# The Transport and Fate of Ethanol and BTEX in Groundwater Contaminated by Gasohol

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ABSTRACT: Ethanol is used a component in all gasoline in Brazil, and its use could increase significantly in the U.S. to meet the requirements of the Clean Air Act Amendments. Recent problems with ground water contamination by methyl tert-butyl ether (MTBE) have made policymakers more cognizant of the need to consider the overall impact of gasoline oxygenates in the environment. Therefore, a thorough understanding of the impact of incorporating ethanol as a gasoline component on the fate and transport of gasoline releases is required. This article provides a comprehensive review of the transport of ethanol and monoaromatic hydrocarbons (BTEX) in the subsurface following a gasohol spill. Two mechanisms related to the presence of ethanol are generally considered to impact BTEX transport. Ethanol can increase the aqueous concentration of BTEX compounds due to a cosolvent effect, and it can inhibit BTEX biodegradation by preferentially consuming electron acceptors and nutrients. Our review illustrates that cosolvent effects should be minor at the ethanol concentrations expected from gasohol spills. Nevertheless, the inhibition of BTEX biodegradation and the possible decrease in sorption-related retardation suggests that ethanol is likely to increase BTEX plume lengths. The net effect of ethanol on natural attenuation of BTEX is likely to be system specific, depending largely on the release scenario and the assimilative capacity of the aquifer.

**KEY WORDS:** oxygenates, ethanol, gasoline, dissolution, biodegradation, natural attenuation, cosolvency, benzene.

# I. INTRODUCTION

Under the Clean Air Act Amendments of 1990, oxygen-containing organic compounds must be added to gasoline in some areas of the U.S. to reduce air

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1064-3389/01/\$.50 © 2001 by CRC Press LLC pollution. Cities that are not in compliance with certain air quality standards must sell oxygenated gasoline (oxyfuel) that has been formulated to contain at least 2.7% oxygen (by weight) to reduce emissions of carbon monoxide during winter months. Other areas of the U.S. are required to use reformulated gasoline (RFG) (2% oxygen) year-round to reduce emissions that contribute to ozone formation. MTBE is the most commonly used fuel oxygenate (BRP, 1999). It is added at up to 15% by volume in oxyfuel or 11% in RFG and is currently used in over 85% of the nation's RFG (BRP, 1999). Ethanol is also widely used in oxygenated gasoline (8% in oxyfuel or 6% in RFG, by volume). It is also sometimes used at 10% volume in gasoline, even in areas that are not required to use RFG, because there is a 0.54 cent/gallon federal subsidy for this gasoline to promote markets for ethanol (RFA, 1999). Gasoline with ethanol added as an oxygenate at 10% or less by volume is referred in this paper as "gasohol".

The regulatory decision-making process that lead to the widespread use of MTBE over the last decade is now quite controversial (BRP, 1999). It has been discovered that MTBE is a ubiquitous contaminant in surface and ground waters throughout the nation (Gullick and LeChavalier, 2000; Moran *et al.*, 1999; Zogorski *et al.*, 1996). Because of this and consumer complaints of the pungent odor and concerns over possible health effects from MTBE (Bedard, 1995; Peaff, 1994), an alternative oxygenate is being sought. The State of California has responded directly to this issue by phasing out the use of MTBE in gasoline by December 2002 (Davis, 1999). In addition, the federally appointed Blue Ribbon Panel on Oxygenates in Gasoline (BRP) has recommended that the EPA reconsider its mandate to require the use of oxygenates (BRP, 1999). In addition, the EPA has announced proposed regulatory action to restrict the use of MTBE under Section 6 of the Toxic Substances Control Act (Federal Register, 2000).

The selection of suitable oxygen-bearing chemicals to add to gasoline will continue to be debated. Due to the problems with MTBE, regulators are somewhat more cognizant of the need to consider the overall impact of oxygenates on the environment. California, for example, has commissioned an environmental fate and transport analysis of ethanol in air, surface water and groundwater (Davis, 1999). This information will be used in conjunction with economic and availability constraints to redefine the fuel oxygenate program in California.

Given the increasing financial and political incentives for expanding its use as an automotive fuel oxygenate, ethanol appears likely to be encountered more frequently in groundwater plumes containing BTEX (benzene, toluene, ethylbenzene, and xylenes). Consequently, a comprehensive understanding of the effects of ethanol on the fate and transport of BTEX compounds is needed to determine if the economic and air-quality benefits of adding ethanol to gasoline outweigh its potential detrimental effects on groundwater quality, environmental and human health.

#### A. Use of Ethanol-Containing Gasoline

Worldwide, the most significant use of ethanol started in Brazil in the 1970s. In that country, the National Alcohol Program was created to cope with the high oil prices of the 70s and 80s. Federal incentives, associated with the participation of the automobile industry and the strong environmental appeal, made the program a success. Ethanol is used as fuel in vehicles in two ways: as sole fuel (hydrated), or mixed with gasoline (anhydrous). In 1985, 95% of all cars produced used hydrated ethanol as the only fuel. When oil prices began to drop, the program was changed because the sale of cars that could run only on ethanol plummeted. In 1999, approximately 75% of all automobiles in Brazil ran on gasoline containing 24% ethanol, with a total fuel alcohol consumption of  $13.8 \times 10^6$  m<sup>3</sup>/year (ANP, 1999).

In the U.S., several recent political decisions have resulted in the increased the use of ethanol in gasoline. This emphasis stems from two different initiatives. First, ethanol is being promoted as a renewable, biomass-based fuel alternative. Second, it is an oxygenate that is perceived to have less impact on the environment than MTBE. Gasohol containing 10% ethanol by volume has been used extensively in the corn-growing states of the Midwest for several years. It can be found as an option at most gasoline stations in Iowa and Nebraska, accounting for 21% of all motor fuel sold in Nebraska (Chambers, 1999). At present, 60% of gasoline sold in Illinois and 90% of gasoline sold in the Chicago area contains 10% ethanol (RFA, 1999). Throughout the country, U.S. consumers use more than 56 million cubic meters (15 billion gallons) of ethanol-blended gasoline each year (ACE, 1999)

Across Canada, there were over 950 retailers of ethanol-blended fuels in 1998 (CRFA, 1999). Gasohol is distributed by most major petroleum companies and several other independent retail outlets. The gasohol is available in all grades of gasoline and for on-farm delivery.

With the current widespread use of gasohol, it is expected that there would be numerous releases of either neat ethanol at a gasoline distribution terminal or gasohol from a leaking underground storage tank. A survey of state and EPA personnel in Midwest States who investigate and remediate leaking underground storage tanks (LUST), however, indicated that there is inadequate information available to identify and investigate the impact of ethanol on the fate of BTEX species at gasoline stations (Powers and Heermann, 1999). Much of the lack of information stems from the regulatory environment controlling the investigation and remediation of gasoline leaks and spills. None of the States requires ethanol concentrations to be measured in groundwater samples because ethanol is not a regulated pollutant. The lack of information is due in part to the perception that there are no important differences between the gasohol and standard blend gasoline. This perception is the same even in Brazil where gasohol has been used for over 20 years.

# B. Overview of the Fate of Gasohol in the Subsurface

The presence of oxygenate chemicals can potentially impact the migration and fate of gasoline in the subsurface following a spill or leak. In general, the public health concerns with gasoline in the subsurface arise from the presence of dissolved species in groundwater that could be used for drinking purposes. Numerous processes affect the concentration of such chemicals in aquifers. Generally, these processes include the infiltration of the gasoline through the unsaturated zone of the subsurface, spreading of the gasoline pool at the water table, dissolution of slightly soluble species from the gasoline into the water, transport of these chemicals with the groundwater toward a potential point of contact such as a groundwater well and losses such as sorption or biodegradation (Figure 1). Differences in the biodegradability and hydrophobicity of ethanol relative to standard gasoline components contribute to the impact of ethanol on the overall fate of BTEX species in groundwater.

Based on our knowledge of fundamental processes, it is expected that ethanol has the *potential* to increase the concentration of BTEX species in groundwater. Equilibrium concentrations of hydrophobic contaminants increase in the presence of alcohols and losses due to sorption are reduced (e.g., Fu and Luthy, 1986b; Heermann and Powers, 1998). At the same time, the readily biodegradable nature



FIGURE 1. General processes governing the fate of gasoline in the subsurface.

of ethanol results in its disappearance in an aquifer, but with a potentially significant consumption of electron acceptors and nutrients required for BTEX degradation (Corseuil et al., 1998). The significance of these impacts in a subsurface setting is not known and the potential impacts of many of the mechanisms are poorly understood.

This review aims to characterize potential impacts of ethanol on groundwater pollution and remediation that could be associated with a possible widespread adoption of this oxygenate in gasoline. This is accomplished by

- Summarizing and critically analyzing the available information on the fate of ethanol in the environment;
- Assessing the potential environmental impacts associated with ethanol releases; and,
- Evaluating their potential effect on natural attenuation of BTEX compounds.

Both abiotic and biotic processes that are affected by the presence of ethanol in gasoline are included in this article. These are organized around processes associated with the gasoline phase itself (Section II) and the subsequent processes affecting the fate of ethanol and BTEX dissolved in the aqueous phase (Section III). The biodegradation processes discussed in Section III include both ethanol degradation pathways and the potential effects of ethanol on the rate and extent of BTEX biodegradation. Section IV provides a broader understanding of the importance of these mechanisms with a review of modeling studies that incorporate the effects of multiple processes. Throughout this article, it is assumed that the bulk of the gasohol quickly migrates to the water table. Thus, the article focuses on nonaqueous and aqueous phases rather than gaseous phase interactions and processes.

# II. EFFECT OF ETHANOL ON MASS TRANSFER OF BTEX FROM GASOLINE TO GROUNDWATER

In a groundwater system, it is critically important to understand the partitioning of soluble or slightly soluble species between a gasoline pool to the aqueous phase. The dissolution process defines ethanol and BTEX concentrations in the groundwater in the direct vicinity of a gasoline pool. This process is a function of the equilibrium concentrations, the rate of species transport through the gasoline and water, and the relative volumes of gasohol and water that are mixed. Thereafter, the concentration of dissolved ethanol and BTEX is controlled by advective and dispersive mass transfer, as well as losses associated with sorption and biodegradation.

#### A. Equilibrium Considerations

Environmental releases of nonaqueous phase liquids (NAPLs), such as gasoline, contribute to the degradation of groundwater quality as components in the organic phase are slowly leached into the aqueous phase and transported with the groundwater. With gasoline, the more highly soluble monoaromatic compounds dissolve into the aqueous phase at appreciable concentrations creating a long-term source of these hazardous constituents. This mass transfer process is dependent on hydrodynamic conditions, chemical composition of both phases, and the specific surface area between phases. The net exchange of chemical species across an interface between two phases will continue until an equilibrium condition has been achieved. There are two ways to look at this equilibrium condition, the partitioning of the whole gasoline phase (Section II.A.1), or the equilibrium partitioning of individual components between the phases (Section II.A.2). Both of these views are relevant for the analysis of the environmental fate of gasohol in the subsurface.

# 1. Overall Phase Partitioning Behavior

While standard formulation gasolines are almost completely immiscible in water, ethanol is completely miscible in both gasoline and water at all concentrations. When ethanol is present with both gasoline and water, the ethanol partitions preferentially into the aqueous phase, increasing the solubility of BTEX in water (Heerman and Powers, 1998) and reducing the gasoline-water interfacial tension. With a sufficiently large proportion of ethanol in a system, the gasoline and water become completely miscible with each other and merge into a single phase.

Ethanol partitioning and the effects of ethanol on solubility are illustrated on a ternary phase diagram (Figure 2). Note that the diagram assumes a completely mixed system that has reached equilibrium and thus ignores complex transport phenomenon that exists in the subsurface. Using the three axes, one can determine the mass fractions of gasoline, water and ethanol for any point on the interior. The shaded region indicates the range of water, gasoline and ethanol fractions where the three components exist as two separate phases while the unshaded region indicates the composition range where these components exist as a single phase. The curve separating the two regions is called the binodal curve. On Figure 2 the binodal curve indicates that gasoline, ethanol and water will exist as a single phase in all relative combinations of water and gasoline provided that the ethanol present in the entire system exceeds 70 weight percent.

Tie lines transect the two-phase region and join water-rich and gasoline-rich segments of the binodal curve. These tie lines indicate the equilibrium compositions of the two phases. The points connected by the lines define the composition of the water-rich phase (on the left side of the two-phase region) and the gasoline-rich phase (on the right side of the two-phase region). The preferential partitioning



**FIGURE 2.** Ternary phase diagram for gasoline-ethanol-water system at 21°C. The shaded region represents the region where the total mass fractions separate into two phases. The ends of the dashed (tie) lines indicate the composition of each phase at equilibrium. Axes represent mass percentages. (Adapted from de Oliveira, 1997.)

of ethanol into water is indicated by the downward left-to-right slope of the tie lines.

As an example, if a gasoline initially contained 10% ethanol (~9% by volume), its composition would be indicated by point A on Figure 2. If that gasoline was exposed to an equal volume of water and the gasohol and water were allowed to equilibrate, nearly all of the ethanol would migrate into the aqueous phase. At equilibrium, the gasoline phase would then have a composition indicated by point A' and the water-rich phase by point B'.

Because gasoline is a highly complex mixture of alkane, cycloalkane, alkene, and aromatic compounds, changes in the gasoline composition may affect the phase behavior. A lower ethanol fraction would be required for phase separation if toluene were the hydrocarbon than if 2,2,4-trimethylpentane were the hydrocarbon (Letcher *et al.*, 1986). Phase relationships for water and ethanol in combination with gasoline or individual gasoline components have been published in numerous papers (de Oliveira, 1997; Letcher *et al.*, 1992; Letcher *et al.*, 1986; Lojkasek *et al.*, 1992; Peschke and Sandler, 1995; Stephenson, 1992). While these diagrams are useful for defining gross changes in the partitioning behavior of gasoline in the

presence of ethanol, they are not suitable for assessing aqueous phase concentrations of individual chemical species.

#### 2. Cosolvency

Aqueous phase concentration of ethanol that has leached from a gasohol spill could be high enough to affect the groundwater concentrations of individual chemical species equilibrated with the gasoline. Of most concern are the monoaromatic hydrocarbons, especially benzene, which is a known carcinogen (Federal Register, 1985). The addition of ethanol to gasoline affects the ideal equilibrium partitioning relationships by the "cosolvent effect", which is caused by the presence of high concentrations of organic compounds, such as alcohols, in the aqueous phase. These cosolvents reduce the polarity of the aqueous phase, causing a reduction in the aqueous phase activity coefficient and allowing higher concentrations of hydrophobic organic compounds in the aqueous phase (Groves, 1988). This can also be explained in terms of changes in the Gibbs excess free energy associated with molecules of hydrophobic organic compounds (HOC) in water being surrounded by cosolvent molecules as well as water molecules (Schwarzenbach *et al.*, 1993).

#### a. Experimental Cosolvency Studies

Many of the studies that have considered the cosolvency effect of alcohols have utilized single hydrophobic organic chemicals (HOCs) as surrogates for gasoline. This approach neglects complexities associated with multicomponent aspects of this organic phase (Groves, 1988; Hellinger and Sandler, 1995; Mihelcic, 1990; Peschke and Sandler, 1995; Stephenson, 1992). The work by Poulson *et al.* (1992) provides substantial information on the partitioning of BTEX compounds from multicomponent gasolines. Methanol and MTBE were considered as oxygenates added to the PS-6 standard API gasoline in this work. They found that for a given volume of gasoline increases in the BTEX concentrations due to a cosolvent effect were balanced by the reduced mass of these species in the gasoline due to the initial presence of the oxygenate. Significant increases in aqueous benzene concentrations were observed only when the volume of gasoline to water was high.

Corseuil and Fernandes (1999) evaluated the effective solubilities of BTX compounds in water equilibrated with a Brazilian commercial gasoline containing 22% ethanol. A range of ethanol concentrations in the aqueous phase was achieved by varying the volume ratio of water to gasoline (20:1 to 1:1) in the batch experiments. Even with this wide range of water to gasoline ratios and the relatively high volume fraction of ethanol in the Brazilian gasoline, the maximum volume fraction of ethanol in the aqueous phase was on the order of 15%. Their

results showed that even a small concentration of ethanol in the aqueous phase increased the solubility of BTX compounds; aqueous ethanol concentration of 10% increased dissolved BTX concentrations by 30% (Figure 3). The relative magnitude of this effect increased with the hydrophobicity of the compound. Thus, xylene had a larger percentage increase in aqueous phase concentration than benzene.

Heermann and Powers (1998) studied the cosolubility effects associated with the use of ethanol in gasolines. BTEX and ethanol partitioning relationships were established by performing batch equilibrium experiments using both simple and complex "gasolines". Three organic solutions incorporating surrogates for the aromatic and alkane compounds comprising the majority of gasoline were utilized to ensure that the entire system was well characterized. Additional experiments with more complex commercial reformulated gasolines containing ethanol were performed to verify results with the surrogate-compound gasolines. These commercial gasolines included a reformulated gasoline containing 5.8% ethanol by volume obtained directly from the Phillips Chemical Company (C2) and a generic gasoline, also containing ethanol, obtained from a local service station. Equilibrium BTEX and ethanol concentrations were measured in both phases. The aqueous phase concentrations displayed an approximate linear trend when plotted on semi-log scale at ethanol volume fractions greater than 0.2 (Figure 4). At lower concentrations, however, there was a distinctly different trend. These differences are attributed to the hydration of the cosolvent molecules at low concentrations



**FIGURE 3.** Concentration of BTX compounds in water equilibrated with a Brazilian gasoline containing 22% ethanol. (Data from Corseuil and Fernandes, 1999.)

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(Banerjee and Yalkowsky 1988). Over the range of the maximum aqueous phase ethanol volume fractions observed by Corseuil and Fernandes (1999) (~15%), BTX concentrations in the aqueous phase that was equilibrated with the C2 gasoline generally increased by approximately 20 to 50%. The smallest percentage increase was observed for benzene, the least hydrophobic of the BTEX compounds.

Unless there is a neat ethanol spill, aqueous phase ethanol concentrations unlikely to exceed 10% in contaminated sites. Therefore, it is unlikely that cosolventrelated increases in BTEX concentrations will be significant at the field scale.

#### b. Modeling Cosolubility Effects

A cosolvent present in the aqueous phase changes the partitioning of slightly soluble organic species between the organic and aqueous phases. Quantification of this cosolvency effect requires a sophisticated equilibrium relationship due to the nonideal solutions formed in the presence of the polar oxygenate. There are two general approaches to deal with this nonideal behavior. An empirical relationship based on experimental measurements can be used to directly estimate the distribution of an organic compound between the two phases, or a more general and rigorous thermodynamic approach can be employed to estimate activity coefficients. The use of both of these methods is complicated by the complex and unknown composition of the organic phase — commercial gasolines.

The empirical models for the solubility of HOCs in nonideal systems involve the use of both linear and log-linear equations. These equations were originally used for the solubility of pharmaceuticals but have also been applied to environmental systems (Banerjee and Yalkowsky, 1988). In general, cosolvents in water generate a logarithmic increase in HOC solubility with increasing cosolvent concentration (Pinal *et al.*, 1990):

$$\log(C_i^m) = \log(C_{si}^w) + \sigma_s f^c \tag{1}$$

where  $C_i^m$  is the equilibrium concentration of HOC *i* in the cosolvent mixture,  $C_{si}^w$  is the solubility of HOC *i* in pure water,  $f^c$  is the volume fraction of the cosolvent in the aqueous phase, and  $\sigma_s$  is termed the *cosolvency power*.

Deviations from the log-linear cosolubility relationship (Eq. 1) have been observed in several studies with a variety of solutes and cosolvents solutions (Li and Andren, 1994; Rubino and Yalkowsky, 1987). Poulson *et al.* (1992) and Heermann and Powers (1998) (Figure 4) also observed such deviations for BTEX concentrations in gasoline-alcohol systems. For short-chained alcohols, these deviations have been attributed to changes in the interactions between water and the cosolvent molecules (Rubino and Yalkowsky, 1987).



**FIGURE 4.** Concentration of BTX compounds in water equilibrated with a certified California test gasoline from Philips Petroleum (a) and an ethanol-gasoline from Ontario (b). (Data from Heermann and Powers, 1998.)

Since the log-linear cosolubility model (Eq. 1) does not incorporate the influence of interactions between the water and cosolvent molecules, this equation is only valid at higher cosolvent concentrations. Incorporating the observed linear relation at lower cosolvent concentrations (e.g., Figure 4), two equations can be written to reflect differences in solubilization mechanisms at low versus high cosolvent concentrations (Banerjee and Yalkowsky, 1988).

$$C_i^m = \left(1 - \frac{f^c}{\beta}\right) C_i^w + f^c C_i^b \qquad \text{for } f^c < \beta \qquad (2a)$$

$$\ln C_i^m = \left(1 - \frac{f^c - \beta}{1 - \beta}\right) \ln C_i^w + \left(\frac{f^c - \beta}{1 - \beta}\right) \ln C_i^c \quad \text{for } f^c \ge \beta$$
(2b)

where  $\beta$  is the volume fraction of ethanol in the aqueous phase at the breakpoint between the two segments of the model, and  $C_i^{\beta}$  is the concentration of *i* in the cosolvent mixture at this ethanol volume fraction. These model equations are referred to as the linear/log-linear model. Heermann and Powers (1998) adapted these equations for multicomponent mixtures such as gasoline to better incorporate non-ideal characteristics of these mixtures.

An alternative approach to modeling the solubilities of HOCs in a cosolvent mixture is to employ a thermodynamic model to estimate activity coefficients of each component in each phase. These activity coefficients are then used in a set of equations that equate the chemical activities of a species between the two phases. The UNIQUAC (universal quasi chemical) model is often used in multicomponent liquid-liquid equilibrium problems (Smith and VanNess, 1987). A modification of this, the UNIFAC (UNIQUAC functional-group activity coefficients) model, allows the necessary parameters to be estimated from the number and type of functional groups that comprise the chemical species. As this model does not require the same extensive database as UNIQUAC, it is more easily implemented.

UNIFAC has been used extensively in environmental applications. Numerous researchers have used this model to estimate the aqueous phase solubilities in organic phase-water systems, both with and without cosolvents. Reasonable prediction capabilities in these 2 to 3 component systems — generally within a factor of two relative to experimental data — have been reported (Arbuckle, 1986; Banerjee, 1985; Fu and Luthy, 1986a; Groves, 1988; Mihelcic, 1990; Pinal *et al.*, 1990). Hellinger and Sandler (1995) examined the quality of both UNIQUAC and UNIFAC to model their measured gasoline-water-oxygenate solubility data. In both experimental and modeling aspects of their work, they considered single alkane species as surrogates for all species in the gasoline and *t*-amyl methyl ether or *t*-amyl alcohol as the added oxygenates. Both models provided qualitative descriptions of trends in the ternary diagrams representing equilibrium compositions of the two phases. However, neither was accurate in a quantitative sense. Three mathematical models were applied to the experimental results obtained by Heermann and Powers (1998). These models were applied in a true predictive manner based on the volumes of gasoline and water equilibrated and the initial concentration in the gasoline. Representative results of these predictions are included in Figure 5. The log-linear (Eq. 1) and UNIFAC models were capable of representing the overall increase in concentration as a function of increasing ethanol content in the aqueous phase. However, neither of them mimicked the observed two-part curve. The piecewise model comprised of a linear relationship for low ethanol volume fractions and a log-linear model for higher concentrations (Eq. 2) was fit to data for a surrogate gasoline comprised of seven compounds. These parameters were then used to predict BTEX concentrations in the aqueous phase equilibrated with commercial gasoline. This model was superior to the UNIFAC predictions, especially at the low ethanol concentrations expected when gasolines presently sold are spilled in the environment.

# **B. Mass Transfer Rate Limitations**

Experimental measurement or application of cosolvency models to estimate the aqueous concentration of ethanol and BTEX is critically important in under-



**FIGURE 5.** Prediction of benzene concentrations that had been equilibrated with C2 gasoline and additional ethanol. "LLL" indicates the piecewise linear-log-linear cosolvency model. (Adapted from Heermann and Powers, 1998.)

standing the overall impact of gasohol on the groundwater systems. However, there are potential mass-transfer resistances in both the aqueous and gasoline phases that will limit the rate of mass transfer. The net result of these mass transfer resistances is a potential for lower groundwater concentrations than predicted by equilibrium models.

#### 1. General Concepts

The interphase mass transfer of ethanol and hydrocarbons between gasoline and groundwater can be most simply expressed as a product of a mass transfer coefficient and a concentration driving force (Cussler, 1984):

$$N_{i} = k_{i} \left( C_{i}^{*w} - C_{i}^{w} \right) \tag{3}$$

where  $N_i$  is the flux of compound *i*,  $k_i$  is the mass transfer coefficient, and  $C_i^w$  and  $C_i^{*w}$  are the actual and equilibrium concentrations of species *i* in the aqueous phase. For practical purposes, the equilibrium concentration is typically expressed in terms of an equilibrium partition coefficient  $(K_{i,i}^{n,w})$ , which describes the aqueous phase concentration that would be in equilibrium with the actual concentration in the second phase  $(C_i^n)$ .

$$C_{i}^{*w} = \frac{C_{i}^{n}}{K_{i}^{nw}}$$

$$\tag{4}$$

The mass transfer coefficient,  $k_i$  reflects limitations to the rate of interphase mass transfer resulting from the noninstantaneous transport of compounds to and away from the phase boundary. Thus for a gasoline pool, ethanol and hydrocarbons must be transported through the gasoline to the phase boundary separating the gasoline and groundwater and must be transported away from the boundary with the groundwater.

In most interphase mass transfer models, the boundary is conceptualized as a two-dimensional surface with no thickness. Therefore mass cannot accumulate at the boundary and the physical constraint exists that the rate of transport to the boundary equal the rate of transport away from the boundary (Taylor and Krishna, 1993). Because of the sequential nature of the mass transfer and the constraints on the transport rates, a single transport process will often govern the overall mass-transfer rate.

The most complete series of studies associated with mass transfer rates of soluble species from an alcohol-gasoline mixture was conducted for the American Petroleum Institute. These studies focused on the fate and transport of monoaromatic petroleum hydrocarbons from gasoline containing 85% methanol (M85) (Barker *et al.*, 1991; Donaldson *et al.*, 1994; Hubbard *et al.*, 1994). This blend has been used to a limited extent to meet the stringent California emission requirements. Com-

puter simulation and laboratory experiments showed that the methanol in a gasoline pool at the water table quickly dissolved into the groundwater. High aqueous phase concentrations of BTEX were also associated with the initial period of contamination due to the cosolvency effect of the methanol creating a slug of highly contaminated groundwater that was transported downgradient by advection. Once the methanol source was depleted from the gasoline, however, the BTEX concentrations were also reduced.

The vast majority of both analytical and numerical mathematical models of mass transfer from NAPL pools assume that the interphase mass transfer of HOC's are limited by the rate of groundwater transport away from the NAPL groundwater boundary (Anderson et al., 1992; Chrysikopoulos, 1995; Hunt et al., 1988; Johnson and Pankow, 1992; Shan and Javandel, 1997). Assumptions that the composition of the NAPL is homogeneous and remains constant over time are inherent in these models. For standard formulation gasolines, these assumptions may be reasonable because the gasoline composition changes very gradually as a result of low solubilities and slow dissolution rates. However, the preferential dissolution of alcohol will result in significant temporal and/or spatial gradients in the gasoline concentration. Because ethanol partitions preferentially into water, it may be nearly depleted from the gasoline at the boundary. For very slow rates of ethanol transport to the boundary, an ethanol concentration gradient develops through the gasoline invalidating the assumption that the chemical composition is homogeneous over the depth of the pool. In contrast, for very rapid rates of ethanol transport, concentration gradients in the gasoline will be small, but the ethanol will be rapidly depleted from the gasoline invalidating the assumption that concentrations do not vary over time. For sufficiently fast ethanol transport through the gasoline, transport via ground water will define the mass-transfer rate-limiting process. These two extreme cases of ethanol dissolution rates depend on the mechanism limiting the overall mass transfer process. Some of the most important transport processes are described below, first for gasoline and then for groundwater.

# 2. Rate Limitations in the Gasoline Phase

Assuming that the bulk of the gasoline phase collects as a pool at the capillary fringe, two transport processes have been identified that contribute to the transport of ethanol and other hydrocarbons through the gasoline. These include molecular diffusion and free convection. Molecular diffusion, which describes the net movement that occurs when molecules undergoing random motion are subjected to a concentration gradient, is a generally well understood process and is fairly easily modeled (*e.g.*, Cussler, 1984; Taylor and Krishna, 1993). Free convection refers to the process where bulk fluid flow occurs as a result of an unstable condition created when the fluid density increases vertically upward (Cussler, 1984). It has been

studied only recently with respect to gasoline and is a much more difficult process to model. Gasoline entrapped at a residual saturation in the smear zone would be subject to other dissolution and mobilization mechanisms (de Oliveira, 1997).

It is generally assumed that molecular diffusion is the rate-limiting step transporting an organic species from a subsurface NAPL pool to groundwater (e.g., Holman and Javendel, 1996). This mechanism is described mathematically with Ficks Law. Heermann and Powers (in preparation) have shown that this assumption can adequately describe the flux of ethanol from a toluene-ethanol mixture to a flowing aqueous phase. Due to the slow rate of ethanol mass transfer observed in this study, a steep ethanol concentration gradient was rapidly established in the organic phase. With diffusion as the primary mass transfer resistance, there was minimal cosolvency effect and the toluene flux quickly attained a steady state condition resulting in a concentration similar to that observed with no ethanol in the system.

Unlike the conditions that existed in the toluene experiments, most gasolines have a lower density than ethanol, promoting the potential for free convection. Free convection occurs when a density gradient exists within a single fluid. If the gradient is such that the fluid is less dense near the bottom, a physically unstable fluid profile is created. As a result, convective flow is established within the fluid, typically as "fingers", thereby blending the high- and low-density portions of the fluid (Cussler, 1984). Gasoline has a density less than that of ethanol because the alkanes, cycloalkanes, and alkenes that comprise the majority of most gasolines have densities less than the density of ethanol ( $\rho_{etoh} = 0.789$  g/mL). Therefore, in contrast with the toluene experiments described above, most gasolines with ethanol will have a greater density than gasoline that does not contain ethanol.

In the subsurface, as ethanol is removed from the gasoline at the gasolinegroundwater interface, the density of the gasoline at the boundary becomes less than its density in the region above the boundary. As a result, the high- and lowdensity gasoline regions become unstable with respect to each other and, consequently, the gasoline with higher ethanol content and greater density flows downward to the phase boundary while the less-dense ethanol-depleted gasoline moves upwards. In a series of column experiments, Heermann and Powers (in preparation) found that free convective flow greatly increased the rate of ethanol transport to the boundary relative to diffusional transport. The higher rate of interphase mass transfer resulting from free convection will likely lead to greater ethanol concentrations in groundwater and therefore to a greater cosolvency effect. However, the higher mass transfer rate will also result in a more rapid depletion of the ethanol in the gasoline.

# 3. Rate Limitations in the Ground Water

The net flux of ethanol and hydrocarbon species from the gasoline into the groundwater may also be limited by the transport of these species via groundwater

away from the gasoline-water interface. Mass transport in ground water is largely controlled by the processes of advection and hydrodynamic dispersion. Advection is the principal means of transporting hydrocarbons horizontally away from the gasoline-pool boundary with the flowing groundwater while hydrodynamic dispersion is the principal means for vertical transport away from the gasoline pool. The net rate of interphase mass transfer increases with increased groundwater flow rates and dispersion because these processes reduce the concentration of solute near the interface. Advective and dispersive transport is site specific, largely controlled by groundwater flow velocities.

# C. Summary of Mass Transfer Processes

Both equilibrium and mass transfer processes will affect the aqueous phase concentrations of ethanol and, therefore, BTEX species. The cosolvent effect will increase concentrations of BTEX in the aqueous phase. With typical ethanol concentrations in gasoline, however, the BTEX concentration increases are expected to be small.

Mass transfer limitations could further reduce the significance of ethanol on BTEX dissolution behavior. Molecular diffusion in gasoline is generally a very slow transport process in comparison to the groundwater transport processes of advection and dispersion. Thus if diffusion were the only transport process in the gasoline, it would likely be the rate-limiting step under most subsurface conditions. Free convection is apparently a much more rapid transport process that exists, in theory, for most ethanol-bearing gasolines. However, there is insufficient knowledge about free convection in subsurface gasoline lenses to determine if this process is likely to be the rate-limiting step. Alternatively, if convection is sufficiently fast, advective/dispersive transport via groundwater could become the ratelimiting process.

# III. FATE OF ETHANOL AND BTEX DISSOLVED IN THE AQUEOUS PHASE

The overall fate of ethanol and BTEX dissolved in groundwater depends on their rates of transport via advection and hydrodynamic dispersion and sources or sinks of dissolved compounds in the groundwater. As described above, rates of mass transfer between the gasoline and groundwater define the source of these constituents. Two critical removal processes include the sorption of the hydrocarbons to sand, clay, or other solid materials in the subsurface, and the biologically mediated chemical transformation of the ethanol and hydrocarbons. Both of these processes contribute to the natural attenuation of groundwater pollutants, a net phenomenon that has been found to be critically important in minimizing the spread of groundwater plumes generated from spills of standard gasoline in the subsurface (e.g., Rifai *et al.*, 1995). The effect of ethanol on BTEX sorption and biodegradation is described below.

### A. Sorption of BTEX in the Presence of Ethanol

Similar to the cosolvent effects described above, the presence of ethanol or other cosolvents in groundwater reduces the extent of sorption due to the reduced polarity of the aqueous phase (e.g., Kimble and Chin, 1994). Thus, the retardation of BTEX concentrations is reduced in the presence of ethanol and the extent of transport with the groundwater may be increased.

Sorption may be described by a number of "isotherms", or mathematical relations between the concentration of a compound dissolved in water and its equilibrium concentration sorbed to a solid. One widely used isotherm is the Freundlich isotherm (Weber et al., 1991), which relates the equilibrium aqueous-phase concentration of compound *i*,  $C_i^w$ , and the concentration of *i* sorbed to the solid phase,  $S_i$ :

$$S_i = K \left( C_i^w \right)^n \tag{5}$$

The sorption capacity, K, and the exponent n, are empirical fitting parameters.

When a cosolvent is present in the aqueous phase, the partition coefficient,  $K_p$ , decreases (Errett *et al.*, 1996; Fu and Luthy, 1986b; Kimble and Chin, 1994; Nkeddi-Kizza *et al.*, 1985; Rao *et al.*, 1985; Rao *et al.*, 1990). Nkeddi-Kizza *et al.* (1985) demonstrated that log-linear cosolvency relationships similar to Eq. 1 could be applied to sorption and showed that  $K_p$  decreased in an approximate logarithmic manner with increasing volume fraction of cosolvent in the aqueous phase:

$$\log \frac{K_{p_i}^m}{K_{p_i}^w} = -\alpha \sigma_s f^c \tag{6}$$

where  $K_{pi}^{m}$  and  $K_{pi}^{w}$  are the sorption partition coefficients for compound *i* with the superscripts indicating equilibrium with pure water (*w*) and with a water-cosolvent mixture (*m*). Rao *et al.* (1985) and Fu and Luthy (1986b) provided theoretical explanations for the observed behavior analogous to those developed for the liquid aqueous-organic phase partitioning in the presence of a cosolvent. Using methanol as a cosolvent, Fu and Luthy (1986b) showed that the sorption partition coefficient decreased in a log-linear manner, much the same as the solubility increases with cosolvent fraction. They compared the effects of cosolvency on sorption and solubility and found that the slope of the log-linear plot for sorption was about half that for solubility. Brusseau *et al.* (1990) showed that the log-linear model could be extended to include the parameters describing rate-limited desorption.

As an alternative to the empirical log-linear approach, one may estimate the effect of ethanol on the partition coefficient using aqueous-phase activity coefficients. Assuming that the ethanol affects only the aqueous-phase hydrocarbon activities and has no effect on the solid surfaces upon which sorption takes place, then one may simply scale the sorption partition coefficient:

$$K_{p_{i}}^{w,c} = \frac{\gamma_{p_{i}}^{w,c}}{\gamma_{p_{i}}^{w}} K_{p_{i}}^{w}$$
(7)

where  $\gamma_{p,i}^{w,c}$  is the activity coefficient of compound *i* in a water-cosolvent solution and  $\gamma_{p,i}^{w}$  is the activity coefficient of compound *i* in pure water (Rixey, 1994). Activity coefficients can be estimated with UNIQUAC or UNIFAC as described above for estimating aqueous phase concentrations equilibrated with gasohol.

One of the chief effects of sorption on the net transport of solutes with groundwater is the retardation of hydrocarbons such that their effective velocities become less than the groundwater that is transporting them. In a one-dimensional modeling study to compare BTEX concentrations down-gradient of an M85 gasoline release, Rixey (1994) showed that when cosolvent-dependent sorption was incorporated into the model, the BTEX compounds moved more rapidly through the porous medium. The methanol and BTEX were assumed to be added instantaneously to the aqueous phase and so the down-gradient concentrations appeared as discrete peaks. The effect was more pronounced for benzene than for other BTEX compounds because benzene is the least retarded of the BTEX compounds and so moved through the porous medium with nearly the same velocity as the methanol and was subjected to higher cosolvent concentrations. Toluene did not move synchronously with the methanol and so the cosolvency concentrations and the effect of the methanol was less than for benzene. These model simulations also suggest that cosolvency effects would be significant only where aqueous methanol concentrations exceed 10 to 13 wt% (Rixey, 1994). Because of the low concentrations of ethanol expected from gasohol spills, especially in the downgradient groundwater plume, it is not expected that the presence of ethanol will significantly reduce the retardation of BTEX species.

#### B. Biodegradation of Ethanol

Quantifying BTEX biodegradation rates is necessary for predicting the net transport of these pollutants from a gasohol spill and therefore the potential risks of aquifer contamination. BTEX biodegradation, however, is integrally linked to the biodegradation of ethanol. With ethanol concentrations expected in the thousands of ppm, this organic solute can exert a significant biochemical oxygen demand. Thus, the presence of ethanol can consume electron acceptors and nutrients that would otherwise be available for the bioattenuation of BTEX. The discussion in this section identifies ethanol biodegradation rates and mechanisms as a necessary step before the effect of ethanol on BTEX biodegradation can be considered (Section III.C).

#### 1. Ethanol Degradation Rates in Aquifers

Ethanol can be degraded in both aerobic and anaerobic environments at a rate faster than other gasoline constituents (Chapelle, 1993; Malcom Pirnie, 1998). Only large concentrations (>100,000 mg/L) of alcohols are not biodegradable due to their toxicity to most microorganisms (Brusseau, 1993; Hunt *et al.*, 1997). Such high concentrations could be encountered near the source of neat ethanol releases. However, as the maximum allowable ethanol content in gasoline is 10% by volume in the U.S., such high concentrations are unlikely to be encountered at sites contaminated with ethanol-gasoline blends (Corseuil and Fernandes, 1999).

Ethanol concentrations should become exponentially more dilute as the distance from the source increases but may inhibit microbial activity near the source. Thus, ethanol plumes should be degraded by indigenous microbes located a sufficient distance beyond the source. The only field-scale studies with fuel-grade alcohol have been performed with methanol and not ethanol. One field study investigated methanol biodegradation in soils from three different sites under various redox conditions. Methanol concentrations of 1000 mg/L were removed in all soils in less than 1 year, at pH values of 4.5 to 7.8 and at temperatures of 10 to 11°C (Butler *et al.*, 1992). A similar study investigated the persistence and fate of M85 fuel (85% methanol, 15% gasoline) in a shallow sandy aquifer (Barker *et al.*, 1998). All of the methanol (approximately 2400 L at an initial concentration of 7000 mg/L) was biodegraded below 1 mg/L in 476 days, yielding a methanol halflife of about 40 days. Because of the similar properties of methanol and ethanol, the biodegradation of ethanol is also expected to be relatively fast.

While there are no known field-scale studies of the fate and transport of ethanol, a few laboratory studies have focused on ethanol biodegradation. Acclimation periods (periods before degradation proceeded) and zero-order biodegradation rates of ethanol and other fuel oxygenates were measured in anaerobic aquifer slurries by Suflita and Mormile (1993). For initial ethanol concentrations of 50 mg/L, an acclimation period of 25 to 30 days and an anaerobic biodegradation rate of  $17.9 \pm 0.6 \text{ mg/L/day}$  were observed. Compared to ethanol, the observed acclimation period for methanol was shorter (5 days), but its biodegradation rate was slower ( $7.4 \pm 0.7 \text{ mg/L/day}$ ). In a subsequent study, these authors illustrated that their initial results could be extrapolated to other redox conditions. They showed that various short chain alcohols were easily degraded in different sediments under different electron acceptor conditions (Mormile *et al.*, 1994).

Biodegradation of ethanol under various redox conditions was investigated in aquifer microcosms at 20 to 25°C by Corseuil *et al.* (1998). First-order biodegradation rate coefficients from this study are summarized in Table 1. Lower micro-

Table 1		
Metabolites and	End Products of Ethanol Biodegradation	

Aerobic	Anaerobic
Acetaldehyde	Acetaldehyde
Acetate	Acetate
Acetyl-CoA	Butyric acid
Carbon dioxide	Propionic acid
	Hydrogen gas
	<i>N</i> -propanol
	Acetone
	Carbon dioxide
	Methane

bial concentrations, colder temperatures, and mass transfer limitations would likely result in longer half-lives *in situ* than those depicted in Table 1. Nevertheless, it is expected that regardless of the available electron acceptors, ethanol will undergo relatively rapid biodegradation in the subsurface under typical pH, temperature, and nutrient conditions.

# 2. Aerobic Degradation Pathways

Most common aerobic bacteria can mineralize ethanol to  $CO_2$  and  $H_2O$  through Kreb's cycle. In this process, ethanol is first oxidized to acetaldehyde by an alcohol dehydrogenase enzyme. Acetaldehyde is converted to acetyl-CoA either directly by an acetylating acetaldehyde dehydrogenase or through acetate by an acetaldehyde dehydrogenase and an acetate-CoA ligase. The acetyl-CoA is oxidized to  $CO_2$  in Krebs cycle. Many bacteria are also capable of operating a modified Krebs cycle, known as the glyoxylate shunt. This shunt enables bacteria to grow on compounds with two carbon atoms (e.g., ethanol), by condensing two C2-compounds (i.e., ethanol-derived acetyl-CoA and glyoxylate) to produce C4-building blocks, such as malate and oxaloacetate (Madigan *et al.*, 1997).

None of the intermediates in the common metabolic pathways are toxic. In addition, these intermediates are metabolized rapidly intracellularly and are rarely excreted in significant amounts, so their accumulation in groundwater is highly unlikely. One exception is acetate, which is excreted by acetic acid bacteria (e.g., *Gluconobacter* and *Acetobacter*) (Gottschalk, 1986, Xia *et al.*, 1999). These bacteria are unlikely to significantly contribute acidity to ethanol-contaminated groundwater, however, because they are obligate aerobes that typically live on the surfaces of plants and fruits (Gottschalk, 1986). Therefore, they are unlikely to thrive in aquifers contaminated with gasoline-ethanol mixtures, where the high biochemical oxygen demand is likely to deplete the available oxygen.

#### 3. Anaerobic Degradation Pathways

Microorganisms that can ferment ethanol are ubiquitous (Eichler and Schink, 1984; Wu and Hickey, 1996). Ethanol is a common intermediate in the anaerobic food chain, where labile organic matter is degraded to nontoxic products such as acetate,  $CO_2$ ,  $CH_4$  and  $H_2$  by the combined action of several different types of bacteria (White, 1995). As illustrated in Figure 6, the anaerobic food chain consists of three stages. In the first stage, fermenters produce simple organic acids, alcohols, hydrogen gas, and carbon dioxide. Other members of the consortium oxidize these fermentation products in the second stage to CO<sub>2</sub>, H<sub>2</sub>, and acetate, such as sulfate reducers and organisms that use water-derived protons as the major or sole electron sink. The latter include the obligate proton-reducing acetogens, which oxidize butyrate, propionate, ethanol, and other compounds to acetate, H<sub>2</sub> and CO<sub>2</sub>. Acetate can also be produced by homoacetogens, which are bacteria that utilize  $CO_2$  and H<sub>2</sub> for this purpose (Madigan et al., 1997). Mineralization occurs in the third stage. This is accomplished by acetoclastic methanogens, which break down acetate into  $CO_2$  and  $CH_4$  and by hydrogenotrophic methanogens, which reduce  $CO_2$  with  $H_2$ to form CH<sub>4</sub>. Some sulfate reducers and other anaerobic microorganisms can also mineralize acetate and participate in the final stabilization stage (Atlas and Bartha, 1997).

Interspecies hydrogen transfer is a critical link in the anaerobic food chain. Hydrogen-producing fermentative and acetogenic bacteria are at a thermodynamic disadvantage if hydrogen accumulates (Conrad *et al.*, 1985; Wolin and Miller, 1982). For example, the fermentation of ethanol to acetate and propionate by *Desulfobulbus* is strongly inhibited by high hydrogen concentrations (Schink *et al.*,



FIGURE 6. The anaerobic food chain. (Modified from White, 1995.)

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1987; Wu, and Hickey, 1996). Therefore, fermenters and acetogens live syntrophically with hydrogen consumers that keep the  $H_2$  levels low (Figure 7).

When sulfate is not limiting, sulfate reducers compete favorably for  $H_2$  and predominate over methanogens (Phelps *et al.*, 1985). Incomplete oxidizers (a.k.a. type I sulfate reducers) can oxidize ethanol, lactate, and other organic acids to acetate, while complete oxidizers (a.k.a. Type II sulfate reducers) can use either a carbon monoxide dhydrogenase pathway or a modified Kreb's cycle to oxidize acetate further to  $CO_2$  (Madigan *et al.*, 1997; Postgate and Campbell, 1966; Thauer *et al.*, 1989; Wu and Hickey, 1996).

Other terminal electron acceptors can be used for ethanol oxidation. An ironreducing bacterium has been shown to couple ethanol oxidation to the reduction of amorphic ferric oxide (Lovley and Phillips, 1988). Ethanol is also used as the carbon source and electron donor in some wastewater denitrification processes for the purpose nitrate removal (Hasselblad and Hallin, 1998; Nyberg *et al.*, 1996). Fermentative microorganisms can also transform ethanol by condensation reactions to form propionate (Braun *et al.*, 1981; Wu and Hickey, 1996) or butyrate (Bornstein and Barker, 1948). These compounds are not toxic, but could adversely affect groundwater quality by impacting its taste and odor.

#### 4. Summary of Metabolic Intermediates from Ethanol Degradation

Potential metabolic intermediates and end products for microbial degradation of ethanol are listed in Table 1. Oxygen is often quickly depleted by microbial respiration in gasoline-contaminated aquifers (Lee *et al.*, 1988; National Research Council, 1993). Therefore, ethanol is likely to be degraded predominantly under anaerobic conditions, and some anaerobic metabolites are likely to be encountered in contaminated groundwater. None of these metabolites is toxic, although some



**FIGURE 7.** Interspecies hydrogen transfer. Anaerobic oxidation of ethanol to acetate [1] is not thermodynamically feasible under standard conditions ( $\Delta G'_0 = + 9.6 \text{ kJ}$ ). This reaction can proceed only if the H<sub>2</sub> produced by acetogens and other fermenters is removed (law of mass action). The removal of H<sub>2</sub> by hydrogenotrophic methanogens [2] or sulfate reducers enhances the thermodynamic feasibility of acetogenesis and the subsequent mineralization of acetate by acetoclastic methanogens and (Type II) sulfate reducers. Thus, interspecies H<sub>2</sub> transfer prevents the accumulation of fermentation products and enhances anaerobic mineralization.

anaerobic metabolites could have adverse aesthetic impacts. In addition, acetate and other volatile fatty acids can cause a decrease in pH if they accumulate at high concentrations in poorly buffered systems. It is unknown whether the pH could decrease to a level that inhibits the further degradation of the ethanol. Such effects are likely to be system specific due to variability in buffering and dilution capacity among contaminated sites.

#### 5. Impact of Ethanol Biodegradation on Aquifer Permeability

Depending on aquifer chemistry and redox conditions, ethanol could stimulate microbial processes that affect the hydrodynamic properties of the aquifer. For example, fuel ethanol would stimulate microbial growth. Therefore, the formation of cell aggregates and biofilms that reduce the available pore space is a potential clogging mechanism of concern (Taylor and Jaffe, 1990; Vandevivere and Baveye, 1992). In theory, microorganisms could also affect aquifer permeability by contributing to mineral dissolution (e.g., CaCO<sub>3</sub>) or precipitation (e.g., FeS). A combination of excessive microbial growth and mineral precipitation could result in a significant reduction in porosity and permeability over a longer period.

An important mechanism by which microorganisms could reduce the effective porosity is the production of gas bubbles that increase the pressure and restrict water flow (Soares *et al.*, 1988, 1989, and 1991). Controlled experiments that address the significance and extent of such phenomena for ethanol contamination are lacking. Therefore, their potential impact is discussed below from a theoretical point of view.

The overall stoichiometry of methanogenesis from ethanol is given by

$$CH_3CH_2OH \rightarrow 1.5 CH_4 + 0.5 CO_2$$

Thus,

Potential methane production = 
$$1.5 \times \frac{16g - CH_4 / mol}{46g - ethanol / mol} = 0.5217 \frac{g - CH_4}{g - ethanol}$$

Based on the ideal gas law, and assuming a typical groundwater temperature of 15°C, the volume of methane produced at 1 atm from 1 g of ethanol is

$$0.5217 \frac{g - CH_4}{g - ethanol} \times \frac{1mol CH_4}{16 gram} \times \frac{22.4 \ liters}{mole (at \ STP)} \times \frac{(273 + 15)K}{273K} = 0.77 \frac{liters CH_4}{gram - ethanol}$$

As discussed in Section III.C.1.b, a 1000-mg/L ethanol concentration is generally not toxic to methanogenic consortia. This concentration could produce up to 0.77 L of methane within a 1 l pore volume, which could increase the pressure and potentially form gas bubbles that restrict groundwater flow near the source zone. Such a reduction in aquifer permeability could also hinder the replenishment of nutrients and electron acceptors by natural or engineered processes into the contaminated zone. Whether sufficient gas would accumulate at the source to create an explosion hazard is unknown and would depend, in part, on whether sitespecific conditions favor extensive methanogenesis.

# C. Potential Effects of Ethanol on BTEX Biodegradation

# 1. Direct (Intracellular) Effects

#### a. Stimulation of Microbial Growth

Ethanol represents a carbon and energy source that is likely to stimulate the growth of a variety of microbial populations, including species that can degrade BTEX compounds. A proliferation of BTEX degraders would be conducive to faster degradation rates, although this positive effect is likely to be offset by the preferential degradation of ethanol and the associated depletion of electron acceptors.

As discussed earlier, ethanol can be degraded by constitutive enzymes associated with central metabolic pathways, and microorganisms that can degrade simple alcohols are more common in nature than microorganisms that degrade BTEX compounds. Therefore, many species that cannot degrade BTEX are likely to proliferate when ethanol is present. In fact, microbial growth is generally faster on ethanol than on BTEX, due to more favorable thermodynamics. Using a thermodynamic model by McCarty (1969), the predicted maximum specific growth rate on ethanol is 45% greater than the predicted maximum specific growth rate with benzene (Hunt, 1999). Therefore, BTEX degraders are also likely to grow faster on ethanol than on BTEX under a given set of conditions. The effect of ethanol on the relative abundance of BTEX degraders has not been investigated.

Corseuil *et al.* (1998) pointed out that there may be some exceptions to the detrimental effect of ethanol on BTEX degradation, and hypothesized that this may be related to ethanol-induced microbial population shifts. Specifically, although ethanol was preferentially degraded under all electron acceptor conditions tested, ethanol enhanced toluene degradation in all three sulfate-reducing microcosms used in this study. The reason for this enhancement was unclear, but the possibility that this enhancement was due to an incidental growth of toluene degraders during ethanol degradation could not be ruled out. This untested hypothesis does not imply that ethanol would select for BTEX degraders, which is highly unlikely. Rather, the concentration of some BTEX degraders could increase after growth on ethanol, although their fraction of the total heterotrophic consortium would likely decrease.

In summary, little is known about the effect of ethanol on microbial population shifts and the resulting catabolic diversity. Considering that the efficiency of bioremediation depends, in part, on the presence and expression of appropriate biodegradative capacities, studying the microbial ecology of aquifers contaminated with gasoline-alcohol mixtures might be a fruitful avenue of research.

## b. Toxicity of Ethanol

The toxicity of alcohols to microorganisms has received considerable attention in the literature, although only a few studies have evaluated the effect of ethanol on subsurface microbial populations. Hunt *et al.* (1997) reported that ethanol concentrations in microcosm experiments higher than 40,000 mg/L were toxic to the microorganisms, as shown by complete lack of oxygen consumption. Other studies have found that some soil microbial activity can occur at ethanol concentrations of 100,000 mg/L, but not at 200,000 mg/L (Araujo *et al.*, 1998).

Ingram and Buttke (1984) conducted a thorough literature review on the effects of alcohol on microorganisms. Disruption of the cellular permeability barrier is thought to be the basis of bacterial killing by high concentrations of alcohols (Brusseau, 1993; Ingram and Buttke, 1984; Harold, 1970). Ethanol concentrations above 100,000 mg/L result in the immediate inactivation of most vegetative organisms, although spore-forming organisms are more resistant (Dagley *et al.*, 1950; Hugo, 1967). Most bacteria exhibit a dose-dependent inhibition of growth over the range of 10,000 to 100,000 mg/L and very few species can grow at ethanol concentrations higher than 100,000 mg/L (Ingram and Buttke, 1984).

The toxicity of alcohols is related to their chain length and hydrophobicity (Harold, 1970; Hugo, 1967). Longer chain alcohols, up to a chain length of around 10 carbon atoms, are much more potent inhibitors than are the shorter-chain alcohols. This is attributed to the fact that alcohols have two basic functional groups, namely, a hydroxyl function and a hydrocarbon tail. Ethanol is very polar and partitions poorly into the hydrophobic cell membrane (Figure 8). In contrast, the longer (hydrophobic) hydrocarbon tail of octanol favors its concentration within the membrane, which increases its toxicity. Thus, relatively high ethanol concentrations are required to cause lethal effects on biological systems (Ingram and Buttke, 1984).

Ethanol can exert a variety of biophysical effects on microorganisms. The basic actions of alcohols on prokaryotic organisms appear to be dominated by the physicochemical properties of alcohols rather than specific receptors. All hydrophobic and electrostatic interactions in the cytosolic and envelope components of cells can potentially be affected. These include cell membranes, conformations of enzymes and macromolecules, activity coefficients of metabolites, ionization potentials, pKa values of functional groups, and intracellular pH (Franks and Ives, 1966; Ingram and Buttke, 1984; Jukes and Schmidt, 1934; Yaacobi and Ben-Naim, 1974). High ethanol concentrations can also inhibit the synthesis of various organelles, including the cell wall (Blumberg and Strominger, 1974), RNA (Mitchell



**FIGURE 8.** Model showing interactions of octanol and ethanol with a cell membrane. (Adapted from Widdel, 1986.)

and Lucas-Leonard, 1980) DNA (Osztovics *et al.*, 1981), and proteins (Haseltine *et al.*, 1972). Ethanol is not mutagenic. However, acetaldehyde, which is a metabolite of aerobic ethanol degradation, increases cell mutation rates (Igali and Gazsó, 1980).

Ethanol has also been reported to adversely affect the activity of some critical enzymes. The addition of low ethanol concentrations at 3350 mg/L did not cause a significant inhibition of the Na<sup>+</sup>, K<sup>+</sup>-dependent ATPase, NADH oxidase or D-lactate oxidase (Eaton *et al.*, 1982). However, 8500 mg/L of ethanol inhibited these enzymes, with ATPase being the most resistant enzyme examined (Eaton *et al.*, 1982). In contrast, succinate dehydrogenase, part of the Kreb's cycle, is more sensitive, showing 20% inhibition with 3350 mg/L ethanol and 50% inhibition with 8500 mg/L ethanol. Transport systems are uniformly more sensitive to inhibition by ethanol. The lactose permease system exhibits a dose-dependent inhibition with increasing concentrations of ethanol (Ingram *et al.*, 1980). Uptake of glutamate, proline, leucine and the lactose permease was reduced by 10 to 30% with 3350 mg/L ethanol and by 60 to 80% with 8500 mg/L ethanol (Eaton *et al.*, 1982). However, inhibition of both the membrane-bound enzymes and transport systems was substantially relieved after removal of alcohol by washing.

Bringmann and Kuhn (1980) developed a cell multiplication test to characterize the inhibitory effect of common water pollutants. This turbidimetric test estimates the concentration at which the inhibitory action of a pollutant starts. The toxicity threshold is taken as the pollutant concentration that yields a biomass concentration that is at least 3% below the mean value of extinction for non-toxic dilutions of the same test culture. This test was applied to the model organism *P. putida*, which is a common BTEX degrader in the subsurface environment. Table 3 compares the

#### Table 2

First-Order Rate Coefficients ( $\lambda$ ) for Anaerobic and Aerobic Degradation of Ethanol by Aquifer Microorganisms (Estimated from laboratory experiments by Corseuil *et al.*, 1998)

Compound	Electron acceptor	λ (day <sup>-1</sup> )	Half-life (days)
Ethanol	O <sub>2</sub>	0.23 - 0.35	2-3
	NO <sub>3</sub> -	0.53	1.3
	Fe <sup>3+</sup>	0.17	4
	SO4-2	0.1	7
	$CO_2$	0.12	6

\* The sources of soil and groundwater in the microcosms were different for each se

# Table 3 Toxicity Thresholds for a *Pseudomonas putida* (from Bringmann and Kuhn, 1980)

Compound	Concentration (mg/L)
Ethanol	6500
Methanol	6600
1-propanol	2700
2-propanol	1050
1-butanol	650
2-butanol	500
Tertiary amyl alcohol	410
Methyl ethyl ketone	1150
Acetic acid	2850
<i>n</i> -butyric acid	875
Benzene	92
Toluene	29
Ethylbenzene	12

toxicity thresholds for several pollutants that could be a involved in a gasoline spill. Based on this study, it can be concluded that indigenous microorganisms are more resistant to high ethanol concentrations than to high BTEX and other fuel constituent concentrations.

#### c. Enzyme Induction and Repression

Often, target pollutants are degraded by inducible enzymes whose expression can be repressed when easily degradable substrates are present at high concentrations (Duetz *et al.*, 1994; Monod, 1949). However, only indirect evidence has been presented in the literature about the potential effects of ethanol on the expression of enzymes involved in BTEX degradation.

Hunt *et al.* (1997) reported that ethanol at 20 mg/L was preferentially degraded under aerobic conditions over benzene, presumably due to repression of the synthesis of enzymes needed to degrade benzene. This retarded the onset of benzene degradation. Additional microcosm studies also suggested that the preferential utilization of ethanol might increase the lag time before *in situ* BTEX biodegradation begins (Corseuil *et al.*, 1998). Specifically, little or no BTEX degradation occurred in aerobic, denitrifying, iron-reducing, sulfate reducing, and methanogenic microcosms while ethanol was present (Corseuil *et al.*, 1998). Therefore, ethanol may prevent the bacteria subpopulation capable of degrading BTEX from fully expressing its catabolic potential, which would hinder BTEX degradation.

Numerous studies show that carbon-limiting conditions are conducive to simultaneous utilization of multiple substrates (for review see Egli, 1995). This suggests that simultaneous ethanol and BTEX degradation is likely to occur when these compounds are present at low concentrations (e.g., in aquifers with low ppb levels of BTEX contamination). Interestingly, a pure culture of *Pseudomonas putida* F1 was reported to simultaneously degrade ethanol and toluene with no apparent inhibitory effect up to 500 mg/L of ethanol (Hunt *et al.*, 1997). This suggests that while high ethanol concentrations are likely to exert a diauxic effect that would inhibit *in situ* BTEX degradation, the metabolic diversity of microorganisms precludes generalizations about the concentration of ethanol that triggers enzyme repression. Such effects are probably species specific.

#### 2. Indirect (Environmental) Effects

#### a. Depletion of Nutrients and Electron Acceptors

Ethanol in groundwater constitutes a significant biochemical oxygen demand compared with that exerted by other soluble components of gasoline and is likely to accelerate the depletion of dissolved oxygen (Corseuil *et al.*, 1998). This would decrease the extent of aerobic BTEX degradation in oxygen-limited aquifers. Such an effect is particularly important for the fate of benzene, which is the most toxic of the BTEX and degrades slowly under anaerobic conditions or not at all (Alvarez and Vogel, 1995; Anderson *et al.*, 1998;Weiner and Lovley, 1998).

Anaerobic processes are believed to play a major role in containing and removing petroleum product releases at sites undergoing natural attenuation, where engineered oxygen addition is uncommon (Rifai *et al.*, 1995; Corseuil *et al.*, 1998). Because ethanol can be degraded under all common electron acceptor conditions, its presence can also contribute to the consumption of dissolved electron acceptors needed for anaerobic BTEX biodegradation (e.g., nitrate, ferric iron, and sulfate). Therefore, depending on aquifer chemistry and the rate of natural replenishment of electron acceptors, ethanol could impede natural attenuation of BTEX compounds by contributing to the depletion of the electron acceptor pool.

The extent to which ethanol is likely to cause the depletion of nutrients and electron acceptors has not been evaluated at the field scale. Nevertheless, a relevant field study was conducted with methanol, which is likely to cause similar effects as ethanol. Barker *et al.* (1992) conducted experiments involving controlled releases of BTEX and methanol mixtures at the Borden site, Canada. At the end of the 476-day experiment, they observed that a greater mass of BTEX remained in the plume from the gasoline with methanol than in the plume from just gasoline. They attributed this effect to oxygen removal by methanol biodegradation as well as to microbial inhibition due to high methanol concentrations.

# b. Accumulation of Volatile Fatty Acids

As discussed previously, the degradation of ethanol by mixed anaerobic cultures can result in the production of volatile fatty acids (VFAs) such as acetic, propionic, and butyric acid. In the absence of adequate interspecies  $H_2$  transfer (Figure 7), such VFAs can accumulate and decrease the pH (Lasko *et al.*, 1997; Speece, 1983). This could inhibit some microbial populations and would be particularly detrimental to methanogens, which are usually the most sensitive group of anaerobic consortia. Methanogens are generally inhibited when the pH decreases below 6 (McCarty, 1964). Because methanogens often mediate the final pollutant-stabilization step in the absence of nitrate- and sulfate-based respiration, an inhibition of methanogens could adversely affect anaerobic BTEX mineralization.

It should be pointed out that methanogens are not significantly inhibited by VFAs in well-buffered systems. For example, methanogens are often exposed up to 2000 mg/L VFAs in anaerobic digesters (McCarty, 1964). Other bacteria, however, might be inhibited by high VFA concentrations, even if the pH does not decrease significantly. For example, protein production by *E. coli* at pH 7 is

inhibited by acetate at about 2400 mg/L, especially in the case of expression of recombinant proteins, and growth is retarded at 6000 mg/L total acetate (Lasko *et al.*, 1997; Sun *et al.*, 1993).

It is unknown whether VFAs would accumulate in aquifers contaminated with alcohol-amended gasoline at sufficiently high concentrations to significantly decrease the pH and inhibit BTEX degradation. Such effects are likely to be systemspecific due to variability in buffering and dilution capacity among contaminated sites. It should be kept in mind, however, that VFAs are easily degraded and should not accumulate at high concentrations when alternative electron acceptors such as nitrate, sulfate, and ferric iron are present.

#### C. Bioavailability

BTEX bioavailability is rarely a limiting factor. However, ethanol might affect the availability of critical nutrients and co-substrates needed for BTEX bioremediation. As discussed in Section III.B, ethanol exerts a significant biochemical demand for nutrients and electron acceptors. In addition, BTEX migration is often retarded by sorption to aquifer solids. If significant retardation occurs, dissolved oxygen and other nutrients and electron acceptors traveling at the groundwater velocity can sweep over the contaminant plume from the upgradient margin. This can replenish nutrients and electron acceptors needed for in situ BTEX biodegradation. In theory, ethanol could decrease the extent to which BTEX compounds are retarded by sorption. As discussed earlier (Section III.A), evidence suggests that ethanol can affect BTEX partitioning between solid and aqueous phases (Brusseau et al., 1991; Kimble and Chin, 1994). A decrease in BTEX retardation would hinder the ability of essential nutrients and electron acceptors transported by bulk flow to catch up with the migrating BTEX compounds. In addition, adsorption of a contaminant to the aquifer matrix increases dilution of the dissolved contaminant plume, which is a process that might also be affected. The extent to which ethanol might hinder these processes, however, is unknown.

#### D. Summary of the Fate of Dissolved BTEX-Ethanol Mixtures

Ethanol that reaches groundwater is likely to be biodegraded preferentially over BTEX compounds. Although none of the potential ethanol metabolites that could accumulate in groundwater is toxic, ethanol may exert a high biochemical oxygen demand that would induce anaerobic conditions and hinder BTEX biodegradation. This is of greatest concern for benzene, which is the most toxic BTEX compound and the most recalcitrant under anaerobic conditions. Ethanol could also hinder the natural attenuation of BTEX plumes by decreasing sorption-related retardation during transport. The overall effect of ethanol on BTEX plume length is likely to be system specific and will depend largely on the release scenario and on the assimilative capacity of the aquifer.

# IV. MODELING EFFORTS QUANTIFYING THE EFFECT OF ETHANOL ON BTEX CONTAMINATION

Although there are numerous uncertainties in the specific mechanisms affecting the migration and dissolution of gasohol and the subsequent transport of ethanol and BTEX species with groundwater, a few studies have been completed to predict the effect of the ethanol on the net transport of soluble species. Table 4 summarizes the studies completed to date. In each case, the modeling studies have presented predictions of the length of BTEX plumes both with and without ethanol in the gasoline. Thus, even though the simulations considered are quite different, the results from all of these studies can be expressed as a percentage increase in the length of the BTEX plumes when ethanol is present versus a standard formulation gasoline.

The modeling approaches used in the studies presented in Table 4 incorporate a wide variety of assumptions. Heermann and Powers (1996) focus only on the impacts of cosolvency and NAPL dissolution rates and, thus, did not incorporate biodegradation. The other studies provide a more comprehensive view of the overall effect of ethanol on benzene plumes, albeit with significant uncertainty in the biodegradation mechanisms they incorporate and model parameters employed. Unfortunately, there are not sufficient data from field studies to verify the findings from any one of these studies. The overall conclusions reached through these studies are summarized in this section.

#### A. Modeling Focus on Cosolvency and Mass Transfer Rates

Heermann and Powers (1996) investigated increases in the transport of BTEX species resulting purely from cosolvency. For this study, a finite difference, cross-sectional flow and solute-transport model was modified to create a source term that simulated the interphase mass transfer of ethanol and xylene from a surrogate gasoline into ground water. Losses due to sorption and biodegradation were not incorporated into this model.

Ethanol and *m*-xylene source rates were computed with a linear mass-transfer rate equation (Eq. 3). To address uncertainties pertaining to mass transport processes in the gasoline, the mass transfer coefficient was varied from  $10^{-8}$  to  $10^{-3}$  m/s. The latter value was sufficiently high to maintain chemical equilibrium between the gasoline and groundwater phases at the boundary. The NAPL-water partition coefficient was estimated using log-linear models for *m*-xylene and ethanol.

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Citation	Conceptual Madel	Mathematical Model	Source Concentrations	Biodegradation	Sensitivity Analysis	Increased Benzene Plame Length
Heermann and Powers (1996)	2-D (X, Z) transport from a pool of gasoline Focus on cusulvency and interphase mass transfer	Finite difference transport models in both planses, coupled by the interphase mass transfer flux	Determined from mass transfer limitations and equilibrium at the interface	nut included	<ul> <li>mass transfer coefficient</li> </ul>	<pre>≤ + 10%   (for xySene not   benzene)</pre>
Malcolm Pirnie (1998)	Stendy-state, 2-D (X, Y) transport from a gasoline pool	Analytical solution with a point source	$\begin{array}{l} C_{code} = 4000 \mbox{ mg/L} \\ C_{B} = 8 \mbox{ mg/L} \\ benzene \end{array}$	Fint-order decay of benzene when C <sub>uad</sub> < 3 mg/L Fint order decay of ethanol	<ul> <li>retardation</li> <li>groundwater</li> <li>velocity</li> </ul>	%tE-11+
McNab et al. (1999)	Continuous slow release of gasoline (up to 3 gpd) to a growing NAPL pool at the water table, 3-D aqueous transport	Analysical solution with numerical averaging and superposition to account for finite source size	C <sub>not</sub> determined from daily input – all ecoh distributed across NAFL pool (C <sub>cash</sub> < 5000 mg/L) C <sub>n</sub> determined from equilibrium rel`n	First-order decay of ethanol and benaone. Benzeme degradation rule constant defined by inverse correlation to BOD cone, at the source	Meete Carlo simulations with • velocity • degradation • retardation garsohol • rate of garahol spill as variables	- + 100%
Molsun et al. (1999)	2-D transport (X-Z) from gasoline source at the water table at a residual saturation	Finite element model, simultaneerus solution of equations for solutes and electrum acceptors (BIONAPL/TD)	C <sub>not</sub> = 2000 mg/L (until depleted) C <sub>0</sub> from Raoult's Law	Aerubic decay with O <sub>2</sub> as the sole electrin acceptor quantified by Monod kinetics. Miscrohial growth incorporated	<ul> <li>Monud parameters</li> <li>retardation</li> <li>C<sub>such</sub></li> <li>spill scenario</li> </ul>	+10-150%

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Contours of simulated aqueous-phase ethanol and *m*-xylene concentrations are shown on Figure 9 for the elapsed period of 180 days. For the case of equilibrium between the gasoline and the groundwater table ( $k_i=10^{-3}$  m/s), the modeling analyses showed an approximate 10% increase in the distance to the leading edge of the *m*-xylene plume at 180 days due to the presence of ethanol in the gasoline. However, when smaller interphase mass-transfer coefficients were used, the size and extent of the *m*-xylene was essentially unaffected by the presence of ethanol. Ethanol was more than 90% depleted from the gasoline within several days under the local equilibrium assumption ( $k_i = 10^{-3}$  m/s) and was more than 99% depleted in less than 90 days. In contrast, ethanol was only about 10% depleted from the gasoline at 180 days for  $k_i = 10^{-8}$  m/s.

The above simulations suggest that the presence of ethanol in gasoline can produce a small but finite increase in the size of a BTEX plume due to cosolvency. Because the cosolvent effect on dissolution is more pronounced for *m*-xylene than benzene, it is expected that increases in the benzene plume due to this mechanism will be even less than predicted for *m*-xylene. Whether the impact is negligible or measurable will depend on transport mechanisms in the gasoline. Because this study did not consider the processes of sorption and preferential ethanol biodegradation (which hinders BTEX natural attenuation), it underestimates the true increase in the length of BTEX plumes. The modeling efforts described below provide a more complete understanding of the significance of these other processes.

# B. Comprehensive Modeling Efforts

Three of the modeling studies included in Table 4 largely ignored mass transfer and cosolvent effects at the NAPL source, but provided a more comprehensive understanding of the importance of other transport phenomena and spill scenarios on the length of benzene plumes in the presence of ethanol. Malcolm Pirnie (1998) arbitrarily defined ethanol concentrations at the source to be 4000 mg/L, while Molson et al. (1999) used 2000 mg/L based on the complete partitioning of ethanol into the aqueous pores within a residual gasoline source. The volume of the residual source corresponded to a residual saturation value of 0.023 for the HOC components of the gasoline. In contrast, McNab et al. (1999), considered a gasoline tank leaking slowly at three gallons per day or less, and assumed that all of the ethanol in the gasoline that leaked from the tank each day was transferred to the groundwater. The range of their predicted ethanol concentrations at the source was on the same order of magnitude as those used by Malcolm Pirnie (1998) and Molson et al. (1999).

Biodegradation rates were handled very differently among these three cases. The Malcolm Pirnie (1998) and McNab et al. (1999) approaches considered the effects of preferential ethanol degradation and the associated depletion of electron



Distance from center of gasoline

**FIGURE 9.** Predicted concentration contours for *m*-xylene and ethanol dissolved from oxygenated gasoline under a) local equilibrium conditions ( $k_i^n = 10^{-3}$  m/s) and b) mass transfer rate limited conditions ( $k_i^n = 10^{-8}$  m/s). All concentrations are in mg/L (time = 180 days). (From Heermann and Powers, 1996.)

acceptors on benzene degradation. However, these models did not consider the resulting changes in microbial concentrations and their effect on biodegradation rates. Molson et al.'s approach is a better representation of the actual biological mechanisms. Although it incorporates Monod kinetics, microbial growth and oxygen transport and consumption, it is still limited in its capacity to model the specific substrate interactions described in Section III of this article. Biodegradation rate coefficients were obtained from values compiled by Schirmer (1998). Molson et al. (1999) and McNab et al. (1999) provided some sensitivity analysis to evaluate the importance of biodegradation rate parameters on the overall benzene plume behavior. The choice of biodegradation parameters is very influential in model predictions. Because these parameters are highly site-specific and variable even within a given site, there is a considerable uncertainty in the accuracy of these simulations.

Results from these modeling studies illustrate that benzene plumes are indeed expected to increase when ethanol is present in the gasoline. The range of increased plume lengths varies between 10 and 150%. Several variables affect these estimates. Most importantly, the consumption of oxygen by ethanol and therefore the drastically reduced benzene degradation rate coefficients (k). Not surprisingly, the background oxygen concentration was an important variable related to this phenomenon. There was less impact of ethanol when the oxygen concentrations are high (Molson et al., 1999). Molson et al. (1999) illustrate that the retardation factor (R) is also a critical variable related to the depletion of oxygen for biodegradation. Higher retardation factors permit separation of the ethanol and benzene plume fronts. Thus, the high rates of oxygen consumption due to the presence of ethanol occur down gradient of the benzene plume front. The highest percent increase in the benzene plume lengths in the Molson et al. study was under the conditions of the lowest retardation factor (Figure 10).

Variability in the spill scenario can also be evaluated with the modeling studies presented in Table 4. With the continuous slow release simulated by McNab et al. (1999), ethanol concentrations at the source remain small, although continuous throughout the simulation period. Larger single-event spills, however, are associated with shorter duration inputs of ethanol to the groundwater, but at higher concentrations (Heermann and Powers, 1996; Molson et al., 1999). Molson et al. (1999) also simulated the release of pure ethanol into soil previously contaminated by gasoline. This spill event would be expected at a gasoline terminal where ethanol and gasoline are blended prior to transport to a filling station. Ethanol concentrations in this scenario are very high, resulting in a greater cosolvency effect for a very limited duration of time. Due to the limited duration of this event, the increased cosolvency appears to be less important than subsequent transport and degradation phenomena on the overall development and migration of a benzene plume.

Because these modeling efforts have not been verified with field data, a significant amount of uncertainty exists in their predictions. There seems to be a



**FIGURE 10.** Benzene plumes at 20 years from gasoline (left) and gasohol (right) sources. Four cases from the sensitivity analysis completed by Molsen et al. (1999) are shown, with k referring to the first-order degradation rate coefficient and R to the retardation factor. Contours are 10, 100, and 1000  $\mu$ g/L.

general agreement that cosolvency will not be a significant impact for gasohol with <10% ethanol by volume. The most substantial uncertainties lie in the mathematical description of and parameters used for the biodegradation rates. Yet, even with this uncertainty, predictions for most cases that are considered "typical" have similar predictions — ~20 to 50% increase in the length of benzene plumes. Substantial efforts to generate biodegradation data at both laboratory and field scales could improve our confidence in these predictions.

# V. SUMMARY AND CONCLUSIONS

Research materials describing the impact of fuel-grade ethanol on the overall fate and transport of gasoline hydrocarbons in the subsurface were critically

reviewed in this article. There is a substantial body of literature from which to draw information. However, while it appears that some aspects of the overall process are very well understood, other aspects are very poorly understood.

Gasohol spills to the subsurface undergo a series of steps: infiltration through the unsaturated zone, spreading and entrapment at the water table, leaching of compounds into the groundwater, and transport of solutes with the groundwater. In turn, several processes and variables affect each of these individual steps. Many of these individual processes are significantly impacted by the hydrophilic characteristics of ethanol in comparison with the more hydrophobic petroleum hydrocarbons. Unlike standard gasolines, the preferential partitioning of ethanol into the aqueous phase can cause significant changes in the volumes and composition of the aqueous and gasoline phases over time, and an increase in the effective solubilities of other petroleum hydrocarbons.

Although nearly all of the ethanol partitions from gasohol to an aqueous phase, concentrations of ethanol in water equilibrated with gasohol containing 10% ethanol or less are expected to be fairly low (<15% by volume). Higher concentrations would be expected for a neat ethanol spill. At these ethanol concentrations, aqueous BTEX concentrations will increase by less than 50% due to the cosolvent effect. The extent of the increase in concentration is least for benzene, which is the least hydrophobic and most toxic petroleum hydrocarbon in gasoline.

Quantifying dissolution from a NAPL pool requires that mass transfer rates also be considered. Relative to diffusion, free convection can increase the dissolution rate of ethanol and BTEX compounds and should be accounted for in modeling the gasoline source term. Significant losses of ethanol during this mass transfer process cause the composition of the gasoline in a pool at the water table to vary with time.

The transport and losses of BTEX dissolved in groundwater are also impacted by the presence of ethanol. Ethanol that reaches groundwater is likely to be biodegraded at much faster rates than other gasoline constituents. If the carbon source is not limiting, a preferential degradation of ethanol over BTEX may be observed under both aerobic and anaerobic conditions. Depending on the extent of the release, ethanol may exert a high biochemical oxygen demand that would contribute to the rapid depletion of dissolved oxygen in the groundwater. Thus, ethanol will likely be degraded predominantly under anaerobic conditions. None of the potential ethanol metabolites that could accumulate in groundwater is toxic, although some potential biodegradation byproducts such as butyrate could adversely affect the taste and odor of drinking water sources. In addition, acetate and other volatile fatty acids could accumulate at high concentrations, causing a pH decrease in poorly buffered systems.

The preferential degradation of ethanol by indigenous microorganisms and the accompanying depletion of oxygen and other electron acceptors suggest that ethanol could hinder BTEX biodegradation. This is particularly important for the fate of benzene, which is the most toxic BTEX compound and the most recalcitrant

under anaerobic conditions. Ethanol could also contribute to longer BTEX plumes by decreasing sorption-related retardation during transport.

The net effect of the ethanol on the length and duration of a contaminant plume requires an understanding of all steps along the series of processes that define the complete fate and transport pathways. This review illustrates that there is substantial knowledge about many mechanisms and data available to quantify many of the fundamental properties in gasoline-water-ethanol systems. At this point, however, the lack of *in situ* biodegradation rate data limits efforts to adequately predict the probable impact of ethanol on BTEX plumes. Specifically, little is known about the subsurface characteristics of ethanol plumes and how ethanol (or its metabolites) affects the stability and dimensions of BTEX plumes. This suggests the need for field studies that provide a stronger basis for risk assessment. The overall effect of ethanol is likely to be system specific and will largely depend on the release scenario and on the buffering and dilution capacity of the aquifer. It is likely that current bioremediation and risk management practices may have to be adapted to the increasing possibility of encountering ethanol as a co-contaminant. Albeit, the water resource impacts associated with the use of ethanol will be significantly less and more manageable than those associated with the continued use of MTBE. The key factor is the biodegradability of ethanol compared to the recalcitrance of MTBE.

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