1987; Wu, and Hickey, 1996). Therefore, fermenters and acetogens live syntrophically with hydrogen consumers that keep the H₂ levels low (Figure 7).

When sulfate is not limiting, sulfate reducers compete favorably for H₂ 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 CO₂ (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 iron-reducing 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](image-url)

**FIGURE 7.** Interspecies hydrogen transfer. Anaerobic oxidation of ethanol to acetate [1] is not thermodynamically feasible under standard conditions (ΔG° = + 9.6 kJ). This reaction can proceed only if the H₂ produced by acetogens and other fermenters is removed (law of mass action). The removal of H₂ 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 H₂ 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., CaCO₃) 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

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow 1.5 \text{CH}_4 + 0.5 \text{CO}_2
\]

Thus,

\[
\text{Potential methane production} = 1.5 \times \frac{16 \text{ g-CH}_4}{46 \text{ g-ethanol}} = 0.5217 \frac{\text{g-CH}_4}{\text{g-ethanol}}
\]

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

\[
0.5217 \frac{\text{g-CH}_4}{\text{g-ethanol}} \times \frac{1 \text{ mol CH}_4}{16 \text{ gram}} \times \frac{22.4 \text{ liters}}{\text{mole at STP}} \times \frac{(273 + 15)K}{273K} = 0.77 \frac{\text{liters CH}_4}{\text{gram - ethanol}}
\]

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 liter 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 pro-
cesses 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 site-specific 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 accep-
tors.

As discussed earlier, ethanol can be degraded by constitutive enzymes associ-
ated 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 thermo-
dynamic 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...
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⁺, K⁺-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

![Figure 8](image-url)
Table 3
Toxicity Thresholds for a *Pseudomonas putida* (From Bringmann and Kuhn, 1980)

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

Table 2
First-Order Rate Coefficients (λ) for Anaerobic and Aerobic Degradation of Ethanol by Aquifer Microorganisms (Estimated from laboratory experiments by Corseuil *et al.*, 1998)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electron acceptor</th>
<th>λ (day⁻¹)</th>
<th>Half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>O₂</td>
<td>0.23 - 0.35</td>
<td>2-3</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.53</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.17</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.1</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.12</td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>

* * The sources of soil and groundwater in the microcosms were different for each se
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 H₂ 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 system-specific 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.
### TABLE 4
Summary of Modeling Efforts to Assess the Effects of Ethanol on Benzene Plume Lengths

<table>
<thead>
<tr>
<th>Citation</th>
<th>Conceptual Model</th>
<th>Mathematical Model</th>
<th>Source Concentrations</th>
<th>Biodegradation</th>
<th>Sensitivity Analysis</th>
<th>Increased Benzene Plume Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heermann and Powers (1996)</td>
<td>2-D (X, Z) transport from a pool of gasoline</td>
<td>Finite difference transport models in both phases, coupled by the interphase mass transfer flux</td>
<td>Determined from mass transfer limitations and equilibrium at the interface</td>
<td>not included</td>
<td>• mass transfer coefficient</td>
<td>≤ + 10% (for xylene not benzene)</td>
</tr>
</tbody>
</table>
| Malcolm Pirnie (1998)     | Steady-state, 2-D (X, Y) transport from a gasoline pool                         | Analytical solution with a point source                 | $C_{\text{max}} = 4000 \text{ mg/L}$  
$C_b = 8 \text{ mg/L}$ benzene                            | First-order decay of benzene when $C_{\text{max}} \leq 3 \text{ mg/L}$  
First order decay of ethanol | • retardation  
• groundwater velocity                                           | +17-34%                                               |
| 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       | Analytical solution with numerical averaging and superposition to account for finite source size | $C_{\text{max}}$ determined from daily input – all ethanol distributed across NAPL pool ($C_{\text{max}} \leq 5000 \text{ mg/L}$)  
$C_b$ determined from equilibrium rel’n             | First-order decay of ethanol and benzene. Benzene degradation rate constant defined by inverse correlation to BOD conc. at the source | Monte Carlo simulations with  
• velocity  
• degradation rates  
• retardation  
• ethanol frac in gasohol  
• rate of gasohol spill as variables | ~ +100%                                               |
| Molson et al. (1999)      | 2-D transport (X-Z) from gasoline source at the water table at a residual saturation | Finite element model, simultaneous solution of equations for solutes and electron acceptors (BIONAPL/3D) | $C_{\text{max}} = 2000 \text{ mg/L}$ (until depleted)  
$C_b$ from Raoult’s Law                                    | Aerobic decay with $O_2$ as the sole electron acceptor quantified by Monod kinetics. Microbial growth incorporated | • Monod parameters  
• retardation  
• $C_{\text{max}}$  
• spill scenario                                          | +10-150%                                              |
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 \((k_i = 10^{-3} \text{ m/s})\), 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 \((k_i = 10^{-3} \text{ m/s})\) 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 \(k_i = 10^{-8} \text{ m/s}\).

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
FIGURE 9. Predicted concentration contours for m-xylene and ethanol dissolved from oxygenated gasoline under a) local equilibrium conditions \((k_i = 10^{-3} \text{ m/s})\) and b) mass transfer rate limited conditions \((k_i = 10^{-8} \text{ m/s})\). 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
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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