similar in composition and properties to JP-8, which the USAF currently uses to power aircraft (Harrison, 2009). The environmental impacts of JP-8, especially on groundwater quality, are well understood. Thus, we can be relatively confident that we understand the groundwater impacts of synfuels which may be used in alternative fuels.

The USAF presently is not considering using alcohol-based fuels to power aircraft, but these fuels have many applications in combustion engines associated with USAF ground equipment and more widely, automotive engines. Alcohol products have been used as fuel oxygenates in gasoline and their usage has increased in recent years. Alcohol blends with petroleum-based fuels will become more prevalent in response to

increasing concerns over greenhouse gas emissions, global warming, and the rising cost of petroleum-based fuels.

At present, there are a number of different formulations of gasoline and alcohol products available in the market, most commonly, gasoline and ethyl alcohol (also known as ethanol) mixture. However, ethanol-based gasoline blends, in which ethanol serves as a fuel oxygenate, introduce a new set of problems for the refinery industry, consumers, and the environment.

Ethanol has physico-chemical properties—low energy content, high vapor pressure, corrosivity, and hydrophilicity—that make the alcohol moderately unsuited for use with the current petroleum-based infrastructure (Cascone, 2008; Wackett, 2008). Furthermore, as mentioned earlier, there are environmental impact concerns that adding ethanol to gasoline will result in larger and more persistent BTEX plumes in groundwater. A field study at Vandenberg Air Force Base (AFB) showed that adding ethanol to gasoline caused a reduction in aromatic hydrocarbon biodegradation, and a lengthening of groundwater plumes of benzene and other aromatic compounds (Mackay et al., 2006). The aromatic components in the fuel persisted longer in the subsurface because the microorganisms degraded the ethanol in preference to the other, less energetically favorable, contaminants. The ability to predict the impact of alternative fuels on groundwater is crucial as we make decisions on which fuels to implement.

Previous modeling has focused on the effects of different ethanol-gasoline blends on the natural degradation of benzene. In agreement with the Mackay et al. (2006) field study results, modeling showed that the contaminant (*e.g.*, benzene) plumes are longer in gasoline-containing ethanol compared to gasoline without ethanol (Gomez et al., 2008)

The modeling suggested that novel processes, which were due to the complex interaction of microorganisms, electron acceptors such as oxygen, ethanol, and the aromatics, resulted in increased aromatic plume lengths. As other alternative fuels are considered for future use (*e.g.*, bioalcohol fuels, Fischer-Tropsch synfuels), it is critical to understand the potential impact of implementation of these fuels on groundwater quality.

As mentioned, the environmental impacts of Fischer-Tropsch synfuels and JP-8 are well understood since the hydrocarbons in both fuels are similar. Due to the problems with gasoline-ethanol formulations discussed above (corrosivity, low energy density, and environmental impact), other alcohol blends are being looked at (Lee et al., 2008; Wackett, 2008). One alcohol in particular, butanol, is a likely candidate for use as a fuel oxygenate and an alternative fuel in combustion engines. The widespread use of butanol, as a replacement for other fuel oxygenates, is imminent (Cascone, 2008; Wackett, 2008; Mariano et al., 2009). Thus, the ability to predict the impact on groundwater of using butanol as an alternative fuel is crucial.

1.3. Research Objective

The primary objective of the research is to evaluate how implementation of butanol in combustion fuels might adversely impact groundwater quality due to the inevitable spills and leakage that will occur.

1.4. Research Problem

Models are important tools that can provide insight into the potentially complex interactions that will affect contaminant fate and transport in the subsurface. The research problem is to develop a numerical model capable of predicting transport and fate

in groundwater of contaminants such as BTEX in the presence of butanol, a compound which is likely to be blended into gasoline in the future.

1.5. Specific Research Questions

1. What subsurface processes impact the fate and transport of an alternative fuel (butanol-gasoline blend) in groundwater?
2. What are the potential impacts of leaks and spills of the butanol-gasoline on groundwater quality?

1.6. Research Approach

The study entails reviewing the literature, developing a model, and then using the model to conduct sensitivity analyses in order to study the potential impacts to groundwater of blending butanol into gasoline. The literature review will survey the alternative fuels that are being considered for implementation in the U.S., and then focus in on butanol blends, which appear very likely to be used in the near future. Further, the literature review will identify processes and parameter values that are important to determining the fate and transport of butanol-blended fuel in groundwater.

The next phase of the study involves developing a model which incorporates the important processes (*e.g.*, advection, dispersion, sorption, degradation kinetics) that were identified in the literature review as influencing the fate of butanol and gasoline components in subsurface water. The model will be developed as a component of the Groundwater Modeling System (GMS) suite of models that DoD uses (COE, 2008).

In the final phase of the study, the revised GMS will be used to simulate different scenarios to determine the potential impact of butanol on groundwater quality. Other

simulations will be conducted to evaluate the sensitivity of the contaminant plume extent and persistence as a function of hydrogeochemical parameters (using realistic values as determined in the literature review) and fuel composition.

1.7. Scope and Limitations of Research

There are a number of limitations associated with this research. First, butanol is the only alternative fuel examined. The decision to focus on butanol was based upon butanol's (1) likelihood of widespread use and (2) potential for groundwater quality impacts. Second, benzene is the only contaminant selected as a target compound because benzene is a known carcinogen, which present a significant environmental health risk. Finally, the reader should understand that application of any model involves numerous simplifying assumptions (*e.g.*, which processes are important, simplified mathematical descriptions of those processes, use of parameters that may be constant in space and time). However, the power of modeling is to assist users in identifying those key factors that may be important in designing future studies as well as providing qualitative insights into how the complex interactions of various processes, chemicals, and environmental conditions can result in environmental impacts.

1.8. Definition of Terms

Aerobes – microorganisms that use oxygen as a terminal electron acceptor.

Anaerobes – microorganisms that use terminal electron acceptors other than oxygen.

Advection – a transport mechanism that describes the displacement of matter by bulk fluid flow. In the subsurface, groundwater is the fluid that transports dissolved compounds (*i.e.*, contaminants, oxygen, sulfate, carbon dioxide, etc.).

Biodegradation – decomposition of contaminants in the environment via microbial activities.

BTEX – aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene isomers) that are components of gasoline.

Butanol (also referred to as *biobutanol* in the literature when produced from biological sources) – an alcohol with four carbon atoms. Other synonyms include propylmethanol, 1-butanol, *n*-butanol, 1-hydroxybutane, and butyl hydroxide.

Butanol-gasoline (butanol-blended gasoline) – mixture of butanol and gasoline as a final fuel blend.

Dispersion – a subsurface transport mechanism that accounts for the spreading of dissolved compounds due to variations in flow velocity in the porous medium.

Methanogens – anaerobes that degrade organic matter using carbon dioxide as a terminal electron acceptor and producing methane.

Monod kinetics – a mathematical model, named after microbiologist Jacques Monod, describing the relationship between microbial growth and concentration of substrate. A dual Monod kinetic model represents the rate of microbial growth as a function of the

concentrations of both an electron donor and an electron acceptor (Rittman and McCarty, 2001).

Redox condition – the redox condition of an aquifer is defined by the primary terminal electron acceptor (TEA) that is present in the aquifer. Thus, if oxygen is the TEA, the redox condition is aerobic; if sulfate is the TEA, the redox condition is sulfate-reducing or sulfidogenic, and if carbon dioxide is the TEA, the redox condition is methanogenic.

Sorption – partitioning of a compound between dissolved and solid phases. In groundwater, sorption results in retarded transport (*i.e.*, retarded advection and dispersion) of a dissolved compound. It is typically assumed that a compound in the sorbed (solid) phase is not available for biodegradation.

Sulfate-reducing bacteria (SRB) – anaerobes that use sulfate as a terminal electron acceptor.

Terminal electron acceptor (TEA) – a compound that is reduced by receiving an electron from a donor compound, typically, a carbon compound or hydrogen, during microbial respiration. Common TEAs found in groundwater include oxygen (O_2), nitrate (NO_3^-), manganic manganese (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2).

2.0. Literature ReviewEquation Chapter 2 Section 1

2.1. Overview

Fossil fuels such as oil and natural gas make up a major component of the energy sources that drive the economy of U.S. and other nations. The domestic supply of petroleum fuel in the U.S. is limited. The U.S. Energy Information Administration (EIA) (2009) indicated domestic fuel production in 2008 was 8.5 million barrels per day (bpd), which only met 43 percent of the nation's demand. The daily petroleum consumption rate in the U.S. is 19.5 million bpd—making the nation the world's top petroleum consumer in 2008 (EIA, 2009). Within the DoD, the USAF is the leading energy user with aircraft consuming nearly 280,000 bpd (Danigole, 2007). Because of the imbalance between U.S. domestic oil production and consumption, the nation must resort to importing the difference from other countries that often are located in regions of the world that are in turmoil. This heavy reliance on foreign energy is a critical national security risk for the U.S.

The cost of fossil fuels has fluctuated unpredictably in recent years. High prices and growing energy demands have heightened concerns on the economic feasibility of using petroleum fuel. As an example, the USAF's expenditure on petroleum fuel increased 50 percent between fiscal year 2004 and 2005 (Danigole, 2007). The high fuel costs constrain operating budgets that negatively impact military readiness and training missions within the USAF as well as other DoD components (Danigole, 2007). Another growing concern with respect to the use of petroleum fuel is global warming, as a result of greenhouse gas emissions. Combustion of fossil fuels has contributed “to the observed

increase in atmospheric carbon dioxide, with concomitant global warming effects” (Wackett, 2008). Furthermore, other combustion byproducts of petroleum fuel include gaseous substances and particulates that are considered detrimental to the environment and may have substantial impacts to human health (Godish, 2004). Environmental concerns, economic constraints, and national security risks have motivated a search for alternative energy sources to replace petroleum-based energy.

Renewable energy (RE) and alternative fuels are two sources that could substitute for fossil fuels. RE refers to energy generated from wind, hydropower, geothermal, wave and tidal, or solar. RE sources have large potential in supplying energy without emissions. These RE sources supplied roughly 13 percent of the total global energy demand in 2004 (Resch et al., 2008). Although RE provides cleaner power, RE suffers some critical technological and cost challenges. Electricity production, for example, is mostly decentralized when using RE sources; this is incompatible with the present centralized electrical grid infrastructure in many countries (Reiche and Bechberger, 2004). Power generation from RE sources is also intermittent and can be unpredictable (Gross et al., 2003). The use of RE sources for electricity production is declining on a global scale (Jefferson, 2006). Despite the maturity of some RE technologies, which are commercially viable, the capital and maintenance costs remain high (Gross et al., 2003; Qu et al., 2008; Resch et al., 2008). As an example, consider solar energy. Solar technologies have become relatively mature, yet they have limited application due to market barriers and inconsistent policy drivers (DOE, 2009). Although RE sources can provide energy supply and reduce dependence on fossil fuels, in the near term, the outlook regarding the expansion of RE sources to meet energy demands is “bleak”

(Jefferson, 2006). More importantly, in the context of this thesis, RE sources are not yet practical for transportation use, while alternative fuels such as biofuels are able to meet near-term transportation demands and their widespread use is predicted as inevitable (Demirbas, 2008; Wackett, 2008; Zidansek et al., 2009). This chapter reviews the characteristics of various alternative fuels, and based on the literature, attempts to predict which fuel has the most potential for future use. In addition, studies regarding the fate and transport in groundwater of the alternative fuel with the greatest potential for application are surveyed.

2.2. Fuel Properties

Conventional combustion fuel commonly used in aviation turbine and automotive engines is an organic liquid comprised of numerous hydrocarbons that may include paraffins, naphthenes, and aromatics (Speight, 2008). The fuel is derived from refining raw crude petroleum. The composition of hydrocarbons in the fuel is related to the crude's origin and refining methods. Further, it should be noted that the fuel used in automotive engines (gasoline) is different than the fuel used in aviation engines (kerosene/jet fuel). Table 2-1 presents the difference in properties between distillates for gasoline and jet fuel (Bartis et al., 2008; Speight, 2008).

Table 2-1: Petroleum Distillates Composition

Composition	Gasoline	Kerosene/ Jet Fuel
Carbon lengths	4-12	10-16
Paraffins (%)	4-8	32
Isoparaffins (%)	25-40	31
Cycloparaffins (%)	3-7	16
Olefins (%)	1-4	Trace
Aromatics (%)	20-50	21

Moreover, the finished fuel blend delivered to end users will also have a different chemical composition than listed in Table 2-1. The final formulation must satisfy standards and regulatory requirements. The overall fuel characteristics (volatility, density, energy content, viscosity, aromatic content, etc.) must meet applicable standard specifications: motor engines—American Society for Testing and Materials (ASTM) D4814 or Federal Specification VV-G-1690C and commercial aviation turbine engines—ASTM D1655. In addition, the fuel must have certain additives to comply with environmental mandates such as the Clean Air Act. DoD has additional requirements for the fuel to be used in various military weapon systems. The finished product must comply with the specification for military jet fuel, MIL-DTL-83188F. Important properties of petroleum-based jet fuel (nominal values) and the military specification for JP-8 are summarized in Table 2-2 (Domen et al., 2009).

Table 2-2: Properties of Petroleum Jet Fuel and JP-8 Specification

Property	Petro Fuel	JP-8 Specification	
		Min	Max
Freezing point (°C)	-46.0	N/A	-47.0
Flash point (°C)	52.0	38.0	N/A
Density at 15°C (kg/L)	0.813	0.775	0.840
Aromatics (volume %)	21.2	N/A	25.0
Olefins (volume %)	1.6	N/A	N/A
Net heat of combustion (MJ/kg)	43.0	42.8	N/A

The end product often contains additives such as oxygenates (ethers or alcohols) and inhibitors (anti-corrosion and/or de-icing compounds). Thus, reformulation of the refined distillates into final combustion fuel is always necessary.

Alternative fuel—regardless whether it is for use as a standalone fuel or as a component to mix with petroleum-derived fuel—must exhibit chemical and physical characteristics that meet or exceed respective specifications. In other words, the fuel

must have the proper chemical composition, density, volatility, etc. to allow a direct substitution or “drop in” to standard petroleum fuel without compromising performance and safety. More importantly, the alternative fuel must have the appropriate energy content and lubricity. According to Danigole (2007), one of the critical aspects in assessing the alternative fuel is its aromatics composition. The presence of aromatics provides lubricity and prevents leakage between connections throughout the fuel system. Although aromatics produce harmful particulates when burned, the aromatics induce swelling of elastomeric gaskets or o-rings to seal fuel components (Danigole, 2007; Hileman et al., 2009). Other criteria to consider when evaluating an alternative fuel for military and consumer uses include: production capacity, transportation infrastructure, long-term storage stability, cost, and whether use of the fuel requires major engine modification (Danigole, 2007; Wackett, 2008). Rigorous research has been conducted to evaluate different classes of alternative fuels that could be used either as a direct replacement for petroleum-derived fuel or as a complementary product for use in conjunction with petroleum. Synthetic and bioalcohol fuels are amongst the most viable alternative fuels that may become commercially available and have widespread uses (Demirbas, 2008; Lee et al., 2008; Wackett, 2008).

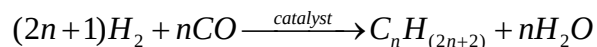
2.3. Types of Alternative Fuel Being Evaluated

Synthetic Fuel

Synthetic fuel is a general term for a fuel that results from liquefaction, and sometimes gasification, of organic matter (typically, coal, natural gas, or biomass). There are numerous synthesis techniques available for transforming feedstock into usable fuel

(*e.g.*, Bergius, Kohleol, Mobil, Fischer-Tropsch (FT), Karrick, Sabatier, or biochemical processes) (Probstein and Hicks, 1982; Speight, 2008). All methods may be employed to catalytically produce fuels needed for both aviation and ground transportation uses. The U.S. has increasingly studied the use of FT and biochemical conversion technologies to generate additional energy supplies from renewable resources (Bartis et al., 2008; Hileman et al., 2009). Hence, the synthetic fuels examined here are limited to those derived from FT synthesis and biochemical processes.

The FT process has been known since the early 1900s (Probstein and Hicks, 1982). The FT process employed catalysts to promote a chemical reaction between hydrogen and carbon monoxide to produce various liquid and gaseous hydrocarbons. The overall chemical conversion is:



The feedstock for the initial reactants in the FT process includes sources such as coal, natural gas, oil shale, and biomass (Speight, 2008). FT synthesis has shown success in large-scale fuel production in South Africa within the last 30 years (Taylor et al., 2008). Hydrocarbons produced from the FT process are primarily paraffins and “exceptionally high-quality diesel and jet fuels that can be sent directly to local fuel distributors” (Bartis et al., 2008). FT fuel is also known as synthetic paraffinic kerosene (SPK). SPK has some olefins but no other hydrocarbon groups such as aromatics or oxygenates, which are important in providing lubrication and preventing leakage in fuel systems (Taylor et al., 2008). Up to 50 percent by volume of SPK has been used in commercial aircraft since 1999 in South Africa (Ott, 2006; Hileman et al., 2009). The combustion of SPK

produces less air pollutants than petroleum fuel. Table 2-3 summarizes some of the chemical and physical characteristics of SPK.

Table 2-3: Properties of SPK

Property	Value
Freezing point (°C)	-57.0
Flash point (°C)	45.0
Density at 15°C (kg/L)	0.747
Aromatics (volume %)	0.0
Olefins (volume %)	0.5
Net heat of combustion (MJ/kg)	44.2

These attributes (environmental benefits, proven commercial application, feedstock readily available domestically, which therefore results in national security benefits) have led the USAF to further investigate the potential of SPK for use in military aircraft (Bartis et al., 2008). The Air Force is proactively pursuing the commercial development of FT-derived fuel for military use (Bartis et al., 2008). As a major participant in DoD's Assured Fuels Initiative, the USAF created the Alternative Fuels Certification Office (AFCO) in 2007 to oversee the effort to certify military aircraft and ground vehicle fleets to use synthetic fuel (Bartis et al., 2008; Rodriguez and Bartsch, 2008). The USAF certification requires a blending of SPK and conventional jet fuel (MIL-DTL-83133F). The current finished fuel blend can only contain up to a maximum of 50 percent synfuel on a volume basis to maintain performance specifications of petroleum jet fuel. The chemical and physical properties of the JP-8/SPK blend have been shown to satisfy the military jet fuel specification for blended fuel (see Table 2-4). Currently, a number of airframes in the USAF have been certified to operate on the 50/50 percent blend of SPK and conventional JP-8 (Bartis et al., 2008). ASTM International (2009) has also recently approved SPK for use in commercial airlines with the

publication of specification, ASTM D7566 “Aviation Turbine Fuel Containing Synthesized Hydrocarbons,” paving the way for widespread use of a blend of conventional jet fuel with SPK.

Table 2-4: Properties of JP-8/SPK Blend and Military Blended Fuel Specification
(Domen et al., 2009; MIL-DTL-83133F)

Property	JP-8/SPK (50/50)	JP-8/SPK Specification	
		Min	Max
Freezing point (°C)	-55.0	N/A	-47.0
Flash point (°C)	47.0	38.0	68.0
Density at 15°C (kg/L)	0.779	0.775	0.840
Aromatics (volume %)	10.5	8.0	25.0
Olefins (volume %)	1.4	N/A	5.0
Net heat of combustion (MJ/kg)	43.6	42.8	N/A

In addition to using coal and natural gas as feedstock to produce synthetic fuel to meet transportation demands, there is also interest in producing synthetic fuels using biomass. The USAF commenced another certification program that would allow aircraft to fly on synthetic fuel derived from plant oils or animal fats (Harrison, 2009). DoD and the commercial sector, particularly, the commercial aviation industry, are investigating the feasibility of alternative fuel production using renewable feedstocks like biomass (DARPA, 2009; Rahmes et al., 2009).

Biomass is a general classification for renewable organic matter; typically algal crops, plants, grasses, agricultural crops, animal fats and wastes, and municipal wastes. Biomass is ubiquitous and features extractable components (*e.g.*, proteins, lipids, lignin, cellulose, starches, and hydrocarbons) that may be chemically processed to produce a fuel that is suitable for use in internal combustion engines.

The chemical process, known as either hydroprocessing or hydrotreating, consists of two stages. In the first stage, oxygen is removed from oil. In the second stage, the

deoxygenated oil is selectively isomerized into the desired end products such as biodiesel and SPK (Rahmes et al., 2009). The catalytic conversion scheme for the production of synfuel mentioned here is rather similar to FT synthesis. The composition of the hydrotreated synfuel is a mixture of paraffinic hydrocarbons with no aromatics or sulfur-containing chemicals (Mikkonen, 2008; Rahmes et al., 2009). With respect to aviation applications, the hydrotreated synthetic fuel is also referred to as hydroprocessed (or hydrotreated) renewable jet (HRJ) fuel. HRJ fuel has characteristics similar to FT-derived SPK (Hileman et al., 2009; Harrison, 2009; Rahmes et al., 2009). HRJ fuel is largely composed of normal and isomeric paraffins with carbon lengths between 9 and 15 (Rahmes et al., 2009). As with FT-derived SPK, except for the lack of aromatic content, the carbon chain composition of HRJ fuel is a near match to commercial jet fuel (Rahmes et al., 2009). Due to the lack of aromatics and its relatively low density, it is necessary to blend HRJ fuels with petroleum-based fuels in order to meet standard fuel specifications (Rahmes et al., 2009).

A series of engine and flight tests were conducted using several blends of commercial jet and HRJ fuel. The tests indicated “the fuel blends displayed no adverse effects on any of the aircraft systems” (Rahmes et al., 2009). Biologically produced synfuel has the ability to power aircraft with performance that is no less than SPK. It appears synthetic fuels made from renewable resources such as biomass, vegetable oils, or animal fats are viable alternatives to FT-derived fuel. HRJ fuel can complement FT-derived fuel and both fuels also have the potential to replace traditional petroleum fuel when appropriate additives are identified to inhibit the decomposition of elastomers and

improve lubricity—enabling the FT and HRJ fuels to be compatible with aircraft fuel systems (Taylor et al., 2008; Hileman et al., 2009).

Note that regardless of whether the synfuel is produced from FT or hydrotreatment, at present, it still must be blended with conventional fuel for use in commercial or military aircraft, as conventional fuels contain important constituents that are required to meet specifications (particularly the aromatics) that synfuels lack.

Bioalcohol Fuels

Bioalcohol, in the present context, refers to biologically produced alcohol rather than alcohols from a petroleum source. It should be noted that there is no chemical difference between alcohols from biological or petroleum sources; the chemical properties of alcohols from both sources are identical.

The concept of using alcohols in the transportation sector is not new. Alcohols have been employed to fuel ground vehicles since the early 1900s. The continued increase in global demand for energy and the unprecedented high costs of imported oil have triggered renewed interest in bioalcohol fuel for transportation, to include aviation. According to Speight (2008), “practically, any of the organic molecules of the alcohol family can be used as a fuel.” Bioalcohols have characteristics that can help both developing and industrialized countries move toward energy independence. The alcohols can power internal combustion engines as well as provide energy sources for generating electricity (Demirbas, 2008; Keeney, 2009). The resources used for alcohol production are easily accessible, sustainable, and regionally available. Bioalcohol fuels could provide another plausible source of alternative energy for transportation purposes.

Among the alcohol compounds, ethanol and butanol are the two fuels with the most potential. Ethanol and butanol may be added to fuel as oxygenates or used as substitute fuels for imported oil (Alvarez and Hunt, 2002; Wackett, 2008). In fact, for a number of years ethanol has been used extensively worldwide as an additive in fuel (as both an oxygenate and as a fuel itself) (Alvarez and Hunt, 2002; Scragg, 2009). Butanol has emerged recently as a potential gasoline replacement or fuel additive (Dagaut and Togbe, 2008; Lee et al., 2008). These alcohols have several desirable attributes which have led to renewed interest in their use as transportation fuels (Lee et al., 2008; Wackett, 2008).

In general, bioalcohol synthesis involves a biochemical process that relies on microorganisms to convert feedstock to products. The overall biological production processes for ethanol and butanol are relatively similar. The production of alcohols can utilize different raw materials. The feedstock sources such as corn, sugar cane, wood, rice, wheat, cellulose, and more broadly, biomass are typically renewable and sustainable. These resources are widely available and readily accessible. The emergence of microbial metabolic engineering has resulted in innovative bioconversion technologies that make alcohol production cost competitive with fossil fuels (Demirbas, 2008; Wackett, 2008). Furthermore, depending on the feedstock, bioconversion may generate other value-added products that can be processed in concurrence with alcohols (Speight, 2008). With respect to fuel production, the combination of technological advances, economic incentives, and concern for the environment has directed global interests toward exploring the feasibility of using ethanol and/or butanol for transportation fuel.

Ethanol is a two-carbon molecule with a hydroxyl (-OH) functional group attached. It is a colorless, volatile, and water-miscible liquid. Ethanol is a versatile alcohol with numerous applications; most notably, as a beverage and fuel additive. The alcohol has been utilized as an additive in gasoline for many years. However, due to compatibility issues, pure ethanol cannot function as a fuel in current combustion engines. The volume percent of ethanol in fuels is limited to 15-20 percent in engines currently in use. To use higher ethanol percentages in fuel, engine fuel system modifications are required (Demirbas, 2008).

In contrast to ethanol, butanol is not currently used as a fuel additive in the U.S. Butanol is a four-carbon alcohol with the molecular formula C_4H_9OH . The alcohol is a colorless liquid and relatively miscible in water. Engine performance tests suggest butanol can be a formidable alternative fuel for ground transportation (Alasfour, 1997; Gautum and Martin, 2000). Additionally, with regards to air emission, butanol may offer significant benefits to the environment (Gautum et al., 2000). Table 2-5 summarizes selected properties and characteristics of traditional aviation fuel, gasoline, ethanol, and butanol.

Table 2-5: Properties of Transport Fuels and Alcohols

Property^a	Ethanol	Gasoline^b	Butanol	Jet Fuel
Specific gravity ^c	0.79	0.72	0.81	0.81
Aromatics (volume %)	0.0	20.0	0.0	21.2
Olefins (volume %)	0.0	2.0	0.0	1.6
Net heat of combustion (MJ/kg)	26.6	44.4	33.3	43.0
Energy density (MJ/L)	21.0	32.0	27.0	34.8

a. Listed properties are nominal values.

b. Aromatics and olefins content can vary up to 50% and 5%, respectively.

c. Values are for temperature in the range: $15\text{ }^{\circ}\text{C} \leq \text{Temperature} \leq 20\text{ }^{\circ}\text{C}$.

As we have discussed, both ethanol and butanol can function as alternative fuels for transportation. However, the bioalcohols are more applicable to ground vehicles than for aviation uses. Fuels for aviation must have high energy content (heat of combustion and energy density). The energy content of both ethanol and butanol is considerably less than jet fuel. The energy densities for ethanol and butanol are approximately 40 percent and 20 percent lower than that of conventional aviation fuel, respectively (see Table 2-5). There are also significant differences in the other chemical and physical properties of alcohols and jet fuel—rendering the alcohols incompatible for application in aviation (Hileman et al., 2009). On the contrary, the alcohols, particularly butanol, are attractive as fuels for use in ground vehicles (Hileman et al., 2009).

2.4. Environmental Impacts

Synthetic Fuel

As briefly indicated earlier, synfuel provides cleaner emissions when burned. Several studies indicated that using blended jet fuel (synfuel/traditional jet fuel mixture) would negligibly impact or perhaps even improve air quality due to the low sulfur and aromatic content of the synfuel (Hileman et al., 2009; Rahmes et al., 2009). Although definitive studies are not available, this thesis assumes that due to the similarities between synfuel and aviation fuels, a synfuel/jet fuel blend would have no worse impact on groundwater than pure aviation fuel does. Further, since the fate and transport of aviation fuels in groundwater has been well documented (Vroblesky et al., 1996; Lu et al., 1999; Namocatcat et al., 2003; Thompson et al., 2004; Bugna et al., 2005), it is assumed that the impact of synfuel on groundwater is also understood.

Bioalcohols

The 1990 CAA Amendments mandated that transportation fuels in most polluted U.S. cities should have oxygenates added to reduce atmospheric pollutants like carbon monoxide and volatile organic compounds (USEPA, 1998). As a result, the use of fuel oxygenates has become widespread (USEPA, 1998). Besides MTBE, ethanol has been added to gasoline as an oxygenate over the last two decades. In addition to its value as an oxygenate, the alcohol is an octane booster. Although ethanol in fuel reduces carbon monoxide emissions, the combustion of ethanol-blended fuel has been shown to increase atmospheric levels of acetaldehyde (a possible carcinogen) and oxides of nitrogen (ozone precursors) (Niven, 2005). The emissions of these combustion byproducts may present greater health risk than gasoline without ethanol (Jacobson, 2007). Additionally, recent research has shown that when ethanol-blended fuel leaks into the subsurface, gasoline with ethanol may be more harmful to groundwater than gasoline without ethanol (Mackay et al., 2006). Ethanol and gasoline components can enter the subsurface in a variety of ways: surface spills, precipitation, and especially storage tanks leaks. A number of studies have shown that the presence of ethanol hampers the natural attenuation of harmful BTEX compounds and facilitates the further migration of these xenobiotics in the subsurface (Corseuil et al., 1998; Mackay et al., 2006).

2.5. Potential Future Fuels

Synthetic Fuel

Based on synfuel production capability and synfuel's chemical similarity to petroleum fuel, synfuel will likely be used in both commercial and military aviation.

Unlike ethanol and butanol, synfuels can be directly blended into petroleum jet fuel and used in aircraft engines, without requiring engine or infrastructure modification (Harrison, 2009). As “...air transportation is likely to continue to rely heavily on petroleum-derived kerosene jet fuel” (Hileman et al., 2009), blending synfuels and petroleum-derived jet fuel is a very practical short-term approach to reducing our reliance on petroleum-based fuel in aviation. Currently, the USAF is committed to using a JP-8/SPK blended fuel to power various weapon systems in order to attain the Air Force’s goal of having aircraft using 50 percent alternative fuels by 2016 (Rodriguez and Bartsch, 2008; Warwick, 2009). At the same time, in order to reduce dependence on oil, the USAF and DoD continue to pursue the development of other alternative fuels that will have higher energy content than current synthetic fuels and biofuels. In addition, it is envisioned that these advanced alternative fuels will be produced using improved techniques that achieve 90 percent conversion of feedstocks (Danigole, 2007; DARPA, 2009). While synfuels will have aviation applications, widespread use of synfuel for ground transportation is unlikely due to other readily accessible, and cheaper, alternative bioalcohol fuels.

Bioalcohol Fuels

As discussed earlier, there are substantial challenges in using ethanol and butanol as aviation fuels. Both alcohols degrade turbine engine performance and pose risks to flight safety (Harrison, 2009; Hileman et al., 2009). An alternative jet fuels feasibility study concluded that “alcohol fuels are clearly better suited for ground-based transportation applications” (Hileman et al., 2009). The use of alcohol fuels within

USAF and DoD to power aircraft is not anticipated. However, the alcohols may play important roles in fueling ground vehicles.

Although ethanol has been blended with gasoline for motor vehicle use throughout the world for a number of years, the alcohol has several important shortcomings. Ethanol can't be transported through existing pipelines, decomposes elastomers that seal connections between fuel system components, attracts water, thereby reducing the usability of the fuel, and causes corrosion (Wackett, 2008). There are also growing concerns on the impact to the environment in using ethanol to fuel ground vehicles (Alvarez and Hunt, 2002; Niven, 2005; Kim and Dale, 2006; Jacobson, 2007; Keeney, 2009). As noted earlier, ethanol in fuel helps lower emissions of some pollutants, but results in increased concentrations of other compounds that may be even more hazardous (Niven, 2005; Jacobson, 2007). Additionally, as noted above, the presence of ethanol in fuel slows the natural attenuation of BTEX compounds, resulting in soil and water contamination when there are fuel leaks (Alvarez and Hunt, 2002; Niven, 2005). Other indirect environmental impacts are related to how ethanol is produced from agricultural feedstocks (*e.g.*, corn and sugarcane), which require significant quantities of water (Keeney, 2009) and nutrients that could lead to "adverse impacts on acidification and eutrophication due to emissions related to nitrogen (and phosphorous) in agricultural processes" (Kim and Dale, 2006). Moreover, as demands for energy intensify, there are doubts that ethanol could supply global requirements (Wackett, 2008). In order to avoid the problems associated with ethanol, other alternative fuels (*e.g.* butanol, hydrogen, and biodiesel) are being considered for use in ground transportation.

Butanol has a number of advantages over ethanol as a ground vehicle fuel. Butanol has an energy density that is nearly equivalent to gasoline, while the energy density of ethanol is 34 percent lower (see Table 2-5). Compared to ethanol, butanol has a lower vapor pressure; is less corrosive; less hygroscopic; and is compatible with the current pipeline and fuel storage infrastructure (Wackett, 2008; Mariano et al., 2009). Butanol is similar enough to gasoline that the alcohol can “be used directly in any gasoline engine without modification and/or substitution” (Lee et al., 2008). Nevertheless, butanol has some deficiencies. Butanol has a higher short-term toxicity to humans and animals than ethanol and gasoline (Cascone, 2008). Historically, the rate of production of butanol was inadequate to meet transportation demands. Butanol production was relatively inefficient and expensive, especially considering the historically low cost of crude oil. Thus, it was not until recently that much effort was expended on developing more efficient biochemical production processes for alternative fuels like butanol (Cascone, 2008; Lee et al., 2008). Due to recent increases in petroleum fuel costs, butanol and ethanol have both become attractive as fuels for ground vehicles. And with the advances in butanol production techniques, along with its environmental advantages, the attractiveness of butanol as a ground vehicle fuel *vis-à-vis* ethanol has increased (Lee et al., 2008; Wackett, 2008; Hileman et al., 2009).

Though, in the short term, ethanol is likely to become a petroleum replacement fuel, butanol can “supersede ethanol as liquid fuel of choice” in the long-term (NAS, 2009; Scragg, 2009). Existing commercial ethanol production facilities can be converted to produce butanol with minimal capital cost (Cascone, 2008). Several commercial entities in the United Kingdom have switched their ethanol production plants to

manufacture butanol (Scragg, 2009). With the growing commercialization of biologically produced butanol, the prospect of using the alcohol in automotive combustion engines is high. In the foreseeable future, butanol and/or butanol-blended gasoline will become prevalent in automobiles (Hileman et al., 2009).

Based on long-term projections, it appears likely that butanol and/or a butanol-gasoline mixture will become dominant as a ground vehicle fuel. However, scientific studies examining the impact of butanol spills on the subsurface environment are limited. In particular, it is important to know if the presence of butanol, like ethanol, in an alcohol-gasoline blend will result in slower natural attenuation of BTEX compounds in the subsurface and therefore, longer and more persistent BTEX groundwater plumes. To answer this question, an understanding of the processes affecting the fate and transport of butanol in the subsurface is necessary.

2.6. Potential Impacts of a Butanol Blend Release on Groundwater Quality

As previously pointed out, spills and leaks of fuel from pipelines and underground storage tanks are inevitable. A number of experimental and modeling studies have been conducted examining the impact of ethanol blend releases on groundwater. This section looks at the results of those studies. It then goes on to look at the physical and biochemical properties of butanol. These properties will be used in Chapter 3 to develop a model to simulate the fate and transport of butanol blends in groundwater, based on the models that have been used to simulate the fate and transport of ethanol blends in groundwater.

Fate and Transport of Ethanol Blends in Groundwater

Petroleum hydrocarbons are generally biodegradable. These contaminants can undergo biotic decay in the subsurface environment (Lu et al., 1999; Mackay et al., 2006). Microbial consortia utilize these organic compounds (substrates) as a source of carbon for growth, as well as a source of electrons for energy. The subsurface environment has microorganisms that are capable of transforming toxic pollutants like BTEX into harmless end-products under both aerobic and anaerobic conditions through reduction-oxidation (redox) reactions (Alvarez and Hunt, 2002; Chakraborty and Coates, 2004). The rate and extent of biodegradation is a function of a number of factors: environmental conditions (*e.g.*, temperature, pH), presence of microbes with abilities to degrade the target compounds, availability of substrates (electron donors), and especially availability of terminal electron acceptors (O_2 , NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-} , and CO_2) (Alvarez and Hunt, 2002; Mackay et al., 2006).

Biotransformation often occurs in sequential order from aerobic (most energetically favorable) to anaerobic redox conditions. Under aerobic redox conditions, oxygen is the primary electron acceptor. Under anaerobic redox conditions, the most thermodynamically favorable reaction is denitrification, where nitrate (NO_3^-) is the electron acceptor. This is followed sequentially, by manganese reduction (Mn^{4+} is the electron acceptor), iron reduction (Fe^{3+} is the electron acceptor), sulfate reduction (SO_4^{2-} is the electron acceptor), and methanogenesis (CO_2 is the electron acceptor) (Rittman and McCarty, 2001).

Looking at reaction rates, consider the degradation of ethanol and benzene in groundwater. Under aerobic conditions, ethanol has a half-life of 13 hours while benzene

has a half-life of 240 hours (Howard et al., 1991). In this case, if there is only a limited amount of electron acceptor (oxygen) available, the oxygen may be consumed degrading the ethanol, and will not be available to serve as an electron acceptor in the benzene degradation reaction. Half-life values for ethanol, butanol, and BTEX in groundwater are summarized in Table 2-6. Unless noted, values reported are based on aerobic biodegradation (Howard et al., 1991).

Table 2-6: Half-life Values of Alcohols and BTEX in Groundwater

Chemical	Low (hour)	High (hour)
Ethanol	13	52
Butanol ^a	48	1296
Benzene	240	17280 ^a
Toluene	168	672
Xylenes (<i>m-,o-,p-</i>) ^b	336	8640

^aBased on aqueous anaerobic biodegradation

^bBased on aqueous aerobic and anaerobic biodegradation

As illustrated in Table 2-6, based on kinetic considerations, alcohols biodegrade faster than the other hydrocarbon components in gasoline. Moreover, aerobes and anaerobes can easily degrade short-chain alcohols in comparison to compounds like BTEX (Alvarez and Hunt, 2002). Thus, when ethanol blended fuel is released into the subsurface, it would be anticipated that the naturally occurring bacteria would preferentially oxidize the ethanol, and therefore, the biodegradation of the other gasoline constituents, particularly the BTEX compounds, would be delayed. Mackay et al. (2006) conducted a field experimental study to evaluate this. The field experiment simulated a slow release of gasoline blended with ethanol into groundwater, such as might result from a fuel storage tank leak or large fuel spill. The study involved two side-by-side experiments conducted simultaneously in an aquifer at Vandenberg AFB where sulfate

had been shown to be the primary electron acceptor (sulfate-reducing conditions). One experiment involved the continuous injection over 9 months of groundwater amended with 1-3 mg/L of benzene, toluene, and o-xylene (BToX). The second experiment was similar, except that 500 mg/L ethanol was added to the groundwater containing the BToX compounds. BToX, ethanol, and electron acceptors were monitored over the course of the study. It was observed that initially both BToX plumes extended the same distance. However, the plume without ethanol retracted, presumably as a result of biodegradation by naturally occurring microorganisms that used sulfate as an electron acceptor and the BToX compounds as electron donors. The BToX compounds in the plume with ethanol persisted, sulfate concentrations dropped, and methane concentrations increased. It appeared that in the plume with ethanol, sulfate was depleted as microorganisms used the ethanol that was present as an electron donor. After the sulfate was depleted, methanogenic conditions prevailed in the aquifer. BToX degradation was slowed. The results indicated that adding ethanol to gasoline may cause reduction in the biodegradation of the aromatic components of the gasoline (Mackay et al., 2006).

A modeling study was conducted to simulate the effects of blending 10 percent ethanol by volume into gasoline (known as E10) on the natural degradation of benzene in groundwater (Gomez et al., 2008). The modeling results confirmed the observations of the Mackay et al. (2006) field study. The model used Reactive Transport in 3-Dimensions (RT3D) and Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW) to examine the fate and transport of contaminants (Clement et al., 1998; Harbaugh et al., 2000). The overall governing expression for the contaminant fate and transport is:

$$R \frac{\partial C}{\partial t} = \left[D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right] - \left[v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} \right] + r \quad (2.1)$$

where

R = contaminant retardation factor (dimensionless)

C = contaminant concentration in aqueous phase (ML^{-3})

D_i = hydrodynamic dispersion coefficient along i axis (L^2T^{-1})

v_i = flow velocity along i axis (LT^{-1})

r = rate of all reactions for the contaminant in aqueous phase ($\text{ML}^{-3}\text{T}^{-1}$)

Equation (2.1) considers concentration changes of the contaminant as a result of advection (second bracketed terms on the right-hand side), dispersion (first bracketed terms on the right-hand side), linear, equilibrium adsorption modeled using a retardation factor, and generation/degradation processes (last term on the right-hand side). The generation/degradation processes simulated in the reaction term included several novel mechanisms, which contribute to the delayed natural attenuation of benzene when ethanol is present: metabolic flux dilution (MFD) and catabolite repression. MFD describes the noncompetitive inhibition that results in a decrease in utilization of a target contaminant (*e.g.*, benzene) when a more favorable substrate (*e.g.*, ethanol) is present. Catabolite repression accounts for the inhibition of genes that grow on a target carbon source (*e.g.*, benzene) in a mixture of contaminants due to the increase of other enzymes that rapidly metabolize the preferred carbon source (*e.g.*, ethanol).

Gomez et al. (2008) modeled the biodegradation of ethanol and benzene based on dual Monod kinetics, in which the rate of substrate utilization is a function of concentrations of substrate, electron acceptor, and active biomass. The general expression is shown in Equation (2.2):

$$r_s = -\hat{q}_s \left(\frac{S}{K_s + S} \right) \left(\frac{A}{K_A + A} \right) X_a \quad (2.2)$$

where

- r_s = rate of substrate utilization ($M_s L^{-3} T^{-1}$)
- $\hat{q}_s$ = maximum specific rate of substrate utilization ($M_s M_x^{-1} T^{-1}$)
- S = substrate (electron donor) concentration ($M_s L^{-3}$)
- A = electron acceptor concentration ($M_A L^{-3}$)
- K_s = half-saturation coefficient of substrate ($M_s L^{-3}$)
- K_A = half-saturation coefficient of electron acceptor ($M_A L^{-3}$)
- X_a = concentration of active biomass ($M_x L^{-3}$)

The authors incorporated MFD and catabolite repression based on the fraction of substrate dissolved in the aqueous phase. The fraction of substrate, f_s (dimensionless), is calculated as follow:

$$f_s = \frac{S_{TOC}}{T_{TOC}} \quad (2.3)$$

where S_{TOC} is the substrate concentration (mg/L) and T_{TOC} is total organic concentration (mg/L) of all dissolved organic species, except biomass. All concentrations are expressed as total organic carbon (TOC). MFD accounts for the decrease in the specific utilization of the target substrate based on the substrate availability; thus, the specific utilization rate, $\hat{q}_s$, is corrected to reflect the actual availability of substrate for utilization by multiplying it by the fraction, f_s . The term $\hat{q}_s$ in Equation (2.2) is therefore replaced by $\hat{q}_{s,act}$ where

$$\hat{q}_{s,act} = f_s \hat{q}_s \quad (2.4)$$

Catabolite repression refers to the inhibition of enzymes that are involved in the decomposition of target substrate due to the availability of a more preferred carbon source. Repression is empirically modeled assuming:

$$\hat{q}_{S,act} \propto f_S \quad (2.5)$$

Hence, the mathematical expression for both catabolic repression and MFD is:

$$\hat{q}_{S,act} = f_S^2 \hat{q}_S \quad (2.6)$$

Microbial population dynamics were also examined by considering four separate populations: aerobic ethanol degraders, aerobic ethanol and benzene degraders, anaerobic ethanol degraders, and anaerobic ethanol and benzene degraders (Gomez et al., 2008).

The general expressions for net microbial growth in aerobic (subscript *Aer*) and anaerobic (subscript *An*) conditions are:

$$r_{X,Aer} = \frac{dX_{Aer}}{dt} = - \left[r_{S,Aer} Y_{S,Aer} \right] \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{Aer} X_{Aer} \quad (2.7)$$

$$r_{X,An} = \frac{dX_{An}}{dt} = - \left[r_{S,An} Y_{S,An} \right] \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{An} X_{An} \quad (2.8)$$

where

$r_{X,j}$ = rate of active biomass growth for *j* condition ($M_X L^{-3} T^{-1}$)

$r_{S,j}$ = rate of substrate utilization for *j* condition ($M_S L^{-3} T^{-1}$)

b_j = endogeneous-decay coefficient of active biomass for *j* condition (T^{-1})

$Y_{S,j}$ = biomass yield coefficient on a substrate for *j* condition ($M_X M_S^{-1}$)

X_j = concentration of active biomass for *j* condition ($M_X L^{-3}$)

The microbial (or active biomass) growth equations represent the increases in microbial concentration with increases in substrate utilization. The active biomass yield

coefficient, Y_s , describes the relationship between substrate utilization and biomass growth. The relationship is related through the maximum specific rate of substrate utilization by

$$\hat{\mu}_s = \hat{q}_s Y_s \quad (2.9)$$

where $\hat{\mu}_s$ is defined as the maximum specific active biomass growth on a substrate (T^{-1}).

In the model, Gomez et al. (2008) restricted the volume of biomass by multiplying the growth terms in Equations (2.7) and (2.8) by:

$$\left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) \quad (2.10)$$

where

$$\begin{aligned} \eta_{bio} &= \text{total biomass saturation} \\ &\quad (\text{volume of biomass per volume of pore space}) \\ \eta &= \text{total porosity} \\ \gamma &= \text{pore space utilization factor} \end{aligned}$$

The total biomass saturation, η_{bio} , is a function of biomass density (ρ = mass of cells per volume of biomass), total aerobic biomass concentration ($X_{Aer,T}$), and total anaerobic biomass concentrations ($X_{An,T}$) as expressed below:

$$\eta_{bio} = \frac{X_{Aer,T} + X_{An,T}}{\rho} \quad (2.11)$$

Table 2-7 lists the values for the parameters that Gomez et al. (2008) employed in simulating the biodegradation of benzene in a release of E10 gasoline.

Table 2-7: Biodegradation Kinetics Parameters

Parameter	Aerobic	Anaerobic
Ethanol		
$\hat{\mu}_s (d^{-1})$	11.0	1.10
Y_s (mg/mg)	0.5	0.07
K_s (mg/L)	63.1	78.9
Benzene		
$\hat{\mu}_s (d^{-1})$	3.2	0.3
Y_s (mg/mg)	0.39	0.05
K_s (mg/L)	7.6	21.6
Other		
$b (d^{-1})$	0.2	0.03
η	0.3	
γ	0.2	
ρ (mg/L)	10^5	
A (mg/L)	6.0	
K_A (mg/L)	0.21	

The simulation study assumed the source of benzene and ethanol is from a light nonaqueous phase liquid (LNAPL). The source dissolved into groundwater flowing past it with a Darcy velocity of 0.9 cm per day (Gomez et al., 2008). The authors examined two release scenarios: a constant concentration of 1000 mg/L ethanol and 10 mg/L of benzene and a decreasing 2000 kg LNAPL source consisting of ethanol and benzene. Simulations indicated the presence of ethanol in E10 gasoline affects benzene degradation. The length of the benzene plume for the constant and decreasing source scenarios increased by 40 percent and 22 percent, respectively, when 10 percent ethanol was present (Gomez et al., 2008).

The model considered contaminant degradation under aerobic and methanogenic conditions within the simulated aquifer. Although the study showed trends that were similar to Mackay et al.'s (2006) field observations, the numerical model only considered

aerobic and methanogenic conditions, whereas in the field study, sulfate reducing and methanogenic conditions were prevalent.

Butanol Physical and Biochemical Properties

Based on the impact of ethanol on the behavior of BTEX compounds in groundwater, it is likely that blending butanol with gasoline would have similar effects. This section looks at the properties of butanol, and the processes that might affect the fate and transport of butanol in groundwater.

Groundwater flow passing a NAPL phase consisting of butanol-blended gasoline is likely to contain high concentrations of butanol relative to other components. Although butanol is not as miscible in water as ethanol; it has a high solubility of 77,000 mg/L, which can be acutely toxic to microorganisms (bacteria have acute toxicity thresholds for butanol between 110 mg/L and 2,250 mg/L (Staples, 2001)). BTEX and other components in gasoline have low solubilities. Hence, near the source area, butanol would be expected to be the dominant dissolved species. Selected properties of butanol and BTEX are listed in Table 2-8 for comparison.

Table 2-8: Selected Properties of Butanol and BTEX

Chemical	MW	Specific gravity	Solubility (mg/L)	log K_{ow}	Vapor Pressure (mm Hg)
Gasoline	~100	0.72-0.74	100-200	N/A	N/A
Butanol	74.12	0.81	77000	0.88	6.70
Benzene	78.11	0.88	1780	2.13	95.2
Toluene	92.13	0.87	535	2.73	28.4
<i>o</i> -Xylene	106.17	0.88	178	3.12	6.61
<i>p</i> -Xylene	106.17	0.86	162	3.15	8.84
<i>m</i> -Xylene	106.17	0.86	161	3.20	8.29

The octanol-water partition coefficients, K_{ow} , is related to the hydrophobicity of the compound. Hydrocarbons with high K_{ow} values are hydrophobic (lipophilic) and do not readily partition into water. Butanol has a low K_{ow} compared to the BTEX components of gasoline; hence, the alcohol partitions into the aqueous phase much more readily than the BTEX compounds. Further, with respect to adsorption onto organic compounds associated with aquifer solids, the BTEX compounds would exhibit higher sorption than butanol, due to the lipophilicity of BTEX in comparison to butanol. Due to higher sorption, the velocity of the BTEX plumes in the groundwater would be retarded in relation to both the velocity of the groundwater itself, and the velocity of the butanol plume.

Biodegradation: Aerobic

Despite the acute toxicity of high concentration of butanol on microorganisms, numerous studies demonstrate that butanol biodegrades under aerobic conditions. Table 2-9 presents a summary list of different microorganisms that were reported to assimilate butanol and their related kinetic parameters. It should be noted that Table 2-9 also contains kinetic parameter values for those aerobic bacteria that produce enzymes such as alcohol dehydrogenase (ADH) and quinoxinoprotein butanol dehydrogenase (BDH) with abilities to transform butanol into other products.

As for biomass yield for bacteria growing on butanol, the *Arthrobacter* sp. strain HA1 was reported to have a growth yield of 20.0 g protein per mole butanol ($Y_s = 0.27$ mg/mg) (Scholtz et al., 1988). Batch and continuous bioscrubber studies indicated a mixed culture had a growth yield of 66.7 g dry cell weight (dcw) and 39.3 g dcw per

mole butanol ($Y_s = 0.90$ mg/mg and $Y_s = 0.53$ mg/mg), respectively (Wubker and Friedrich, 1996).

Table 2-9: Aerobic Butanol Degraders

Species	$\hat{\mu}_s$	$\hat{q}_s$	K_s	Reference
<i>Enterobacter</i> sp. VKGH12	6.48	N.R.	N.R.	(Veeranagouda et al., 2006)
<i>Gardonia</i> sp. MTCC4818	N.R.	0.0012	N.R.	(Chatterjee et al., 2005)
<i>Pseudomonas butanovora</i> (BDH)	N.R.	4.8	0.52	(Vangnai and Arp, 2001)
<i>Arthrobacter</i> sp. HA1	4.56	N.R.	N.R.	(Scholtz et al., 1988)
<i>Pseudomonas putida</i> HK5				
ADH I	N.R.	21.5	120.1	(Toyama et al., 1995)
ADH IIB	N.R.	17.1	7.78	(Toyama et al., 1995)
ADH IIG	N.R.	14.7	11.12	(Toyama et al., 1995)
<i>Pichia pastoris</i>	N.R.	4.8	N.R.	(Borzeix et al., 1995)
Mixed culture (trickle-bed reactor)	16.8	0.10	42.2	(Heinze and Friedrich, 1997)

$\hat{\mu}_s (d^{-1})$; $\hat{q}_s \left(\frac{\mu mol}{min \cdot mg \text{ protein}} \right)$; $K_s \left(\frac{mg}{L} \right)$; N.R.: not reported

Mariano et al. (2009) evaluated the aerobic degradation potential of gasoline and butanol blends in laboratory experiments. Two separate experimental conditions were studied that simulated soil contamination (50 mL fuel/kg of soil) and water contamination (20 mL fuel/L of river water), respectively. Four different butanol-gasoline fuel blends were examined: 5, 10, 15, and 20 percent butanol by volume. Additionally, Mariano et al. (2009) performed a similar experiment using a 20/80 ethanol-gasoline blend to compare with the butanol-gasoline blend results. The experiments quantified degradation by measuring the production of CO₂ from aerobic respiration for each experimental condition. The soil contamination experiment showed all butanol/gasoline blends readily degraded while degradation of pure butanol exhibited a lag of 54 days before starting to degrade. The authors also noted that the degradation of the 20/80 butanol/gasoline blend in soil started one week after the 20/80 ethanol-gasoline blend (Mariano et al., 2009).

The water contamination experiment indicated butanol/gasoline blend degradation began almost immediately while the degradation pure butanol (at a dissolved concentration of 20,000 mg/L in water) had a lag of 92 days before degradation commenced. After the lag period, biodegradation of butanol remained active even though butanol concentrations were 10 times higher than the reported maximum acute toxicity threshold (2,250 mg/L). In addition, it was demonstrated that in water, ethanol biodegraded faster than butanol which biodegraded faster than gasoline (Mariano et al., 2009). Furthermore, the research demonstrated that butanol-blended gasoline is more biodegradable than gasoline without alcohol in both water and soil. Butanol present in gasoline may have increased the solubility of the hydrocarbons and subsequently, could increase the gasoline hydrocarbons' availability to microorganisms (Mariano et al., 2009). However, the study did not examine the effects of butanol on the attenuation of fuel components like benzene under natural conditions; specifically when the electron acceptor supply may be limited. In the Mariano et al. (2009) study, aerobic conditions were maintained, which would not necessarily be the case in the subsurface.

Biodegradation: Anaerobic

Anaerobic biodegradation studies specifically examining butanol-gasoline blends were not available. However, there were several studies conducted that showed that anaerobic microorganisms (Table 2-10) have the abilities to metabolize butanol via sulfate-reduction and/or methanogenesis. Kinetic data on biodegradation of butanol under anaerobic conditions were also limited. Only two studies examined microbial kinetics with butanol as an electron donor in an anaerobic environment. Kuever et al. (1993) noted the sulfate reducing bacteria (SRB) in their study grew on butanol with a

doubling time of 12 to 14 hours. Microbial growth yield data were limited to *Acetobacterium carbinolicum* strain WoProp1 (3.85 g dry cell per mole butanol) and *Methanospirillum hungatei* in coculture with strain WoProp1 (7.71 g dry cell per mole butanol) (Eichler and Schink, 1984). Stoichiometric conversion of butanol under sulfate-reducing and methanogenic conditions are as follows (Eichler and Schink, 1984):

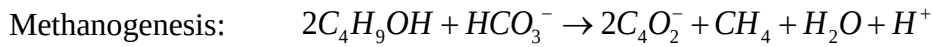
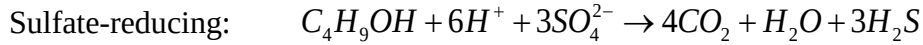


Table 2-10: Anaerobic Butanol Degraders

Species	Reference
<i>Acetobacterium carbinolicum</i>	(Eichler and Schink, 1984)
<i>Desulfatirhabdium butyrativorans</i>	(Balk et al., 2008)
<i>Desulfobacterium indolicum</i>	(Bak and Widdel, 1986)
<i>Pelobacter carbinolicus</i>	(Lovley et al., 1995)
<i>Desulfotomaculum</i> sp. strain Groll	(Kuever et al., 1993)
<i>Clostridium beijerinckii</i> (butylicum)*	(Hui et al., 1987)

*Reported $\hat{q}_s \left(\frac{\mu\text{mol}}{\text{min} \cdot \text{mg protein}} \right)$ values of 0.85×10^{-3} and 2.3×10^{-3} .

Impact to BTEX Degradation

As is apparent from the preceding review of the literature, many questions regarding the impact of butanol-gasoline blends on groundwater quality remain unanswered. While the impact of ethanol-gasoline blends on groundwater has been studied in the field and through model simulations, with the exception of a soon to be published modeling study by Gomez and Alvarez (2010), similar work has not been conducted for butanol-gasoline blends. Gomez and Alvarez (2010) examined the potential effects of several alcohols to include butanol on BTEX transport using model simulations. The study concluded that “reformulated fuels blends can have a significant

impact on the fate and transport of other gasoline constituents” (Gomez and Alvarez, 2010). As use of butanol as an additive to gasoline appears to be likely in the future, research into the environmental impact of these butanol-gasoline blends is important; particularly with regard to the impact of these blends on groundwater quality. In the next chapter a model is developed, which is based upon the multispecies reactive transport modeling that was done to study the fate and transport of ethanol-gasoline blends, to simulate the fate and transport of butanol-gasoline blends in groundwater.

3.0. Methodology Equation Chapter 3 Section 1

3.1. Overview

This chapter provides details of the approach to study the potential impact of butanol on the natural attenuation of benzene in groundwater as a result of butanol-blended fuel leaks and/or spills. The approach includes development of a model to simulate the important subsurface processes affecting the fate and transport of different butanol/gasoline blends, and use of the model to evaluate how varying fuel blend characteristics and hydrogeochemical parameters impacts the extent and persistence of the benzene plume.

3.2. Model Development

The model used in this research builds upon a model that has been used to simulate the fate and transport of ethanol blends in groundwater (Gomez et al., 2008). The general expression governing the fate and transport of dissolved contaminants in the subsurface is:

$$R \frac{\partial C}{\partial t} = \left[\frac{\partial}{\partial x} \left(D_{xx} \frac{\partial C}{\partial x} + D_{xy} \frac{\partial C}{\partial y} + D_{xz} \frac{\partial C}{\partial z} \right) + \frac{\partial}{\partial y} \left(D_{yx} \frac{\partial C}{\partial x} + D_{yy} \frac{\partial C}{\partial y} + D_{yz} \frac{\partial C}{\partial z} \right) + \frac{\partial}{\partial z} \left(D_{zx} \frac{\partial C}{\partial x} + D_{zy} \frac{\partial C}{\partial y} + D_{zz} \frac{\partial C}{\partial z} \right) \right] - \left[v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} \right] + r \quad (3.1)$$

where the first bracketed terms on the right-hand side represents dissolved contaminant concentration changes as a result of dispersion, the second bracketed terms on the right-hand side represents dissolved contaminant concentration changes as a result of

advection, and the last term on the right-hand side is a generic reaction term (discussed below). Sorption is assumed to be a linear, reversible, equilibrium process, modeled using a retardation factor R .

Equation (3.1) is implemented using DoD's Groundwater Modeling System (GMS). GMS incorporates a suite of groundwater models, including MODFLOW to simulate flow and RT3D to simulate dissolved contaminant transport. MODFLOW determines the steady-state groundwater flow field by applying the main equation of flow and Darcy's Law to a given set of hydraulic head boundary conditions and hydraulic conductivities. RT3D incorporates the steady-state flow field from MODFLOW into the advection term in Equation (3.1) and then uses Equation (3.1) to compute dissolved contaminant concentration variations in space and time that result from advection, dispersion, and reaction. Below, the formulation for the reaction term, r , is described.

With the incorporation of metabolic flux dilution (f_s), retardation due to sorption (R_s) (and assuming sorbed contaminant is not degraded), and defining the maximum specific rate of substrate utilization ($\hat{q}_s$) as the ratio of the maximum specific active biomass growth on a substrate ($\hat{\mu}_s$) and the biomass yield coefficient (Y_s) (see Equation 2.9), the generalized dual Monod substrate utilization expression (Equation 2.2) becomes:

$$r_s = -\frac{f_s}{R_s} \left(\frac{\hat{\mu}_s X_a}{Y_s} \right) \left(\frac{S}{K_s + S} \right) \left(\frac{A}{K_A + A} \right) \quad (3.2)$$

In contrast to the model presented by Gomez et al. (2008), which assumes biodegradation under aerobic and methanogenic conditions only, the model in this study also accounts for degradation of a target contaminant under sulfate-reducing conditions, where SO_4^{2-} is

available as an electron acceptor. The equations describing substrate utilization under aerobic, sulfate-reducing, and methanogenic redox conditions are shown in Equations (3.3) to (3.5), respectively.

$$\text{Aerobic:} \quad r_{S,Aer} = -\frac{f_S}{R_S} \left(\frac{\hat{\mu}_{S,Aer} X_{Aer}}{Y_{S,Aer}} \right) \left(\frac{S}{K_{S,Aer} + S} \right) \left(\frac{O}{K_O + O} \right) \quad (3.3)$$

Sulfate-reduction:

$$r_{S,SRB} = -\frac{f_S}{R_S} \left(\frac{\hat{\mu}_{S,SRB} X_{SRB}}{Y_{S,SRB}} \right) \left(\frac{S}{K_{S,SRB} + S} \right) \left(\frac{SO_4}{K_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \quad (3.4)$$

Methanogenic:

$$r_{S,Met} = -\frac{f_S}{R_S} \left(\frac{\hat{\mu}_{S,Met} X_{Met}}{Y_{S,Met}} \right) \left(\frac{S}{K_{S,Met} + S} \right) \left(\frac{I_{SO_4}}{I_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \quad (3.5)$$

where O and SO_4 corresponds to the dissolved concentrations of oxygen and sulfate, respectively. The last term in Equation (3.4) and the last two terms in Equation (3.5) are used to simulate “switching” from aerobic, to sulfate-reducing, to methanogenic metabolism. The values of the empirical parameters I_O and I_{SO_4} are chosen such that when dissolved oxygen levels are high, the last terms in Equations (3.4) and (3.5) are small, so degradation by sulfate-reduction and methanogenesis is negligible (compared to aerobic oxidation). When oxygen levels are low, but sulfate concentrations are high, degradation described by Equation (3.4), sulfate-reduction, is dominant, and when both oxygen and sulfate concentrations are low, degradation described by Equation (3.5), methanogenesis, is dominant.

The active biomass (X) used in the degradation equations is divided into six different populations (Table 3-1). It is assumed that all microbes have the ability to metabolize and grow on butanol, yet only a subset can metabolize and grow on benzene.

Table 3-1: Microbial Population Divisions

X_1	concentration of aerobes that degrade butanol only
X_2	concentration of aerobes that degrade butanol and benzene
X_3	concentration of SRB that degrade butanol only
X_4	concentration of SRB that degrade butanol and benzene
X_5	concentration of methanogens that degrade butanol only
X_6	concentration of methanogens that degrade butanol and benzene

All microbial communities are considered to be immobile. The contaminant degradation and microbial growth equations used in this study follow.

Butanol (Bu) biodegradation

Six microbial populations utilize butanol for cell synthesis. The overall utilization rate for butanol, Equation (3.6), is based on two separate microbial communities degrading butanol for each redox condition (aerobic, sulfate-reducing, and methanogenic).

$$r_{Bu} = \left[\frac{dBu}{dt} \right] = -\frac{f_{Bu}}{R_{Bu}} \left[r_{Bu,Aer1} + r_{Bu,Aer2} + r_{Bu,SRB1} + r_{Bu,SRB2} + r_{Bu,Met1} + r_{Bu,Met2} \right] \quad (3.6)$$

$$\begin{aligned} r_{Bu,Aer1} &= \frac{\hat{\mu}_{Bu,Aer1} X_1}{Y_{Bu,Aer1}} \left(\frac{Bu}{K_{Bu,Aer1} + Bu} \right) \left(\frac{O}{K_O + O} \right) \\ r_{Bu,Aer2} &= \frac{\hat{\mu}_{Bu,Aer2} X_2}{Y_{Bu,Aer2}} \left(\frac{Bu}{K_{Bu,Aer2} + Bu} \right) \left(\frac{O}{K_O + O} \right) \\ r_{Bu,SRB1} &= \frac{\hat{\mu}_{Bu,SRB1} X_3}{Y_{Bu,SRB1}} \left(\frac{Bu}{K_{Bu,SRB1} + Bu} \right) \left(\frac{SO_4}{K_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \\ r_{Bu,SRB2} &= \frac{\hat{\mu}_{Bu,SRB2} X_4}{Y_{Bu,SRB2}} \left(\frac{Bu}{K_{Bu,SRB2} + Bu} \right) \left(\frac{SO_4}{K_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \\ r_{Bu,Met1} &= \frac{\hat{\mu}_{Bu,Met1} X_5}{Y_{Bu,Met1}} \left(\frac{Bu}{K_{Bu,Met1} + Bu} \right) \left(\frac{I_{SO_4}}{I_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \\ r_{Bu,Met2} &= \frac{\hat{\mu}_{Bu,Met2} X_6}{Y_{Bu,Met2}} \left(\frac{Bu}{K_{Bu,Met2} + Bu} \right) \left(\frac{I_{SO_4}}{I_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \end{aligned} \quad (3.7)$$

Benzene (B) biodegradation

Benzene can also be used for growth and energy by microorganisms. However, in this study, it is assumed that not all microorganisms utilize benzene. As shown in Table 3-1, the microbial populations that metabolize benzene under aerobic, sulfate reducing, and methanogenic conditions are denoted as X_2 , X_4 , and X_6 respectively. The benzene utilization rate under each redox condition, Equation (3.3) to Equation (3.5), is empirically multiplied by f_B , to account for the catabolite repression of enzymes that degrade benzene because butanol is simultaneously available as another carbon source. Hence, the overall rate of utilization for benzene is expressed as:

$$r_B = \left[\frac{dB}{dt} \right] = -\frac{f_B^2}{R_B} \left[r_{B,Aer} + r_{B,SRB} + r_{B,Met} \right] \quad (3.8)$$

$$\begin{aligned} r_{B,Aer} &= \frac{\hat{\mu}_{B,Aer} X_2}{Y_{B,Aer}} \left(\frac{B}{K_{B,Aer} + B} \right) \left(\frac{O}{K_O + O} \right) \\ r_{B,SRB} &= \frac{\hat{\mu}_{B,SRB} X_4}{Y_{B,SRB}} \left(\frac{B}{K_{B,SRB} + B} \right) \left(\frac{SO_4}{K_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \\ r_{B,Met} &= \frac{\hat{\mu}_{B,Met} X_6}{Y_{B,Met}} \left(\frac{B}{K_{B,Met} + B} \right) \left(\frac{I_{SO_4}}{I_{SO_4} + SO_4} \right) \left(\frac{I_O}{I_O + O} \right) \end{aligned} \quad (3.9)$$

Oxygen (O) depletion

The rate of oxygen depletion as a result of degradation of butanol and benzene under aerobic conditions is:

$$r_O = \left[\frac{dO}{dt} \right] = - \left[f_{Bu} \left(r_{Bu,Aer1} F_{O/Bu} + r_{Bu,Aer2} F_{O/Bu} \right) + f_B^2 \left(r_{B,Aer} F_{O/B} \right) \right] \quad (3.10)$$

where $F_{O/Bu}$ represents the stoichiometric mass ratio of oxygen to butanol and similarly,

$F_{O/B}$ is the stoichiometric ratio of oxygen to benzene.

Sulfate (SO4) depletion

The equation that describes the consumption rate of sulfate is analogous to the oxygen depletion rate. The rate of sulfate consumption, in terms of the utilization rates of butanol and benzene under sulfate-reducing conditions is:

$$r_{SO_4} = \left[\frac{dSO_4}{dt} \right] = - \left[f_{Bu} \left(r_{Bu,SRB1} F_{SO_4/Bu} + r_{Bu,SRB2} F_{SO_4/Bu} \right) + f_B^2 \left(r_{B,SRB} F_{SO_4/B} \right) \right] \quad (3.11)$$

where $F_{SO_4/Bu}$ and $F_{SO_4/B}$ correspond to the stoichiometric ratios of sulfate to butanol and sulfate to benzene, respectively.

Microbial growth

Active biomass growth depends on the rate of substrate utilization; thus, the growth for each microbial community is related to the assimilation of substrate under the respective redox condition. Equations (3.12) through (3.17) describe the net biomass growth of butanol and benzene degraders under the various redox conditions.

$$r_{X_1} = \left[\frac{dX_1}{dt} \right] = f_{Bu} \left(r_{Bu,Aer1} Y_{Bu,Aer1} \right) \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{Aer} X_1 \quad (3.12)$$

$$r_{X_2} = \left[\frac{dX_2}{dt} \right] = \left[f_{Bu} \left(r_{Bu,Aer2} Y_{Bu,Aer2} \right) + f_B^2 \left(r_{B,Aer} Y_{B,Aer} \right) \right] \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{Aer} X_2 \quad (3.13)$$

$$r_{X_3} = \left[\frac{dX_3}{dt} \right] = f_{Bu} \left(r_{Bu,SRB1} Y_{Bu,SRB1} \right) \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{SRB} X_3 \quad (3.14)$$

$$r_{X_4} = \left[\frac{dX_4}{dt} \right] = \left[f_{Bu} \left(r_{Bu,SRB2} Y_{Bu,SRB2} \right) + f_B^2 \left(r_{B,SRB} Y_{B,SRB} \right) \right] \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{SRB} X_4 \quad (3.15)$$

$$r_{X_5} = \left[\frac{dX_5}{dt} \right] = f_{Bu} \left(r_{Bu,Met1} Y_{Bu,Met1} \right) \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{Met} X_5 \quad (3.16)$$

$$r_{X_6} = \left[\frac{dX_6}{dt} \right] = \left[f_{Bu} \left(r_{Bu, Met 2} Y_{Bu, Met 2} \right) + f_B^2 \left(r_{B, Met} Y_{B, Met} \right) \right] \left(1 - \frac{\eta_{bio}}{\gamma \cdot \eta} \right) - b_{Met} X_6 \quad (3.17)$$

Note that the volume of biomass is restricted by multiplying the growth terms in Equations (3.12) through (3.17) (first terms on the right-hand side) by the term defined in Equation (2.10), where the total biomass saturation, η_{bio} , associated with microbial growth on butanol and benzene is determined as:

$$\eta_{bio} = \frac{X_1 + X_2 + X_3 + X_4 + X_5 + X_6}{\rho} \quad (3.18)$$

The biodegradation of butanol and benzene is described by the system partial differential equations (PDEs) that has been discussed above. Table 3-2 summarizes the system of PDEs that are being used to model the fate and transport of the four dissolved components (*i.e.*, butanol, benzene, oxygen, and sulfate) and the immobile biomass.

Table 3-2: Model Equations

Species	Fate/Transport	Reaction, r
Butanol	Equation (3.1)	Equation (3.6)
Benzene	Equation (3.1)	Equation (3.8)
Oxygen	Equation (3.1)	Equation (3.10)
Sulfate	Equation (3.1)	Equation (3.11)
Microbes		
X_1		Equation (3.12)
X_2		Equation (3.13)
X_3		Equation (3.14)
X_4		Equation (3.15)
X_5		Equation (3.16)
X_6		Equation (3.17)

This coupled system of PDEs was solved numerically by implementing a user defined reaction module within the RT3D package in GMS.

3.3. Simulation Conditions

Transport and degradation of contaminants in groundwater were simulated in a two-dimensional (2-D) single-layered aquifer. A schematic of the simulation domain is shown in Figure 3-1.

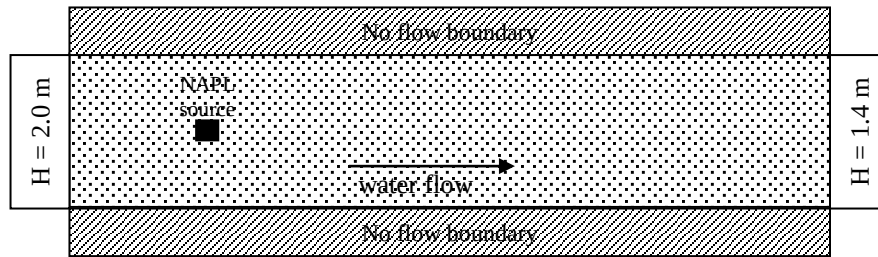


Figure 3-1: Schematic of simulation domain

The 2-D single-layered aquifer is 200 m by 80 m with constant hydraulic head boundaries (H) at two ends, and no flow boundaries along the sides. As shown in Figure 3-1, a constant source, representing a non-aqueous phase liquid (NAPL), is located 40 m from the left constant head boundary and midway between the two no flow boundaries. Both oxygen and sulfate concentrations are specified initially and at the left boundary at values of 6.0 mg/L and 96.0 mg/L, respectively. Other important hydrogeological properties pertaining to the aquifer are presented in Table 3-3 and Table 3-4.

Table 3-3: Hydrogeophysical Parameters of the Aquifer
(Gomez et al., 2008)

Parameter	Unit	Value
<i>Hydrogeology</i>		
Total porosity, η		0.3
Pore space utilization, γ		0.2
Hydraulic conductivity, K	m/d	3.0
Hydraulic gradient, i	m/m	0.003
Water Darcy velocity, q	cm/d	0.9
Water pore velocity, v	cm/d	3.0
Dissolved oxygen, O	mg/L	6.0
Dissolved sulfate ^(*) , SO_4	mg/L	96

^(*) (Mackay et al., 2006)

Table 3-4: Additional Hydrogeophysical Parameters of the Aquifer
(Gomez et al., 2008)

Parameter	Unit	Value
<i>Dispersivity</i>		
Longitudinal	m	7.0
Transverse	m	0.7
<i>Adsorption^a</i>		
Soil bulk density, ρ_b	kg/L	1.7
Partitioning coefficient (butanol) ^b , $K_{d,Bu}$	L/kg	0.072
Partitioning coefficient (benzene), $K_{d,B}$	L/kg	0.095
Partitioning coefficient (ethanol), $K_{d,EtOH}$	L/kg	0.001
Retardation factor (butanol), R_{Bu}		1.41
Retardation factor (benzene), R_B		1.54
Retardation factor (ethanol), R_{EtOH}		1.01
Organic content weight fraction, f_{oc}		0.001
<i>Simulation Domain</i>		
Modeled area length	m	200
Modeled area width	m	80
X space discretization	units	50
Y space discretization	units	100
Cell width	m	0.8
Cell length	m	4.0
Simulation time	years	30
Time step	d	0.02

^aRetardation factors are calculated, $R_s = 1 + \rho_b K_{d,s} / \eta$

^bEstimated using $K_d = K_{oc} f_{oc}$ and reported $K_{oc} = 72 \text{ mL/g}$
(Staples, 2001)

Table 3-5 outlines the simulation scenarios that were run. All simulations used the same set of hydrogeophysical parameters (Table 3-3 and Table 3-4).

Table 3-5: Simulation Scenarios

Scenario	Chemicals	Degradation Condition
A	Benzene	Aerobic → Methanogenic
B	Benzene/Ethanol	Aerobic → Methanogenic
C	Benzene/Butanol	Aerobic → Methanogenic
D	Benzene	Aerobic → Sulfate-reducing → Methanogenic
E	Benzene/Butanol	Aerobic → Sulfate-reducing → Methanogenic

Scenarios A and B were run to verify that the current model implementation successfully reproduced the results reported in the published study of Gomez et al.

(2008). In scenarios A and B, the same kinetic and hydrogeophysical parameters used in Gomez et al. (2008) to simulate benzene and ethanol fate and transport (Tables 3-3 and 3-4), assuming a continuous release of contaminants at constant concentrations (ethanol at 1000 mg/L and benzene at 10 mg/L), are used in the current model implementation. Table 3-6 and Table 3-7 list the biodegradation kinetic parameter values used in simulating the degradation of benzene and ethanol (Gomez et al., 2008). Other pertinent values can be found in Table 2-7. It should also be noted that the stoichiometric ratio, $F_{O/Bu}$, was set to 1.27 mg oxygen per mg ethanol.

Table 3-6: Benzene Biodegradation Kinetic Parameters

Parameter	Unit	Value
<i>Aerobic</i> (Gomez et al., 2008)		
$\hat{\mu}_{B,Aer}$	d ⁻¹	3.2
$Y_{B,Aer}$	mg/mg	0.39
$K_{B,Aer}$	mg/L	7.6
<i>Sulfidogenic</i> (Godeke et al., 2008)		
$\hat{\mu}_{B,SRB}$	d ⁻¹	0.15
$Y_{B,SRB}$	mg/mg	0.002
$K_{B,SRB}$	mg/L	4.5
<i>Methanogenic</i> (Gomez et al., 2008)		
$\hat{\mu}_{B,Met}$	d ⁻¹	0.3
$Y_{B,Met}$	mg/mg	0.05
$K_{B,Met}$	mg/L	21.6

Table 3-7: Ethanol Biodegradation Kinetic Parameters

Parameter	Unit	Value
Aerobic (Gomez et al., 2008)		
$\hat{\mu}_{EtOH,Aer1} = \hat{\mu}_{EtOH,Aer2}$	d ⁻¹	11.0
$Y_{EtOH,Aer1} = Y_{EtOH,Aer2}$	mg/mg	0.5
$K_{EtOH,Aer1} = K_{EtOH,Aer2}$	mg/L	63.1
Sulfidogenic (Boonchayaanant et al., 2008)		
$\hat{\mu}_{EtOH,SRB1} = \hat{\mu}_{EtOH,SRB2}$	d ⁻¹	0.4
$Y_{EtOH,SRB1} = Y_{EtOH,SRB2}$	mg/mg	0.03
$K_{EtOH,SRB1} = K_{EtOH,SRB2}$	mg/L	478
Methanogenic (Gomez et al., 2008)		
$\hat{\mu}_{EtOH,Met1}$	d ⁻¹	1.1
$\hat{\mu}_{EtOH,Met2}$	d ⁻¹	0.8
$Y_{EtOH,Met1} = Y_{EtOH,Met2}$	mg/mg	0.07
$K_{EtOH,Met1} = K_{EtOH,Met2}$	mg/L	78.9

The initial microbial concentration values specified to simulate Scenarios A and B are shown in Table 3-8. Furthermore, as Gomez et al. (2008) did not consider sulfate reduction, sulfate reduction is excluded in Scenarios A and B by specifying initial and boundary sulfate concentrations in groundwater as zero. Thus, all reactions that require sulfate as an electron acceptor (Equations (3.4), (3.11) (3.14), and (3.15)) are not included in the simulations of Scenarios A and B.

Table 3-8: Initial Microbial Concentration (Scenarios A & B)

Microbes	Notation	Initial Conc. (mg/L)
Aerobes (ethanol degraders)	X_1	1.0
Aerobes (ethanol/benzene degraders)	X_2	0.1
SRBs (ethanol degraders)	X_3	0.0
SRBs (ethanol/benzene degraders)	X_4	0.0
Methanogens (ethanol degraders)	X_5	0.1
Methanogens (ethanol/benzene degraders)	X_6	0.001

The degradation of ethanol and benzene under sulfate redox condition was also considered and simulated in a separate simulation scenario. The simulation used the same contaminant source as scenarios A and B. The biodegradation kinetic parameters used are listed in Tables 3-6, 3- 7, and 3-8. The initial concentrations for SRBs were specified at 0.1 mg/L for ethanol degraders and 0.001 mg/L for ethanol/benzene degraders.

Simulations of the butanol and benzene transport and degradation (Scenarios C, D, and E) in groundwater are also implemented using the same 2-D single-layered aquifer described earlier. Scenarios C, D, and E enable the assessment of the impact of butanol on benzene degradation. To assess impact, the steady-state lengths of the benzene plumes (defined as the length of the 5.0 µg/L benzene concentration contour) are compared for the different scenarios. The 5.0 µg/L contour was chosen, as 5.0 µg/L is the maximum contaminant level for benzene in drinking water. Table 3-9 lists the different butanol-gasoline blends that were considered as source zone concentrations, which were based on the effective solubilities of butanol and benzene in water (see Appendix A). The effective solubility, $S_{eff,i}$, was estimated using Raoult's law:

$$S_{eff,i} = X_i^O S_i^w \quad (3.19)$$

where X_i^O is molar fraction of chemical i in NAPL (organic phase) and S_i^w is the pure phase solubility of chemical i in the water phase. The molar fraction of benzene in gasoline was determined assuming benzene is 1.3 percent by volume of the gasoline (USEPA, 2007).

Table 3-9: Contamination Sources Considered

Notation	Butanol/Gasoline (% volume)	Effective Solubility (mg/L)	
		Butanol	Benzene
Bu0	0/100	0	36.2
Bu20	20/80	21,181	26.3
Bu50	50/50	46,418	14.4
Bu85	15/85	68,980	3.8

Even though three butanol-gasoline blends (Bu20, Bu50, and Bu85) were considered as NAPLs which serve as constant sources for simulation, only Bu20 blend was used to assess the impact of butanol on benzene degradation. Both Bu50 and Bu85 blends have butanol concentrations that are 20 to 30 times higher than the maximum acute toxicity threshold for bacteria of 2,250 mg/L. In contrast, the Bu20 blend has butanol concentrations within the 20,000 mg/L, a level that is above toxicity threshold, but can be biodegraded, as noted in Chapter 2. Therefore, the effective solubilities of butanol and benzene in Bu20 are used as constant source concentrations at the NAPL/water interface. Additionally, following Gomez et al. (2008), the input concentrations for both constituents were taken as the average between the value at the NAPL/water interface and zero (assuming the concentrations decrease quickly across a boundary layer adjacent to the NAPL/water interface). The resulting input concentrations used in the simulation with Bu20 as a contaminant source are 10500 mg/L for butanol and 13 mg/L for benzene. Similarly, the input concentration of benzene for Bu0 is 18 mg/L.

Simulation scenarios C, D, and E use the same set of hydrogeophysical and kinetic parameters. As discussed earlier, six populations of immobile microorganisms are included in the model, along with equations describing the advective, dispersive,

sorptive, and reactive transport of four dissolved compounds (butanol, benzene, oxygen, and sulfate). However, Scenario C employs the same technique used in Scenarios A and B to eliminate all sulfate reduction mechanisms from the simulation—initial and boundary concentrations of sulfate and SRB were specified as zero. Therefore, for Scenario C, the biodegradation of butanol and benzene only occurs under aerobic and methanogenic conditions. Pertinent values for the biodegradation variables used in this study are listed in Table 3-6 and Table 3-10 to Table 3-12.

Table 3-10: Butanol Biodegradation Kinetic Parameters

Parameter	Unit	Low	High	Value Used	Comments ^a
<i>Aerobic</i>					
$\hat{\mu}_{Bu,Aer1} = \hat{\mu}_{Bu,Aer2}$	d ⁻¹	4.6	16.8	6.5	Median of reported values
$Y_{Bu,Aer1} = Y_{Bu,Aer2}$	mg/mg	0.27	0.90	0.5	Median of reported values
$K_{Bu,Aer1} = K_{Bu,Aer2}$	mg/L	0.04	120	7.8	Median of reported values
<i>Sulfidogenic</i>					
$\hat{\mu}_{Bu,SRB1} = \hat{\mu}_{Bu,SRB2}$	d ⁻¹	1.19	1.39	1.28	Based on doubling time (Kuever et al., 1993)
$Y_{Bu,SRB1} = Y_{Bu,SRB2}$	mg/mg	N/A	N/A	0.10	Assumed
$K_{Bu,SRB1} = K_{Bu,SRB2}$	mg/L	N/A	N/A	10	Assumed
<i>Methanogenic</i>					
$\hat{\mu}_{Bu,Met1} = \hat{\mu}_{Bu,Met2}$	d ⁻¹	N/A	N/A	0.015	Calculated ^b
$Y_{Bu,Met1} = Y_{Bu,Met2}$	mg/mg	0.052	0.104	0.078	(Eichler and Schink, 1984)
$K_{Bu,Met1} = K_{Bu,Met2}$	mg/L	N/A	N/A	20	Assumed

^aSee Chapter 2 for additional references.

^bBased on median value of Y_s and median value of $\hat{q}_s$ using Equation 2.9.

Table 3-11: Microbial Initial Concentrations

Microbes	Notation	Initial Conc. (mg/L)
Aerobes (butanol degraders)	X_1	1.0
Aerobes (butanol/benzene degraders)	X_2	0.1
SRBs (butanol degraders)	X_3	0.1
SRBs (butanol/benzene degraders)	X_4	0.001
Methanogens (butanol degraders)	X_5	0.1
Methanogens (butanol/benzene degraders)	X_6	0.001

Table 3-12: Other Degradation Kinetic Parameters

Parameter	Unit	Value	Reference/Comment
<i>Biomass</i>			
Biofilm density, ρ	mg/L	10^5	(Gomez et al., 2008)
b_{Aer}	d ⁻¹	0.2	(Gomez et al., 2008)
b_{SRB}	d ⁻¹	0.002	(Godeke et al., 2008)
b_{Met}	d ⁻¹	0.03	(Gomez et al., 2008)
<i>Others</i>			
Initial O	mg/L	6.0	(Gomez et al., 2008)
K_O	mg/L	0.21	(Gomez et al., 2008)
Initial SO_4	mg/L	96	(Mackay et al., 2006)
K_{SO_4}	mg/L	10	(Godeke et al., 2008)
I_O	mg/L	0.1	Empirical
I_{SO_4}	mg/L	0.1	Empirical
$F_{O/B}$	mg/mg	3.07	Stoichiometry
$F_{O/Bu}$	mg/mg	2.59	Stoichiometry
$F_{SO_4/B}$	mg/mg	4.62	Stoichiometry
$F_{SO_4/Bu}$	mg/mg	3.89	Stoichiometry

3.4. Sensitivity Analysis

As discussed in Chapter 2, the degradation of contaminants is highly dependent on environmental conditions, as well as the assumed biodegradation kinetic parameter values. The effect of decay parameter for methanogens (b_{Met}) on benzene degradation was examined. Other parameters such as hydraulic conductivity, microbial growth

kinetics, and biofilm density had been previously studied (Gomez et al., 2008). A continuous release scenario with butanol at 1000 mg/L and benzene at 10 mg/L was employed for the sensitivity analysis. Values used for b_{Met} in the sensitivity analysis were 0.003/d and 0.00045/d, corresponding to 10 and 1.5 percent of the baseline value of 0.03/d, respectively.

4.0. Results and Discussion

4.1. Overview

This chapter implements the model that simulates subsurface processes affecting the fate and transport of butanol-blended fuel and analyzes the model results. First, the model will be verified by comparing model simulations for ethanol-blended fuels with the results reported in the published study of Gomez et al. (2008). Second, the model is used to see the effect of varying parameters on the extent and persistence of plumes resulting from spills of ethanol-blended fuels. Third, the model will be used to assess the impact of butanol on the natural attenuation of benzene in groundwater as a result of butanol-blended fuel leaks and/or spills. Finally, a sensitivity analysis will be conducted to evaluate how varying biodegradation kinetic parameters impacts the extent and persistence of the benzene plume.

4.2. Model Validation

The conditions simulated in Gomez et al. (2008), a continuous release of dissolved contaminant consisting of ethanol (1000 mg/L) and benzene (10 mg/L), were used to verify the model developed for this study. The model, using the parameters presented in Chapter 3 for scenarios A (only benzene) and B (benzene and ethanol) reproduced the results presented in Gomez et al. (2008). Results of model simulations are shown in Figure 4-1 through Figure 4-4 (see Appendix B for the kinetics parameters used in simulations). Figures 4-1 and 4-3 show benzene and oxygen depletion plumes, respectively, for Scenario A, while Figures 4-2 and 4-4 show benzene and oxygen depletion plumes, respectively, for Scenario B.

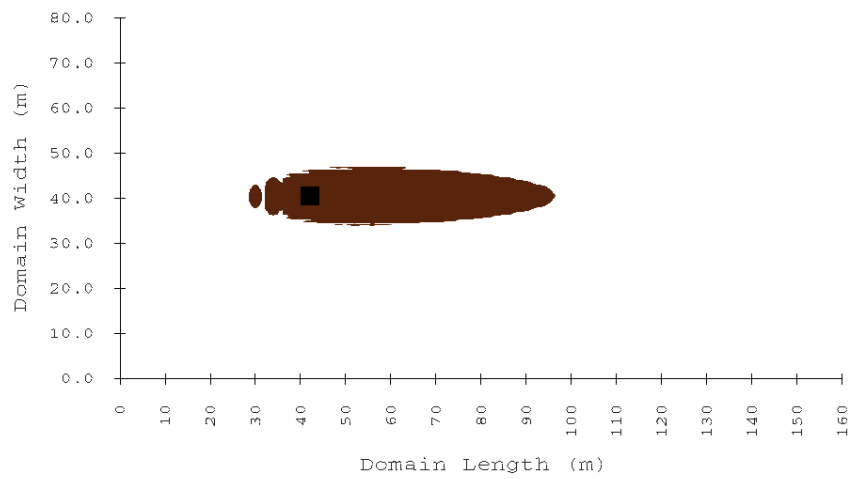


Figure 4-1: Benzene plume 0.005 mg/L contour after 30 years (Scenario A)

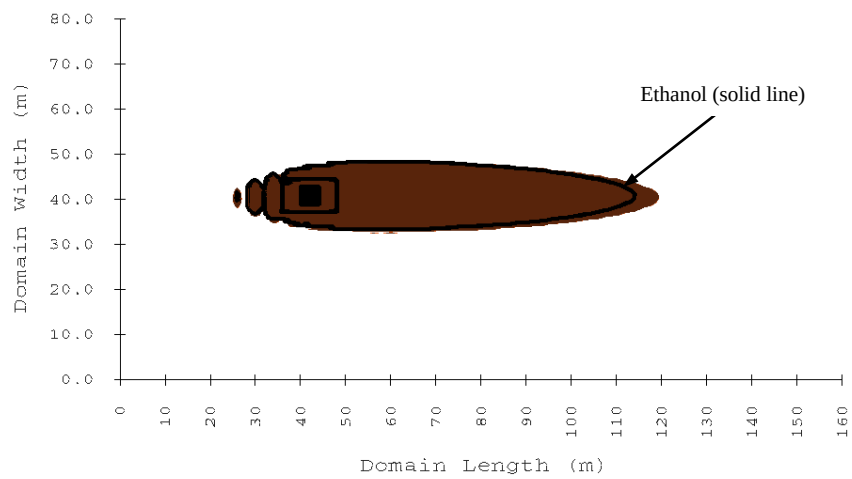


Figure 4-2: Benzene and ethanol plume 0.005 mg/L contours after 30 years (Scenario B)

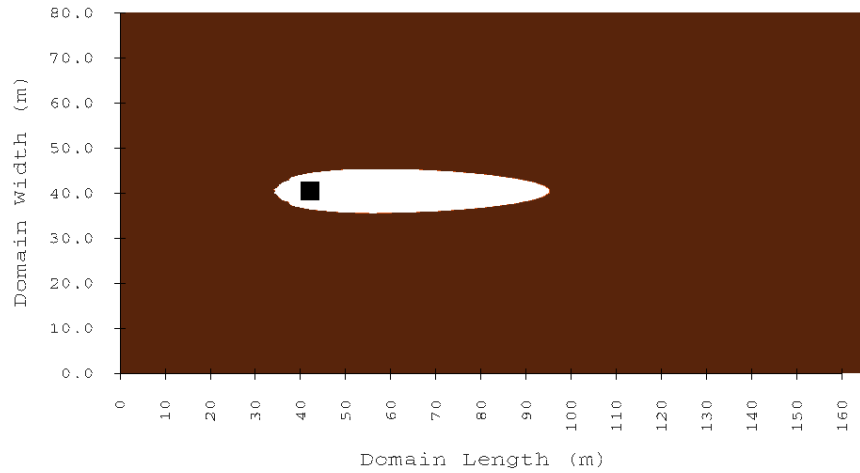


Figure 4-3: Oxygen depletion 0.1 mg/L contour after 30 years (Scenario A)

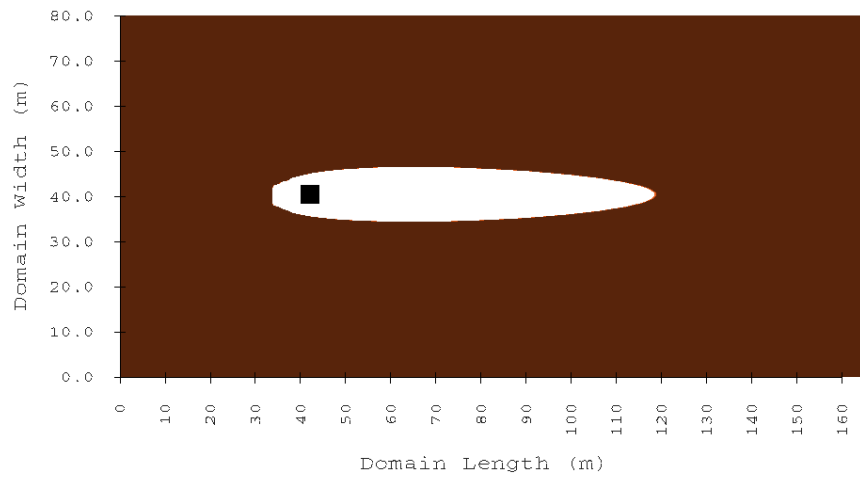


Figure 4-4: Oxygen depletion 0.1 mg/L contour after 30 years (Scenario B)

Ethanol-Blended Fuel Simulations

Several simulations of Scenario B were performed to determine the effects of the specific growth rate of methanogenic ethanol and benzene degraders, $\hat{\mu}_{EtOH, Met2}$, on benzene plume length. Table 4-1 shows how the length of the benzene plume along the centerline, at the end of the 30-year simulation, depends on the specific growth rate. Note the benzene plume length is normalized to the benzene plume length without ethanol (Scenario A), which is 68 m. Furthermore, as the methanogens specific growth rate ($\hat{\mu}_{EtOH, Met2}$) increases, simulations indicated the benzene plume length decreases.

Table 4-1: Effects of Specific Growth Rate on Benzene Length

$\hat{\mu}_{EtOH, Met2}$ (1/d)	Normalized Length
0.1	2.12
0.6	1.71
0.8	1.41
1.1	0.59

Based on simulations of scenarios A and B, the current model reproduced the results shown in Gomez et al. (2008). Table 4-2 compares the benzene, oxygen depletion, and ethanol centerline plume lengths simulated by the model for both Scenarios A and B with the results of Gomez et al. (2008). Scenario B is based on the specific growth rate of methanogens (ethanol and benzene degraders), $\hat{\mu}_{EtOH, Met2} = 0.8/\text{d}$.

Table 4-2: Summary of Plume Lengths of Scenario A & B Simulations

	Scenario A		Scenario B	
	Current Study	Gomez et al. (2008)	Current Study	Gomez et al. (2008)
Benzene plume (m)	68	75	96	100
Oxygen depletion plume (m)	61	64	90	90
Ethanol plume (m)	N/A	N/A	92	90

Additional simulations were performed to include biodegradation of contaminants under sulfate redox condition as sulfate is also a major dissolved electron acceptor in aquifers throughout the U.S. (Mackay et al., 2006). These additional simulations considered biodegradation occurring in an aerobic environment where, due to the contamination, redox conditions changed to sulfate-reducing and ultimately, to methanogenic. The simulations utilized the same contaminant source as was used above, in Scenarios A and B. Figure 4-5 to 4-11 illustrate the resulting electron donor plumes, as well as electron acceptor depletion plumes, at the end of a 30-year simulation.

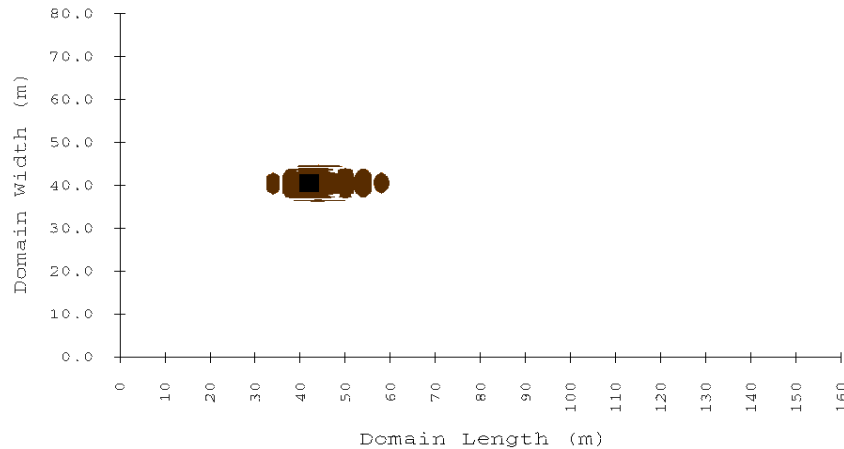


Figure 4-5: Benzene plume 0.005 mg/L contour after 30 years (Scenario A). Model includes sulfate reduction.

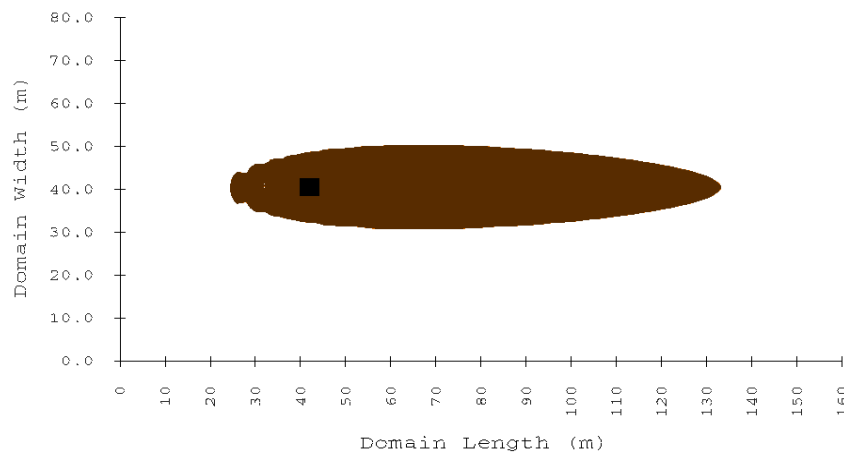


Figure 4-6: Benzene plume 0.005 mg/L contour after 30 years (Scenario B). Model includes sulfate reduction.

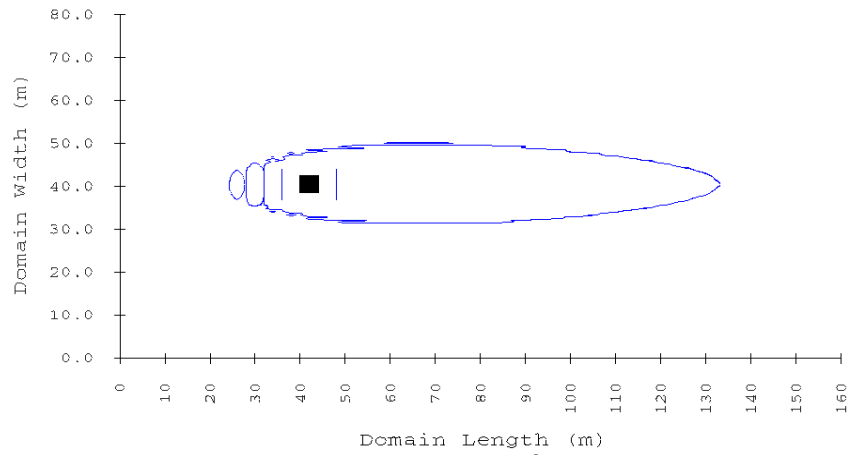


Figure 4-7: Ethanol plume 0.005 mg/L contour after 30 years (Scenario B). Model includes sulfate reduction.

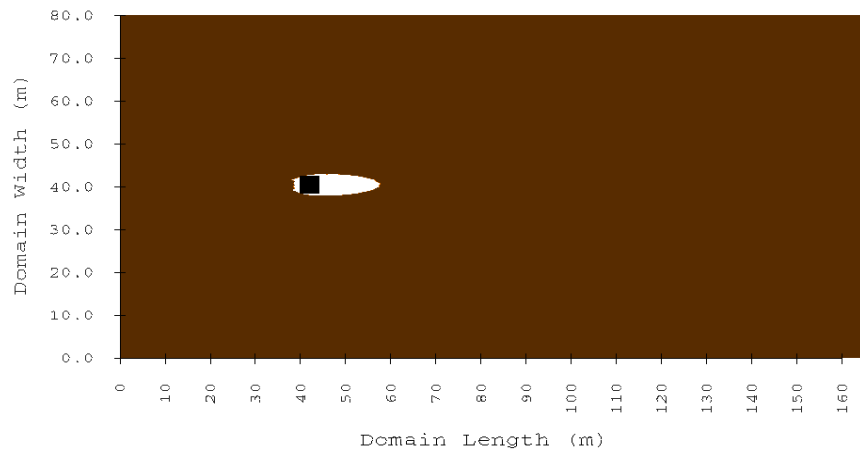


Figure 4-8: Oxygen depletion plume 0.1 mg/L contour after 30 years (Scenario A). Model includes sulfate reduction.

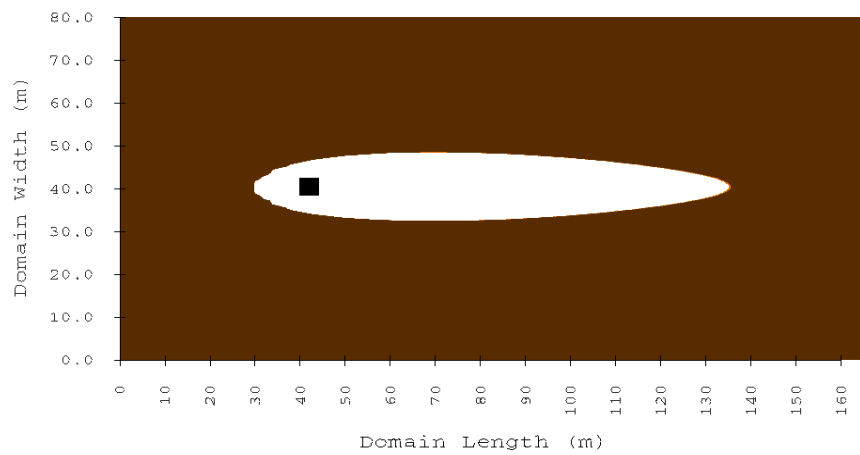


Figure 4-9: Oxygen depletion plume 0.1 mg/L contour after 30 years (Scenario B). Model includes sulfate reduction.

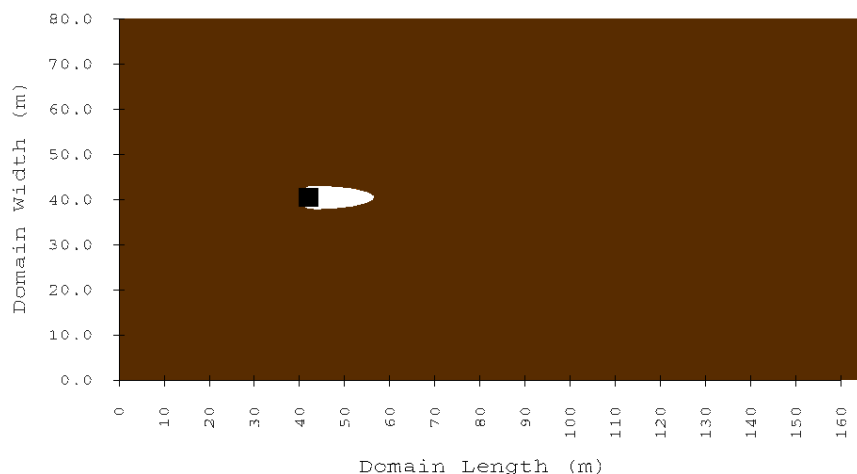


Figure 4-10: Sulfate depletion plume 9.6 mg/L contour after 30 years (Scenario A).
Model includes sulfate reduction.

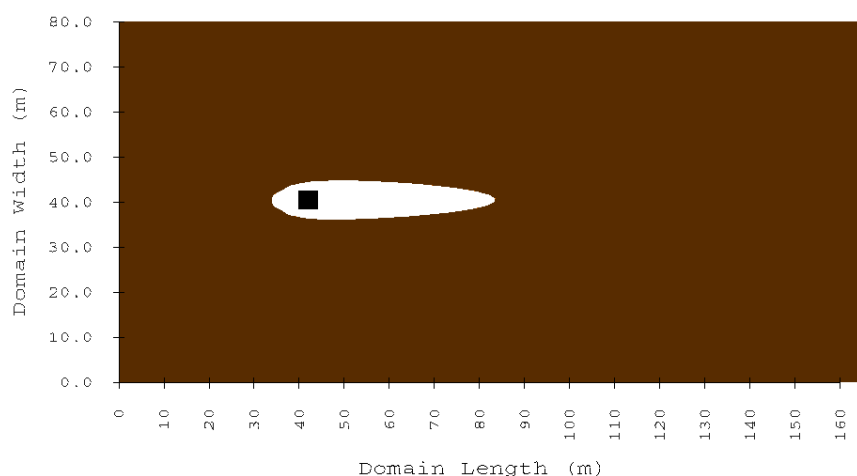


Figure 4-11: Sulfate depletion plume 9.6 mg/L contour after 30 years (Scenario B).
Model includes sulfate reduction.

In the case without ethanol (Scenario A), biodegradation of contaminants with dissolved sulfate available as an additional electron acceptor significantly reduced benzene's downgradient migration (compare Figure 4-1, where sulfate reduction is not simulated, with Figure 4-5, where it is). The modeling results appear to qualitatively match the field observations of Mackay et al. (2006). In the field study at Vandenberg AFB, Mackay et al. (2006) observed a very short benzene plume when no ethanol was present. The plume extended only 3.3 m downgradient of the source (compared to a

plume that was 50 m when ethanol was present. The simulation in Figure 4-5 showed that the benzene plume reached a maximum length of 28 m after 30 years (in fact, the simulated plume reached its steady-state length after approximately 6 years). This compares with a simulated benzene plume length of 110 m when ethanol was present (see Figure 4-6).

With the relatively high concentration of available sulfate (96 mg/L), the simulation showed that degradation of benzene resulted in a relatively small portion of the aquifer with depleted sulfate (Figure 4-10). Mackay et al. (2006) similarly noted that at the Vandenberg AFB site, where sulfate concentrations were comparable to the concentrations used in the model simulation (mean of 96 mg/L), the zone of depleted sulfate in the aquifer was small. In addition, the availability of high dissolved sulfate concentrations (96 mg/L) slows down the development of methanogenic conditions. Methanogenic degradation is noticeable after 300 days (Figure 4-12a) and a methanogenic zone remains within 4-6 m downgradient from the source (Figure 4-12b).

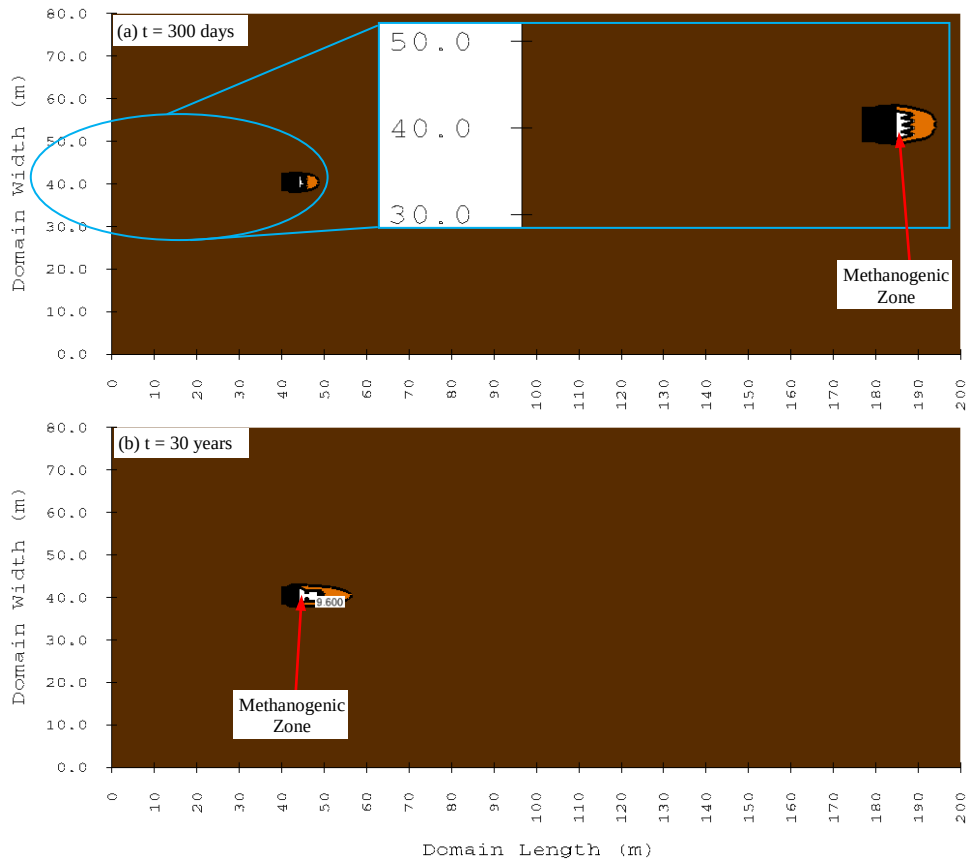


Figure 4-12: Depleted sulfate 0.1 mg/L and 9.6 mg/L contours (Scenario A) at: (a) $t = 300$ days and (b) $t = 30$ years. Model includes sulfate reduction. Methanogenic zone defined as the area where the dissolved sulfate concentration is less than 0.1 mg/L.

In contrast, the ethanol-blended fuel has more profound effects on benzene degradation under sulfate-reducing conditions. In the presence of high concentrations of ethanol, dissolved oxygen and sulfate are quickly diminished. Comparing Figure 4-10 and Figure 4-11, it's obvious that the sulfate depleted zone is more pronounced when ethanol is present. Methanogenic conditions occur much earlier (within 30 days) when ethanol is present (Figure 4-13a). Additionally, the methanogenic zone extends up to 8 m downgradient from the source zone by day 300 (Figure 4-13b); then the zone gradually decreases to 4 m at the end of the 30-year simulation (Figure 4-13c).

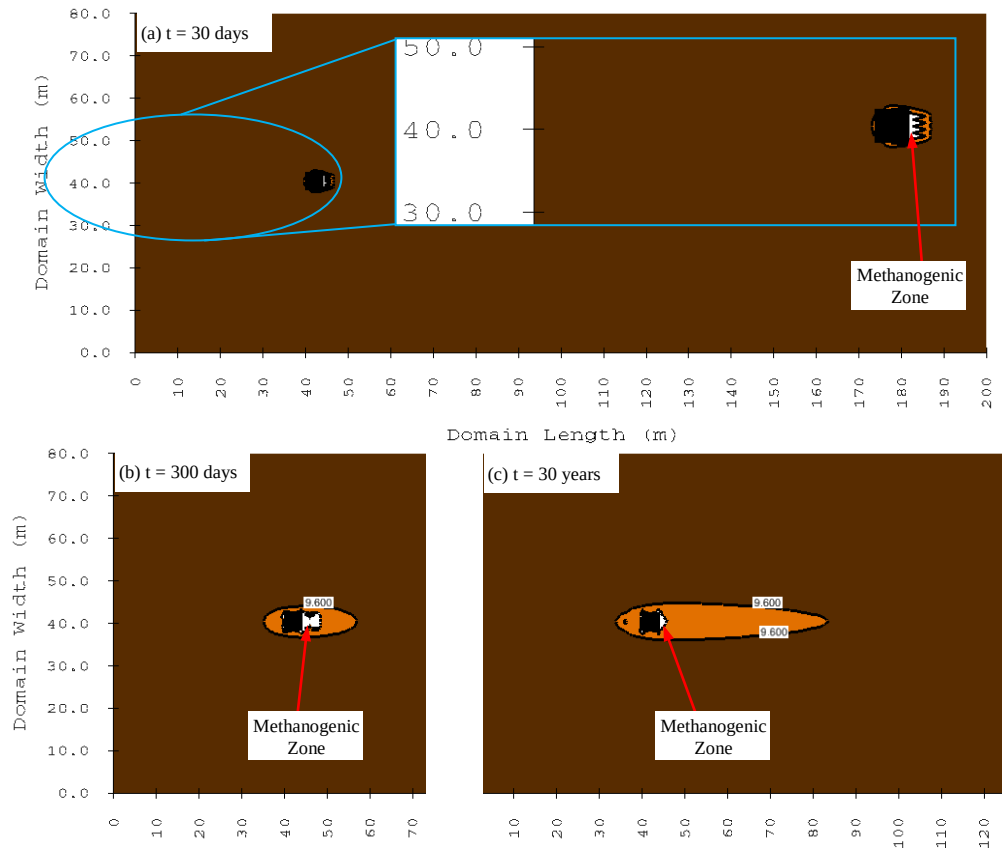


Figure 4-13: Depleted sulfate 0.1 mg/L and 9.6 mg/L contours (Scenario B) at: (a) $t = 30$ days, (b) $t = 300$ days, (c) $t = 30$ years. Model includes sulfate reduction. Methanogenic zone defined as the area where the dissolved sulfate concentration is less than 0.1 mg/L.

The model simulations produced results that were qualitatively similar to what was observed in the field study at Vandenberg AFB, which indicated the presence of ethanol considerably diminished dissolved sulfate concentrations, subsequently leading to the development of methanogenic conditions (Mackay et al., 2006). Simulation estimated that the benzene plume approached its steady-state length of 108 m (385 percent longer than the plume without ethanol) at ~ 20 years. Further, the model simulation found that the plume is 12 m longer than the plume in Scenario B without sulfate reduction. This may be due to the fact that the growth rate of methanogens, using benzene as a substrate in Scenario B, is twice the growth rate of sulfate-reducing bacteria

(Table 3-6); hence, a longer benzene plume is simulated when sulfate reduction dominates. However, the difference in growth rates between sulfate-reducing bacteria and methanogens noted above may not be realistic. Although the Table 3-6 parameter values were obtained from experimental studies, the fact that the values were obtained from different studies may mean they are not directly comparable. Thus, the Figure 4-2 and Figure 4-6 simulations should be compared with caution. In the field, Mackay et al. (2006) observed “the shortening of the ethanol-impacted benzene plume” after seven months, an observation that the model was not able to predict. Several environmental factors may have helped to shorten the benzene plume in the field study: increased availability of sulfate and other electron acceptors resulting from several large rain events (Mackay et al., 2006). Overall, the model produced sulfate depletion and benzene plume footprints that were qualitatively analogous to field observations—the presence of ethanol rapidly depletes the terminal electron acceptors and causes benzene to be more persistent in groundwater.

4.3. Model Prediction: Butanol-blended Fuel

The potential environmental impact of butanol-blended fuel was evaluated by simulating scenarios C, D, and E using a constant contaminant source as described in Chapter 3. Scenario C considered contaminant degradation under aerobic and methanogenic redox conditions. The model initially simulated the scenario with benzene and butanol concentrations specified at 10 mg/L and 1000 mg/L, respectively. Figure 4-14 provides a snapshot of butanol and benzene footprints at ~9.25 years. Beyond 9.25 years, both plumes continue to expand outside the simulation domain. Figure 4-15 shows

the butanol footprint overlapping the depleted oxygen zone (non-shaded area). It is evident that butanol reduces the availability of oxygen needed for the aerobic biodegradation of benzene and generates a substantial methanogenic zone. Simulation of Scenario C with Bu20 blend was not performed because the large butanol concentration (10500 mg/L) source would exert an extremely high demand for oxygen—the benzene plume would persist longer in groundwater and extend well beyond the simulation boundaries.

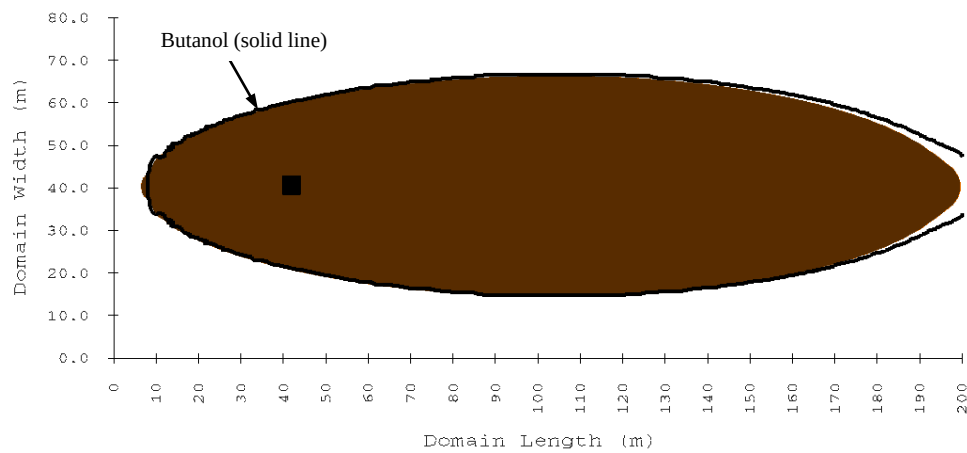


Figure 4-14: Benzene and butanol 0.005 mg/L contours at 9.25 years (Scenario C)

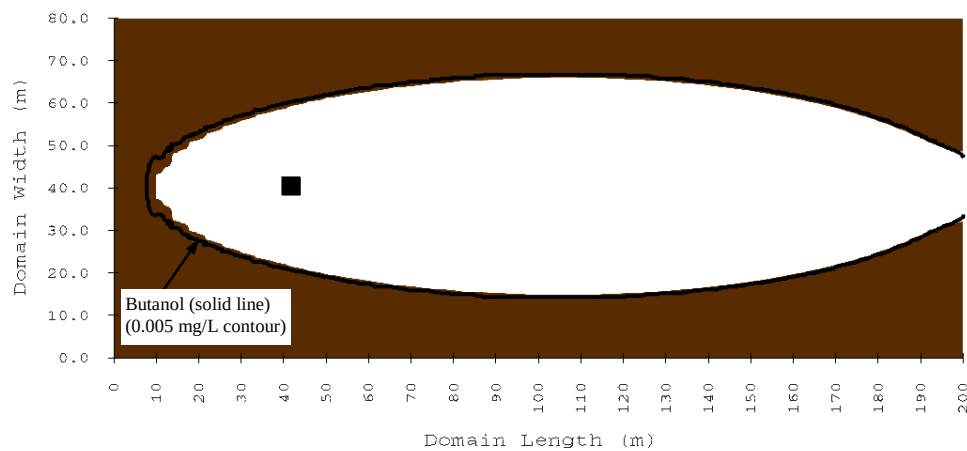


Figure 4-15: Butanol 0.005 mg/L contour and depleted oxygen zone (0.1 mg/L contour) at 9.25 years (Scenario C)

Scenarios D and E evaluated the fate and transport of benzene and butanol under aerobic, sulfidogenic, and methanogenic redox conditions. Bu0 and Bu20 blends were used as continuous NAPL sources for these simulations. As discussed in Chapter 3, the input benzene concentration for Scenario D is 18 mg/L while Scenario E has benzene at 13 mg/L and butanol at 10500 mg/L as input concentrations. The results for these simulations are as follows.

The model indicated that a Bu0 fuel blend would result in a benzene plume length of 32 m after ~4.9 years. At that time, steady-state conditions are attained, and the benzene plume remains at 32 m for the remaining 25 years (Figure 4-16). Figure 4-17 and Figure 4-18 show that the extent of the depleted oxygen and sulfate plumes are small. These results are similar to the results in Scenario A with sulfate reduction (see Figures 4-5, 4-8, and 4-10) despite a slightly larger initial benzene concentration here.

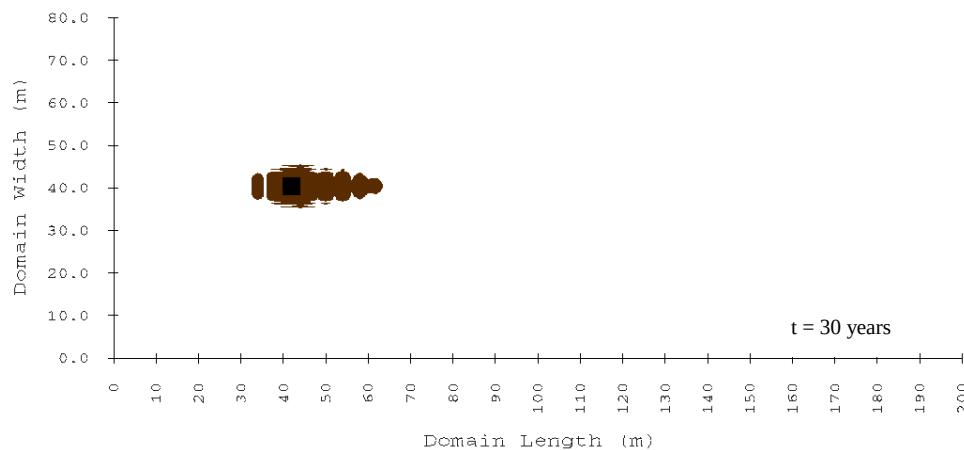


Figure 4-16: Benzene plume 0.005 mg/L contour with Bu0 as a continuous NAPL source at 30 years (Scenario D)

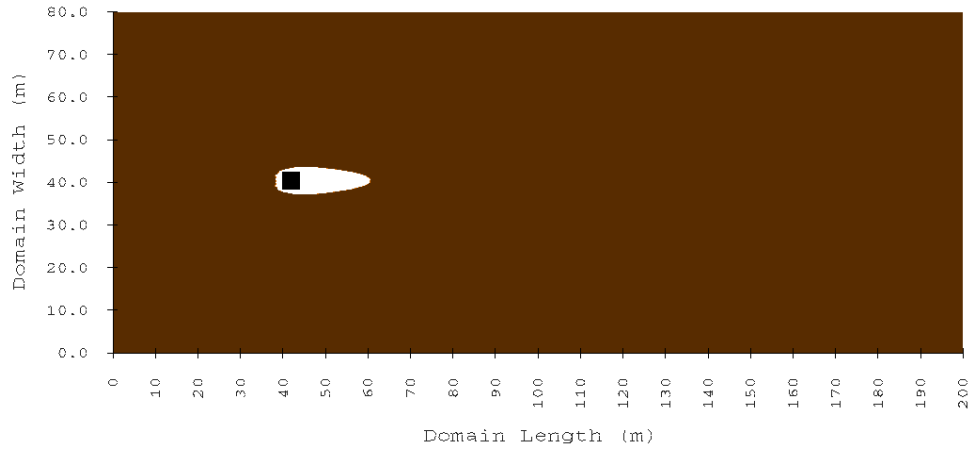


Figure 4-17: Depleted oxygen 0.1 mg/L contour with Bu0 as a continuous NAPL source at 30 years (Scenario D)

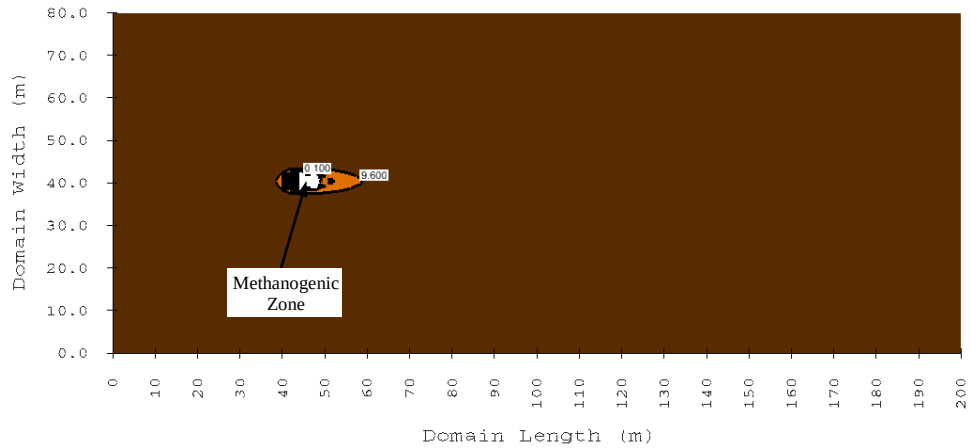


Figure 4-18: Depleted sulfate 0.1 mg/L and 9.6 mg/L contours with Bu0 as a continuous NAPL source at 30 years (Scenario D). Methanogenic zone defined as the area where the dissolved sulfate concentration is less than 0.1 mg/L.

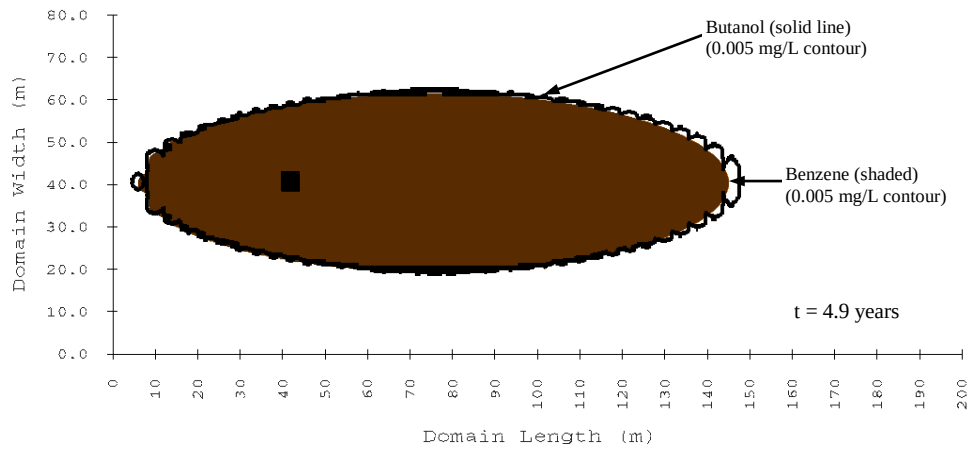


Figure 4-19: Benzene and butanol footprints with Bu20 as a continuous NAPL source after 4.9 years (Scenario E)

Gasoline with 20 percent butanol by volume (Bu20) generates a sizeable benzene footprint (Figure 4-19). The model simulation showed a Bu20 fuel blend (benzene concentration at source = 13 mg/L; butanol concentration at source = 10500 mg/L) leads to a continuously growing benzene plume. A recent publication also noted this effect at even a smaller butanol concentration (3800 mg/L) (Gomez and Alvarez, 2010).

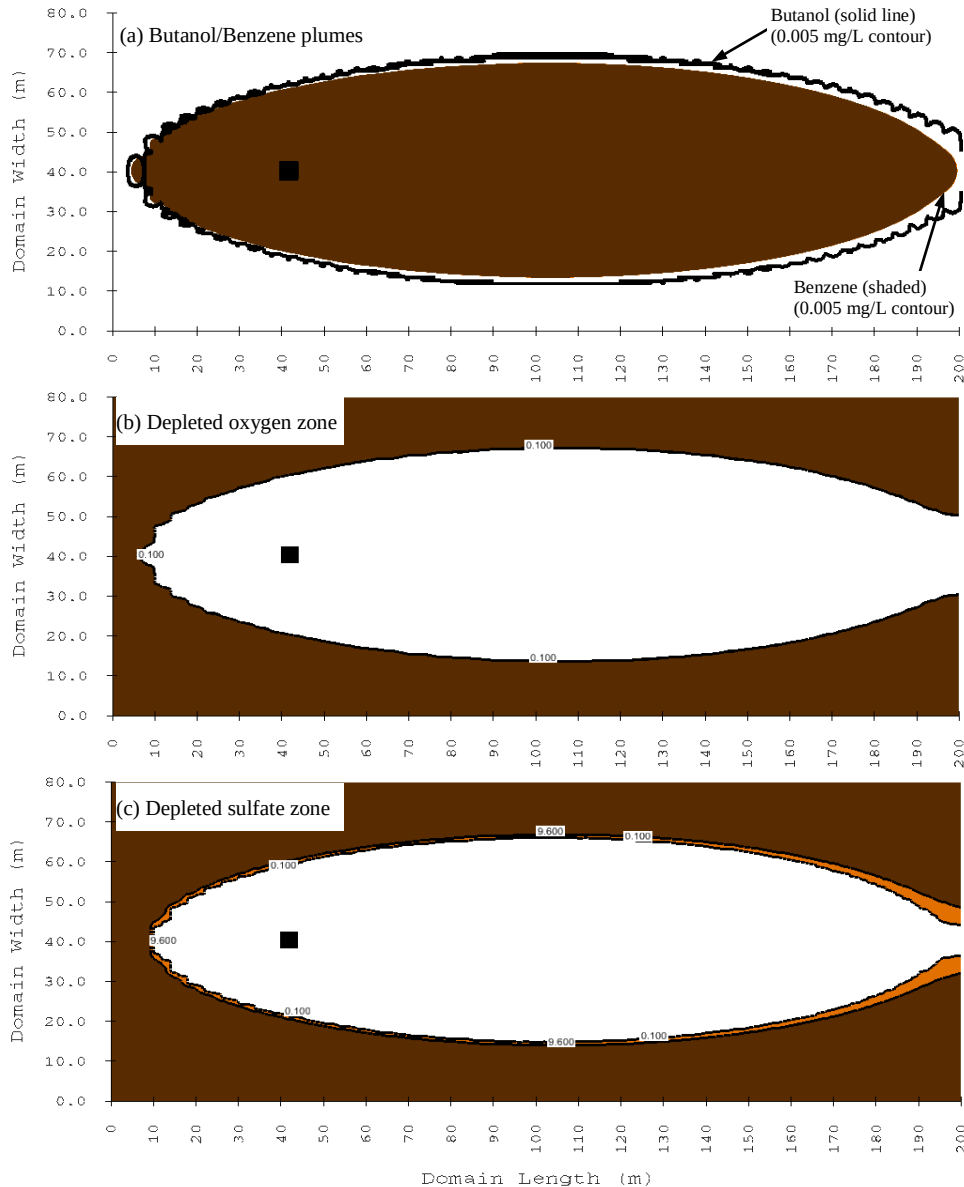


Figure 4-20: (a) Butanol and benzene, (b) depleted oxygen, and (c) depleted sulfate plumes with Bu20 as a continuous NAPL source after 8.5 years (Scenario E)

Comparing Figures 4-16 and 4-19 (recalling that in Figure 4-16, steady-state benzene concentrations were attained after 4.9 years) it is evident that addition of 20 percent butanol has an extremely large impact on the length of the benzene plume (32 m without butanol versus >140 m with butanol). Furthermore, butanol and benzene plumes increasingly grow and extend beyond the simulation domain after 8.5 years. Figure 4-20 illustrates that as the butanol plume expands, electron acceptors (*i.e.*, dissolved oxygen and sulfate) are increasingly depleted downgradient. Both simulation Scenarios C and E suggest that butanol in gasoline hinders the natural degradation of fuel components like benzene. The hazardous aromatic components of gasoline would persist longer in groundwater, degrading water quality and increasing the risk of exposure.

4.4. Sensitivity Analysis

The model includes 48 biodegradation kinetic parameters. Although a thorough sensitivity analysis for each parameter was considered, only one parameter was analyzed in this study, specifically, microbial decay rate of methanogens (b_{Met}). Aquifer properties (*i.e.*, hydraulic conductivity, porosity, and hydraulic gradient) and other biodegradation kinetic parameters had been shown to affect benzene degradation and consequently, benzene plume length (Gomez et al., 2008; Gomez and Alvarez, 2010). Furthermore, there is a rather considerable difference between specific growth rates of methanogens ($\hat{\mu}_{Bu, Met1}$ and $\hat{\mu}_{Bu, Met2}$) in utilizing butanol (Table 3-10) and decay rate, b_{Met} (Table 3-12). Both specific growth rates are half of the decay rate (0.015/d vs. 0.03/d). Typically, growth rates are larger than decay rates. Hence, the sensitivity of the results (*i.e.*, benzene plume length) to reducing b_{Met} was examined.

Scenario C was simulated with 1000 mg/L butanol and 10 mg/L benzene as a continuous NAPL source. Table 4-3 lists the lengths of the benzene plume centerline simulated by the model at 9 years for various values of the methanogen decay rate. As expected, the benzene plume length becomes shorter as the decay rate becomes smaller.

Table 4-3: Sensitivity of Plume Length to Microbial Decay Rate

b_{Met} (1/d)	Plume Length at 9 years (m)	Comments
0.03	188	Baseline
0.003	138	10% of baseline
0.00045 ^a	118 ^b	1.5% of baseline

^aValue is 3.0% of $\hat{\mu}_{Bu, Met1}$ and $\hat{\mu}_{Bu, Met2}$.

^bPlume splits at 3.5 years—length was taken as the distance traveled by the downgradient plume (see Figure 4-25).

Simulations with decay rates of 0.003/d and 0.00045/d show that the benzene plume begins to retreat after ~12.7 and ~9 years, respectively. With a decay rate at 0.003/d, the benzene plume travels to a maximum length of 150 m after 12.7 years (Figure 4-21a) and then recedes to a steady-state length of 118 m (Figure 4-21b). The simulation showed the concentration of methanogens that degrade both butanol and benzene (X_6) significantly increases in the first 12.7 years. Butanol (and benzene, to some extent) stimulates microbial growth that enables an increase in substrate utilization. As a result, a gradual decrease of the benzene plume begins. Figure 4-22 shows the concentration profile for the methanogens (X_6) after 30 years. Note from Table 3-8 that the initial concentration of methanogens is 0.001 mg/L. Clearly, the methanogens have grown within the benzene and butanol plumes, eventually attaining a level that prevents the benzene from migrating further downgradient.

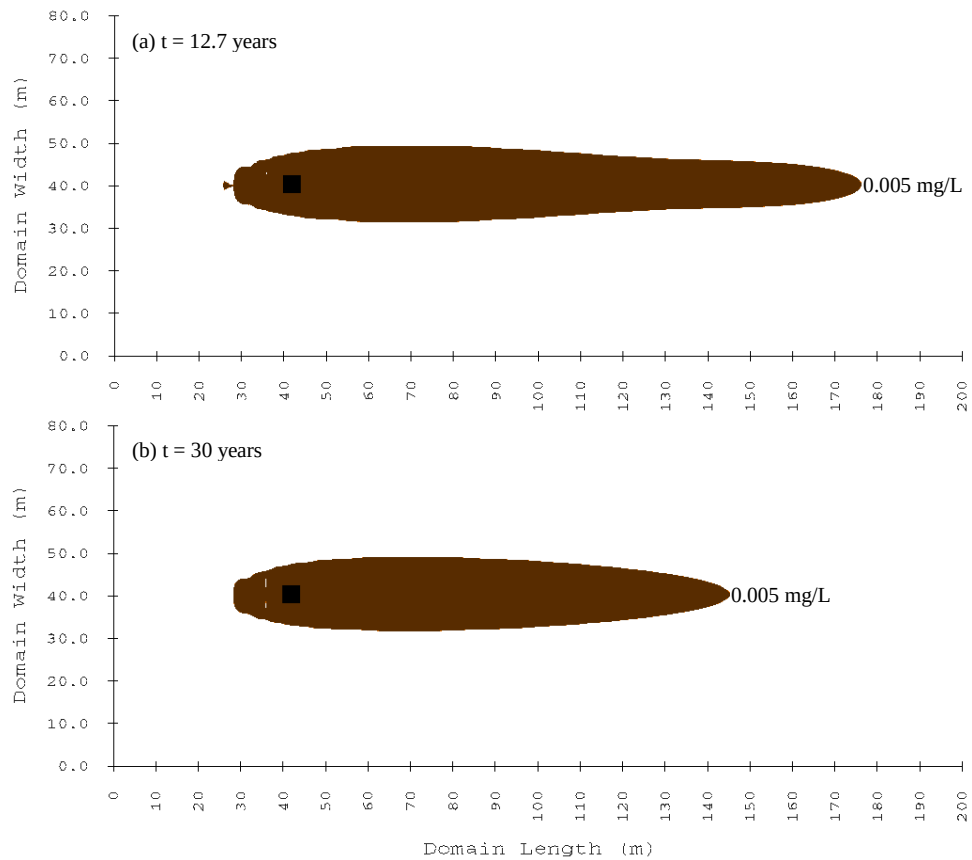


Figure 4-21: Benzene plumes after (a) 12.7 years, and (b) 30 years simulated with $b_{Met} = 0.003/d$

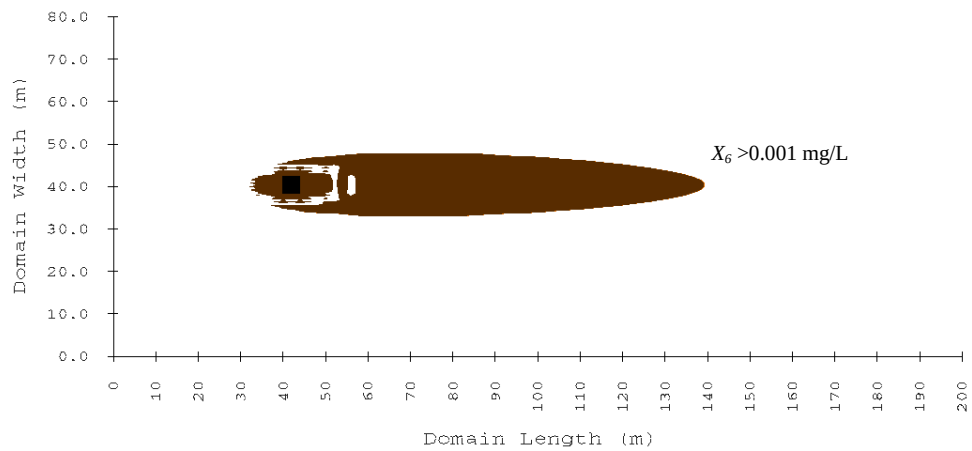


Figure 4-22: Concentration profile of X_6 at 30 years ($b_{Met} = 0.003/d$)

With the decay rate specified at a very low rate, 1.5 percent of the baseline decay rate, the benzene plume exhibits some interesting behavior; separating after 3 years and forming two distinct plumes at 3.5 years, as shown in Figure 4-23b. When the plumes

originally form and the initial concentration of butanol/benzene degraders is low, the benzene plume expands. As more and more butanol/benzene degraders grow, especially near the source where there are high concentrations of butanol (see Figure 4-24), the microbes start to degrade the benzene and therefore, the plume splits. This splitting behavior is similar to the degradation of benzene that was observed under sulfate redox conditions in the aquifer at Vandenberg AFB (Mackay et al., 2006) and the results of a modeling study that was published recently (Gomez and Alvarez, 2010).

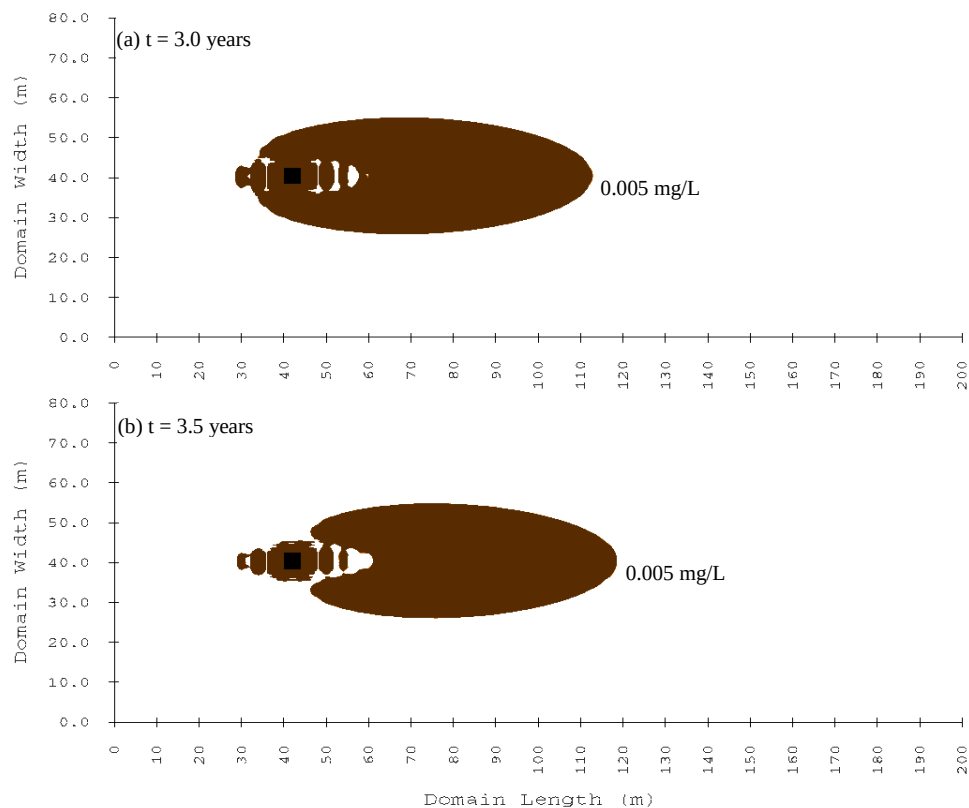


Figure 4-23: Benzene plumes after (a) 3 years, and (b) 3.5 years simulated with $b_{Met} = 0.00045/d$

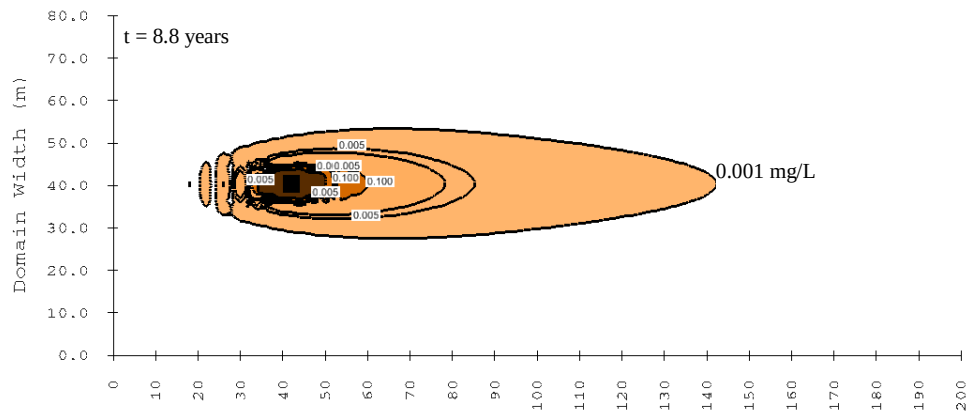


Figure 4-24: Butanol/benzene degraders concentration (X_6) contours after 8.8 years ($b_{Met} = 0.00045/\text{d}$)

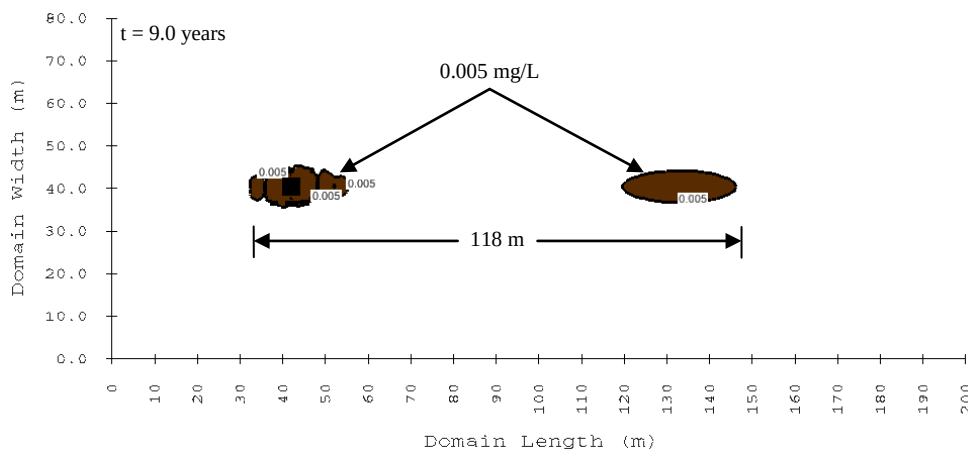


Figure 4-25: Benzene plumes 0.005 mg/L contours at $t = 9.0$ years ($b_{Met} = 0.00045/\text{d}$)

After the plumes split, the leading plume continues to migrate downgradient with continual degradation. The plume travels as far as 110 m from the contaminant source in 9.0 years as depicted in Figure 4-25 and completely degrades by 9.5 years. The plume closest to the source (Figure 4-25) continues to expand, but ultimately, reaches steady-state length of 28 m at 20 years (Figure 4-26). At steady-state, benzene is being degraded by the butanol/benzene degraders near the source at the same rate that benzene enters the aquifer from the source. Figure 4-27 shows the concentration contours of methanogens that degrade both benzene and butanol at steady-state (X_6). It appears that a microbial

barrier is formed consisting of methanogenic benzene and butanol degraders that are at high enough concentrations to completely degrade benzene emanating from the source zone.

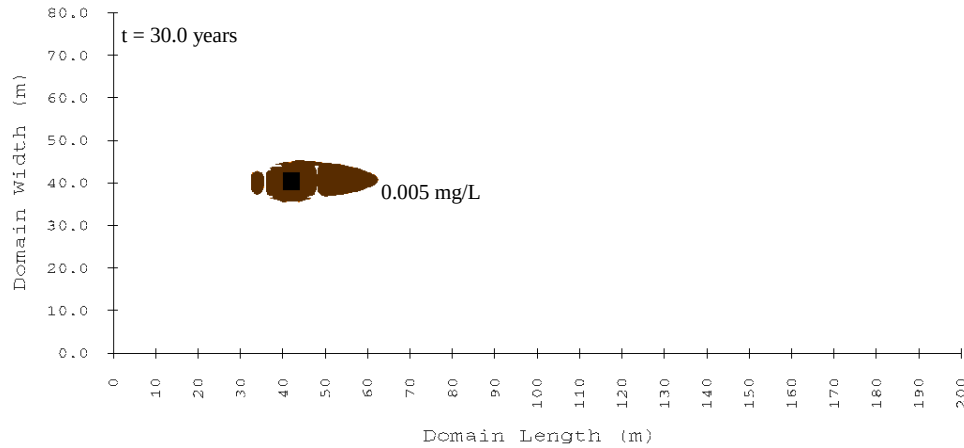


Figure 4-26: Steady-state benzene concentration contour at 30 years ($b_{Met} = 0.00045/d$)

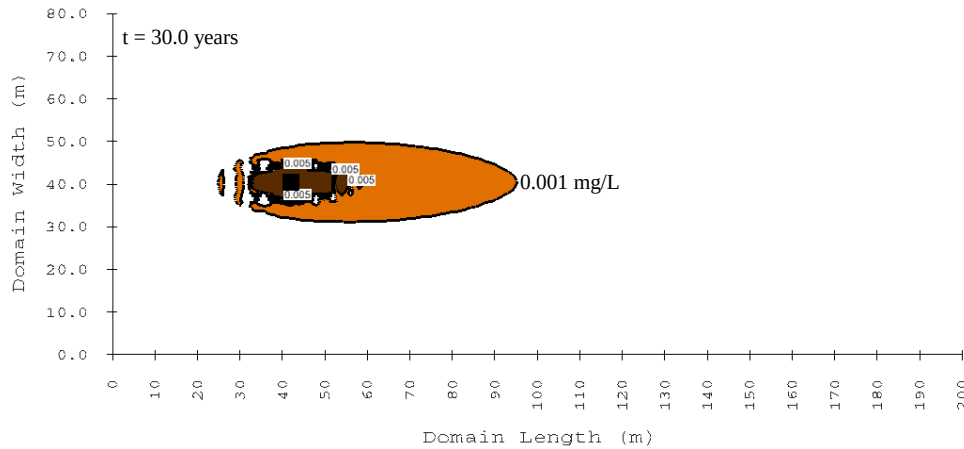


Figure 4-27: Steady-state methanogens concentration (X_6) contours at 30 years ($b_{Met} = 0.00045/d$)

As indicated earlier, the model has a fairly large number of parameters. In the above analysis, it was found that changing only one of these parameters, the microbial decay rate, led to very different benzene plume behaviors. Clearly, due to the complexity of the system that is being modeled (*e.g.*, the number of parameters and processes, the complex interaction between processes), a number of very different results with regard to

benzene plume extent and persistence can be envisioned. The value of a model is that it allows the user to test different system components, and evaluate their influence on results.

5.0. Conclusions and Recommendations

5.1. Summary

Reducing our dependence on imported oil, environmental concerns, and rising energy costs have sparked the development of alternative fuels. This study examined the potential impact to the subsurface environment of replacing ethanol, which is currently being added to gasoline, with biologically derived butanol. For various reasons, butanol is being seriously considered as an ethanol replacement. The addition of ethanol to gasoline has been observed to interfere with the natural processes that reduce the mass and concentration of aromatic hydrocarbons, especially the carcinogen benzene, in groundwater. It is possible that spills and leaks of butanol-blended fuel may have a similar, or even a more pronounced effect, and result in more persistent hazardous aromatic hydrocarbon groundwater plumes. The thesis examined the potential impacts of butanol-blended gasoline on the subsurface environment. A model was developed to evaluate how adding butanol into combustion fuels, as is likely in the near future, might adversely impact groundwater quality due to the inevitable spills and leaks that will occur. The model was incorporated as a component of DoD's suite of models—the Groundwater Modeling System—to simulate the fate and transport of contaminants in the subsurface and to assess potential impacts on groundwater supplies.

5.2. Conclusions

Fuel spills and leaks from storage tanks can contaminate groundwater. Biodegradation is an essential process that can prevent the spreading of contaminants and reduce the extent of environmental damage. The main focus of this research was to use a

numerical model to evaluate how adding butanol into combustion fuels might interfere with the degradation of hazardous contaminants and adversely impact groundwater quality. The following highlight important aspects in regard to the model and the potential impact of butanol-blended fuel.

Model

1. A version of the model that simulated an ethanol-blended fuel release into groundwater was verified with comparison to the previous modeling studies of Gomez et al. (2008) and Gomez and Alvarez (2010).
2. The model qualitatively simulated observations made in a field experiment at Vandenberg AFB (Mackay et al., 2006).
3. The model developed in this study extended the work of Gomez et al. (2008) by accounting for sulfate reduction. It was found that when sulfate-reduction is accounted for, the benzene plume length for release of a fuel without ethanol decreases from the plume length simulated when sulfate reducing conditions are ignored. It was also found that when sulfate reduction is accounted for, the benzene plume length for release of a fuel with ethanol is approximately four times greater than the length of a plume without ethanol.

Butanol-blended Fuel

Model simulations indicate that releases of butanol-blended gasoline would have significant impacts on groundwater quality because:

1. Spills or leaks resulted in longer and more persistent benzene plumes compared to gasoline without butanol.

2. Butanol remains in the environment longer than ethanol; thereby facilitating depletion of electron acceptors and inhibiting benzene biodegradation.

5.3. Recommendations for Future Study

Based on the above conclusions from this thesis, it is apparent that additional study is necessary to thoroughly assess the impacts on groundwater of a decision to blend butanol with gasoline. Here are some recommendations for these additional studies:

Model Validation

The model involves numerous simplifying assumptions (*e.g.*, which processes are important, simplified mathematical descriptions of those processes, use of parameters that may be constant in space and time). Thus, it is important to validate the model by comparing model results with field or laboratory experimental data.

Additional Sensitivity Analyses

Although sensitivity analyses have been done on some hydrogeochemical parameters by others and were not examined in this study, the model uses a large number of parameters, many of which are difficult to measure. In order to guide future studies and site investigations, additional sensitivity analyses should be conducted to identify those parameters that have the most significant effects on subsurface fate and transport.

Integrating Other Processes

A continuous contaminant source was employed for all simulation scenarios considered in this study. Simulation of a finite release of contaminants into the subsurface might better reflect some real world fuel leaks or spills. In addition, it might be useful to examine fuel blends with higher butanol content and expand the model to

incorporate the effects of butanol toxicity on microbial communities, particularly under sulfate redox conditions. This would be similar to the work done by (Gomez and Alvarez, 2010), who examined the effect of toxicity of different alcohols, but in the absence of sulfate reduction. It is also recommended that future studies assess the impact on BTEX fate and transport of butanol as a solvent. Butanol may dissolve aromatic hydrocarbons like BTEX, which could enhance BTEX migration and further impact groundwater quality. Other important processes that may be incorporated into models simulating the fate and transport of butanol-blended fuels could include: potential of microbial growth to cause bioclogging; the production, decay, and transport of intermediate biodegradation products; and buoyancy effects of butanol.

Appendix A: Contaminant Source Input Concentrations Estimation

Volume of Water (L) = 48000

	Butanol	Gasoline	Benzene
S.G.	0.81	0.72	0.88
MW	74.12	100	78.11
Solubility (mg/L)	77000		1780

	Volume (L)				Mass (kg)			Conc. (mg/L)	
	Total	Butanol	Gasoline	Benzene	Butanol	Gasoline	Benzene	Butanol	Benzene
Bu0	100	0	100	1.3	0.000	72.000	1.144	0.00	23.83
Bu20	100	20	80	1.04	16.200	57.600	0.915	337.30	19.07
Bu50	100	50	50	0.65	40.500	36.000	0.572	843.75	11.92
Bu85	100	85	15	0.195	68.850	10.800	0.172	1434.38	3.58

	Mole				Mole Fraction		Effective Solubility (mg/L)		Input Conc. (mg/L)	
	Butanol	Gasoline	Benzene	Total	Butanol	Benzene	Butanol	Benzene	Butanol	Benzene
Bu0	0	720	14.6	720	0.0000	0.0203	0	36	0	18
Bu20	219	576	11.7	795	0.2751	0.0147	21181	26	10590	13
Bu50	546	360	7.3	906	0.6028	0.0081	46418	14	23209	7
Bu85	929	108	2.2	1037	0.8958	0.0021	68980	4	34490	2

$$mass_i (kg) = V_i (L) \cdot SG_i$$

$$mole_i = \frac{mass_i (kg)}{MW_i} \cdot \left(\frac{1000g}{kg} \right)$$

$$mole_{TOT} = mole_{BuOH} + mole_{Gasoline}$$

$$X_i^O = \frac{mole_i}{mole_{TOT}} = \text{mole fraction of } i$$

$$S_{eff,i} = X_i^O S_i^w = \text{effective solubility}$$

Appendix B: Biodegradation Kinetics Parameters Used in Simulations

VALUES USED TO PRODUCE THE FOLLOWING FIGURES									
Parameter	Unit	F.4-1	F.4-2	F.4-5	F.4-6	F.4-14	F.4-16	F.4-19	See (*)
$\hat{\mu}_{B,Aer}$	d ⁻¹	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
$Y_{B,Aer}$	mg/mg	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39
$K_{B,Aer}$	mg/L	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.6
$\mu_{B,SRB}$	d ⁻¹	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
$Y_{B,SRB}$	mg/mg	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
$K_{B,SRB}$	mg/L	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
$\mu_{B,Met}$	d ⁻¹	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
$Y_{B,Met}$	mg/mg	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
$K_{B,Met}$	mg/L	21.6	21.6	21.6	21.6	21.6	21.6	21.6	21.6
$\mu_{Bu,Aer1}$	d ⁻¹	11.0	11.0	11.0	11.0	6.5	6.5	6.5	6.5
$Y_{Bu,Aer1}$	mg/mg	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$K_{Bu,Aer1}$	mg/L	63.1	63.1	63.1	63.1	7.8	7.8	7.8	7.8
$\mu_{Bu,Aer2}$	d ⁻¹	11.0	11.0	11.0	11.0	6.5	6.5	6.5	6.5
$Y_{Bu,Aer2}$	mg/mg	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$K_{Bu,Aer2}$	mg/L	63.1	63.1	63.1	63.1	7.8	7.8	7.8	7.8
$\mu_{Bu,SRB1}$	d ⁻¹	0.4	0.4	0.4	0.4	1.28	1.28	1.28	1.28
$Y_{Bu,SRB1}$	mg/mg	0.03	0.03	0.03	0.03	0.10	0.10	0.10	0.10
$K_{Bu,SRB1}$	mg/L	478	478	478	478	10	10	10	10
$\mu_{Bu,SRB2}$	d ⁻¹	0.4	0.4	0.4	0.4	1.28	1.28	1.28	1.28
$Y_{Bu,SRB2}$	mg/mg	0.03	0.03	0.03	0.03	0.10	0.10	0.10	0.10
$K_{Bu,SRB2}$	mg/L	478	478	478	478	10	10	10	10
$\mu_{B,Met1}$	d ⁻¹	1.10	1.10	1.10	1.10	0.015	0.015	0.015	0.015
$Y_{B,Met1}$	mg/mg	0.07	0.07	0.07	0.07	0.078	0.078	0.078	0.078
$K_{B,Met1}$	mg/L	78.9	78.9	78.9	78.9	20	20	20	20
$\mu_{B,Met2}$	d ⁻¹	1.10	1.10	1.10	1.10	0.015	0.015	0.015	0.015
$Y_{B,Met2}$	mg/mg	0.07	0.07	0.07	0.07	0.078	0.078	0.078	0.078
$K_{B,Met2}$	mg/L	78.9	78.9	78.9	78.9	20	20	20	20

VALUES USED TO PRODUCE THE FOLLOWING FIGURES									
Parameter	Unit	F.4-1	F.4-2	F.4-5	F.4-6	F.4-14	F.4-16	F.4-19	See (*)
b_{Aer}	d ⁻¹	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
b_{SRB}	d ⁻¹	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
b_{Met}	d ⁻¹	0.03	0.03	0.03	0.03	0.03	0.03	0.03	See (*)
K_O	mg/L	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
K_{SO_4}	mg/L	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
I_O	mg/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
I_{SO_4}	mg/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Initial Conditions:									
O	mg/L	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
SO_4	mg/L	0.0	0.0	96.0	96.0	0.0	96.0	96.0	0.0
X_1	mg/L	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
X_2	mg/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
X_3	mg/L	0.0	0.0	0.1	0.1	0.0	0.1	0.1	0.0
X_4	mg/L	0.0	0.0	0.001	0.001	0.0	0.001	0.001	0.0
X_5	mg/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
X_6	mg/L	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Benzene	mg/L	10	10	10	10	10	18	13	10
Butanol	mg/L	0	0	0	0	1000	0	10500	1000
Ethanol	mg/L	0	1000	0	1000	0	0	0	0

(*) Figure 4-21 ($b_{Met} = 0.003$) & Figure 4-23 ($b_{Met} = 0.00045$).

Values in **bold** and shaded cells indicate differences between the figures.

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14. ABSTRACT Fuel spills and leaks from storage tanks can contaminate groundwater. Typically in groundwater, hazardous aromatic hydrocarbons like benzene are attenuated through natural processes. However, it is possible that adding butanol to gasoline will interfere with these natural attenuation processes, so that spills and leaks of alternative fuels containing biobutanol may result in more persistent hazardous aromatic hydrocarbon plumes. This effect has already been observed with ethanol, which is currently added to gasoline. A numerical model was developed to simulate the subsurface fate and transport of butanol-blended fuel to assess the potential impacts of butanol on the natural attenuation of benzene. The model incorporated advection, dispersion, sorption, and biodegradation of contaminants in groundwater. The biodegradation of benzene and butanol was modeled using dual Monod kinetics with degradation occurring under aerobic and anaerobic (sulfate-reducing as well as methanogenic) redox conditions. Model simulations indicated that spills of butanol-blended gasoline resulted in benzene plumes that were longer and more persistent than plumes which resulted from spills of gasoline alone. Electron acceptors (oxygen and sulfate) are more available for biodegradation of benzene in fuel without butanol. The presence of butanol decreased the availability of electron acceptors—limiting benzene's degradation and causing longer plumes.					
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