

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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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 5.4 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 and consider other approaches for reducing air emissions from automobiles (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 13.8×10^6 m³/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

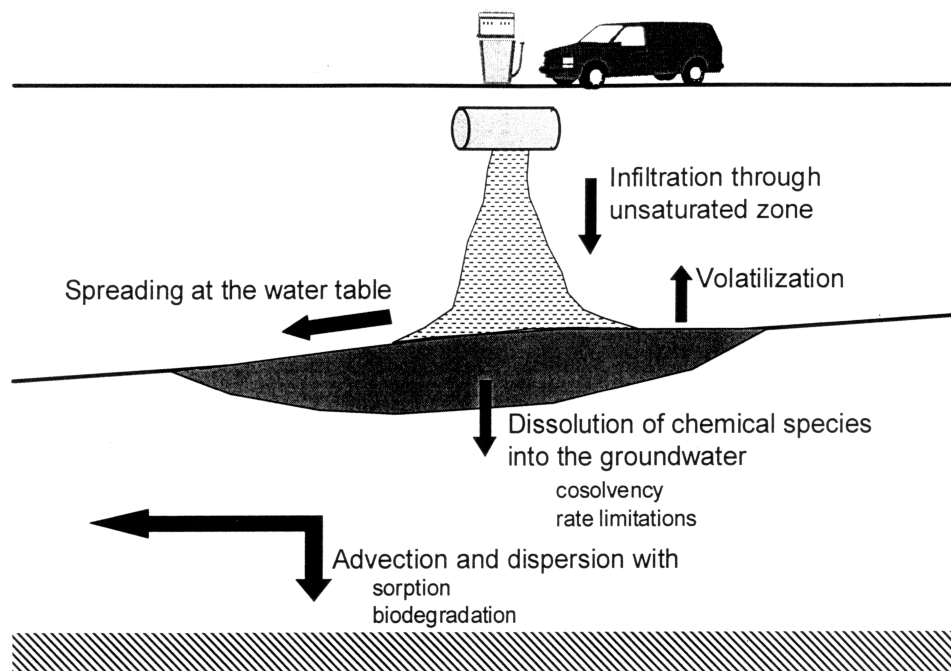


FIGURE 1. General processes governing the fate of gasolines in the subsurface.

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

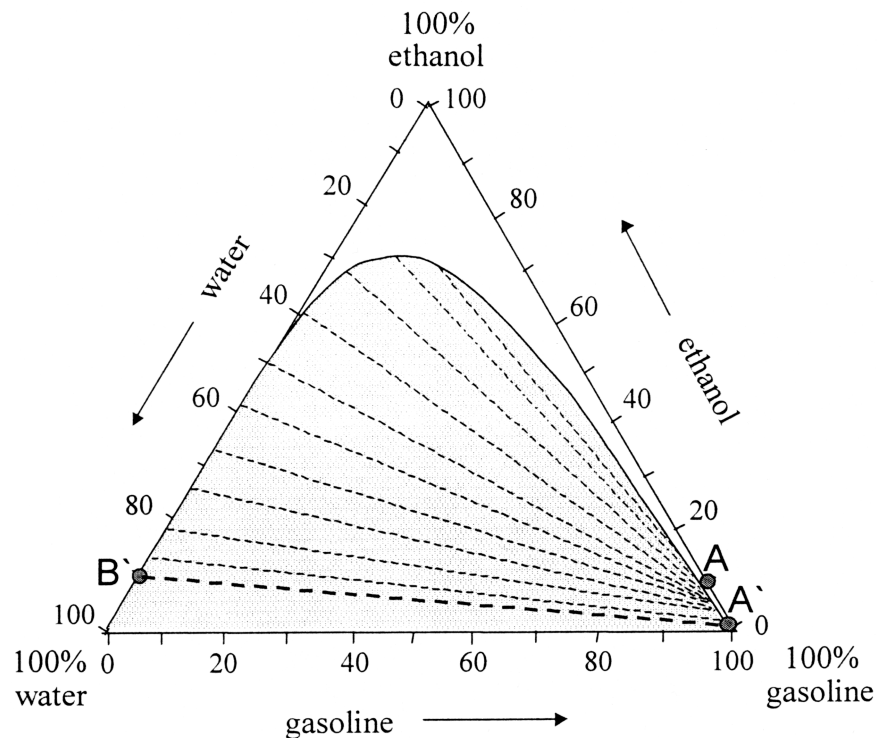


FIGURE 2. Ternary phase diagram for gasoline-ethanol-water system at 21°C. The shaded region represents the region where the total mass fractions separate into two phases. The ends of the dashed (tie) lines indicate the composition of each phase at equilibrium. Axes represent mass percentages. (Adapted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

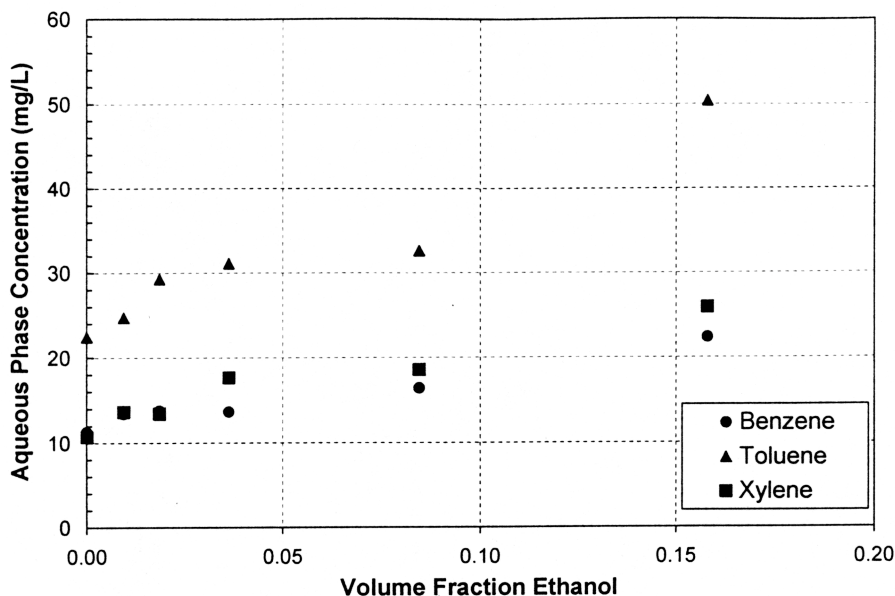


FIGURE 3. Concentration of BTX compounds in water equilibrated with a Brazilian gasoline containing 22% ethanol. (Data from Corseuil and Fernandes, 1999.)

(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 cosolvent-related 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):

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

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 σ_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).

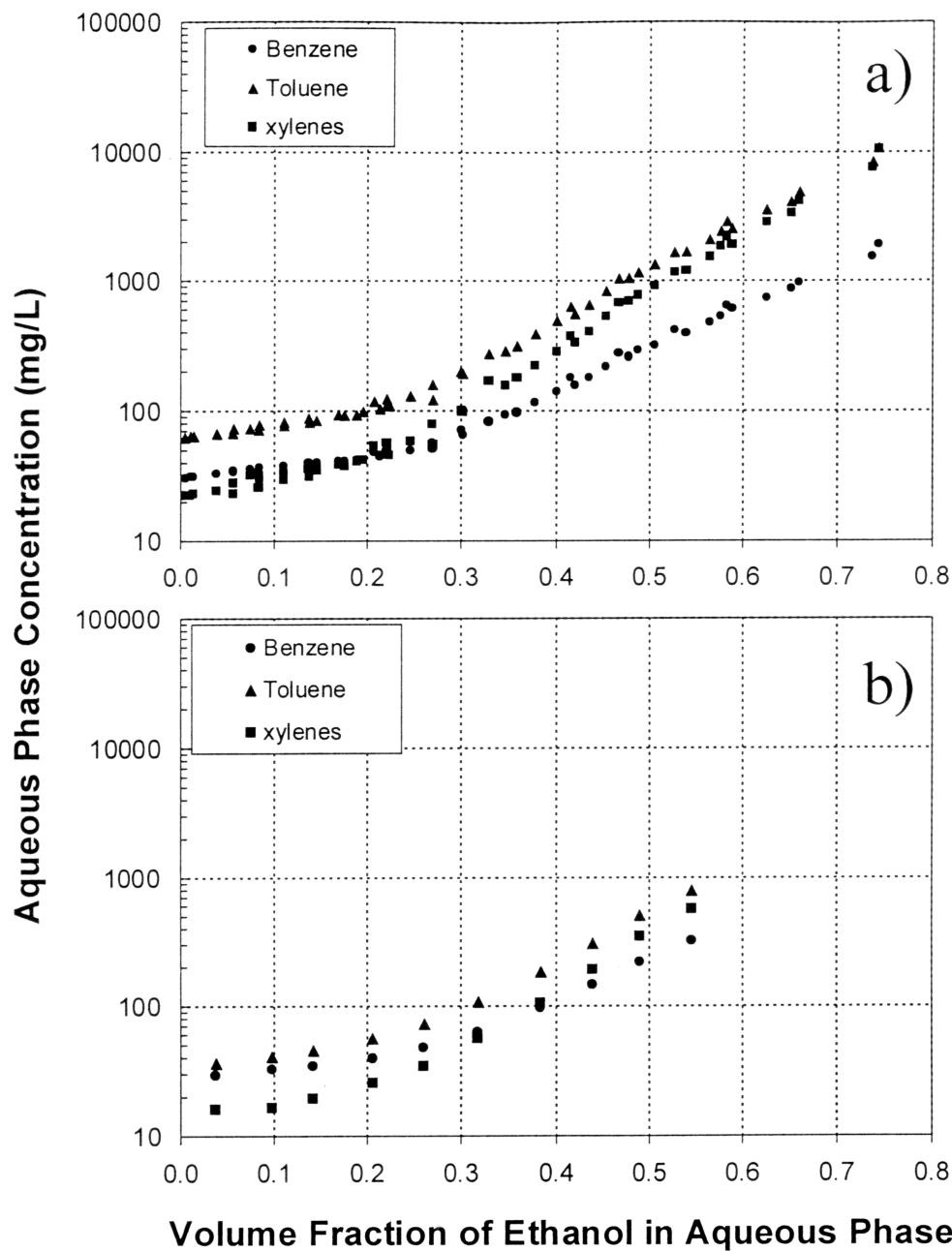


FIGURE 4. Concentration of BTX compounds in water equilibrated with a certified California test gasoline from Philips Petroleum (a) and an ethanol-gasoline from Ontario (b). (Data from Heermann and Powers, 1998.)

Since the log-linear cosolubility model (eqn. [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).

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

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

where, β is the volume fraction of ethanol in the aqueous phase at the breakpoint between the two segments of the model, and C_i^b 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. Since 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 (Eqn. 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-

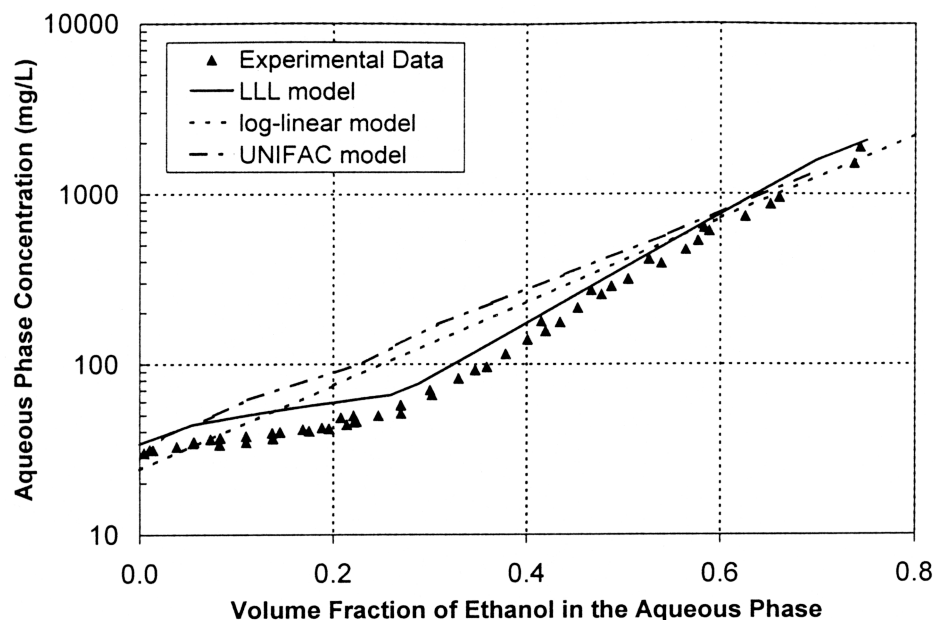


FIGURE 5. Prediction of benzene concentrations that had been equilibrated with C2 gasoline and additional ethanol. “LLL” indicates the piecewise linear-log-linear cosolvency model. (Adapted from Heermann and Powers, 1998.)

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):

$$N_i = k_i (C_i^{*w} - C_i^w) \quad (3)$$

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 ($K_i^{n,w}$), which describes the aqueous phase concentration that would be in equilibrium with the actual concentration in the second phase (C_i^n).

$$C_i^{*w} = \frac{C_i^n}{K_i^{nw}} \quad (4)$$

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 Javandel, 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 ($\rho_{eth} = 0.789 \text{ g/mL}$). 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 gasoline-groundwater 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 low-density 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 rate-limiting 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 :

$$S_i = K(C_i^w)^n \quad (5)$$

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 eqn. (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:

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

where $K_{p_i}^m$ and $K_{p_i}^w$ 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:

$$K_{p_i}^{w,c} = \frac{\gamma_{p_i}^{w,c}}{\gamma_{p_i}^w} K_{p_i}^w \quad (7)$$

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 (Brusseu, 1993; Hunt *et al.*, 1997). Such high concentrations could be encountered near the source of neat ethanol releases. However, since 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 half-life 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 ± 0.6 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 ± 0.7 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
	N-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 CO₂ and H₂O through Krebs'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 CO₂ 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_2 , H_2 , 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_2 and CO_2 . Acetate can also be produced by homoacetogens, which are bacteria that utilize CO_2 and H_2 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_4 . 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.*,

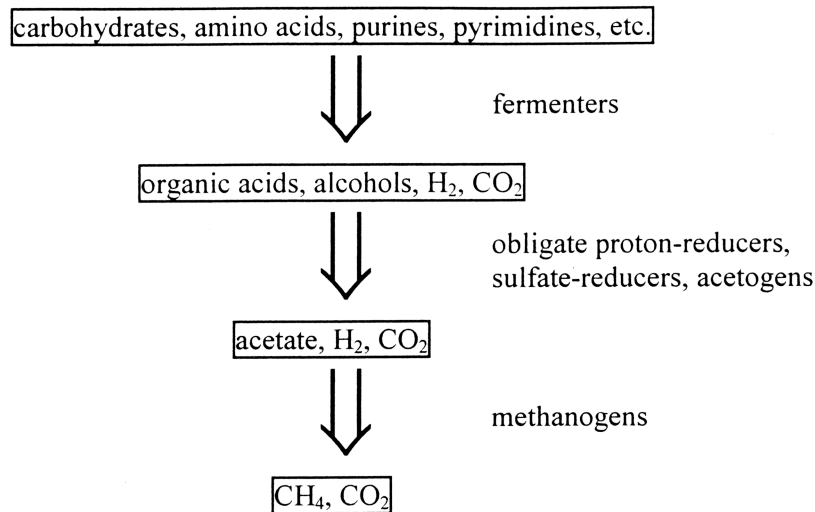


FIGURE 6. The anaerobic food chain. (Modified from White, 1995.)