Oxygenates

The Subsurface Fate of Ethanol

A Look at the Emerging Oxygenate Alternative to MTBE

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In response to the widespread contamination caused by MTBE-blended reformulated gasoline (RFG), legislative initiatives in several states and at the federal level have phased out, or are trying to phase out, the use of MTBE as a gasoline oxygenate. Ethanol is currently the most likely gasoline oxygenate alternative to MTBE. This potential for increased use of ethanol has been most widely acknowledged by California. The California Executive Order requiring the phase-out of MTBE also required that an analysis of the fate, transport, and health risks associated with the use of ethanol as a gasoline oxygenate be conducted. It is clear that California and many other states now recognize the need to understand the environmental fate of gasoline oxygenates before any policy decisions are made regarding their widespread adoption.

The material included in this article begins to summarize findings of the study completed for California. The full report is available at http://www-erd.llnl.gov/ethanol/. The primary physical and biological properties of ethanol that have implications for groundwater contamination are identified in this article. Future articles will focus on the uncertainties in our understanding and research required to make sound policy decisions. (For an overview on ethanol, see LUSTLine *#32, June 1999, "With the Possible Phase-Out of MTBE, What Do We Know About Ethanol?" by Bruce Bauman.)*

Ethanol Use in Gasoline

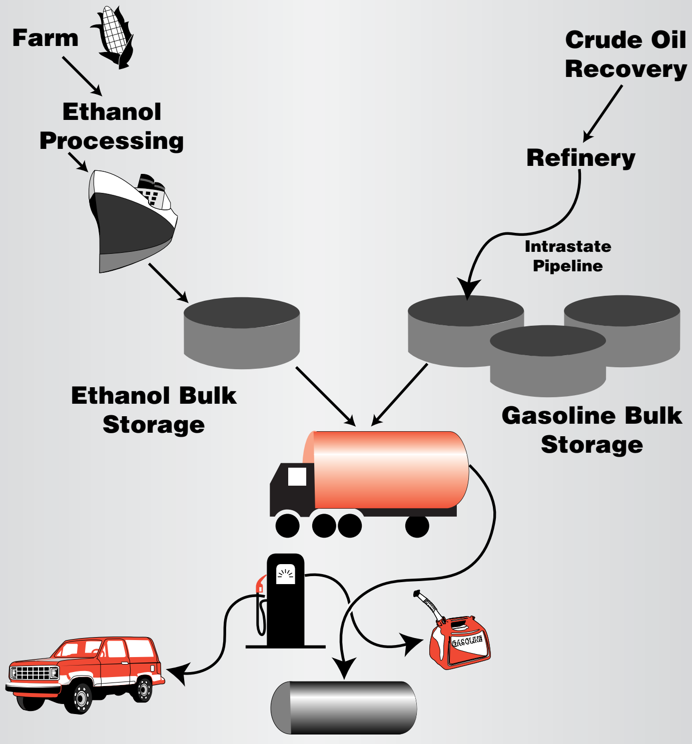
Ethanol is currently used in oxygenated gasoline, albeit not as widely as MTBE. Meeting the federal oxygen requirement would call for 8 percent (by volume) ethanol for oxyfuel and 6 percent for RFG. However, because of a 54 cents per gallon of ethanol used federal subsidy, the blending of ethanol at 10 percent with gasoline is popular. Several states provide additional subsidies for ethanol produced and used in their own states. (See sidebar on page 9.)

In Nebraska, 21 percent of all motor fuel sold contains 10 percent ethanol. At present, 60 percent of gasoline sold in Illinois, and 90 percent of gasoline sold in the Chicago area, contains 10 percent ethanol. Throughout the country, U.S. consumers use more than 56 million cubic meters (15 billion gallons) of ethanol-blended gasoline each year.

The ethanol used for fuel is made primarily from grains or other renewable agricultural and forestry feedstocks. One advantage of ethanol is that it can be made from liquid or solid waste, such as wood by-products, or agricultural waste, such as rice straw. The ethanol used for fuel is a high-octane, water-free alcohol produced from the fermentation of sugar or converted starch.

Unlike most gasoline hydrocarbons, ethanol loves water. These two fluids are completely miscible. This property has important implications, both for the manner in which we use ethanol-blended RFG and its environmental impacts. For example, it is difficult to distribute ethanol-blended RFG because of the propensity for water to absorb into the gasoline. Gasoline distribution terminals receive gasoline and ethanol separately; the two are then mixed as they are pumped into the tanker truck for delivery to a gasoline station (Figure 1). With current ethanol production capabilities, most of the ethanol used would be produced in

Figure 1

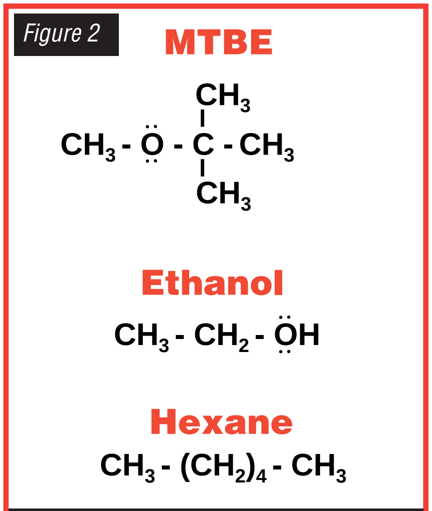


The life cycle of ethanol-RFG has some components that are significantly different than other gasoline formulations.

the Midwest and shipped by rail or marine cargo and then by rail or truck delivery to a final destination terminal.

Given the nature of the ethanol life cycle, the most likely spill scenarios associated with the use of ethanol as a primary fuel oxygenate would involve leaks of ethanol-blended RFG from tanker accidents or USTs or spills of neat ethanol at distribution terminals.

Figure 2



$$\mathrm{CH_3-\underset{..}{\ddot{O}}-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_3}$$

$$\mathrm{CH_3-CH_2-\underset{..}{\ddot{O}}H}$$

$$\mathrm{CH_3-(CH_2)_4-CH_3}$$

Molecular structure of gasoline oxygenates and hexane, a representative component of gasoline. The electrons (˙˙) on the oxygen atoms make the MTBE and ethanol molecules polar and, therefore, much more water-loving (hydrophilic) than hexane or other gasoline hydrocarbons.

Potential Impacts of Ethanol on Groundwater Quality

Many of the chemical properties and, therefore, the environmental transport properties of ethanol are similar to those of MTBE. The chemical structures of these two molecules can help us understand their environmental fate (Figure 2). The oxygen atom in both MTBE and ethanol makes these molecules more polar than other petroleum hydrocarbons. This polarity is the reason that they "love" water, a property described by the term "hydrophilic." Thus both MTBE and ethanol have a relatively high solubility in water and high mobility in the subsurface relative to more hydrophobic (water-hating) gasoline constituents such as hexane.

The key difference in the environmental fate of these two oxygenates is caused by the tert-butyl group on the MTBE molecule. This branched structure makes biodegradation of MTBE very difficult. Thus, while the ethanol molecule can be degraded and naturally attenuated in the subsurface, the MTBE molecule is not effectively attenuated, allowing it to travel significant distances from a spill site. The net effect of these properties results in very different environmental impacts associated with these two gasoline oxygenates:

- MTBE deleteriously affects groundwater quality for extended periods.
- Ethanol is not expected to be a significant groundwater contaminant for extended periods.

Although we do not expect ethanol to contaminate groundwater as much as MTBE, it is possible that its presence in gasoline and groundwater near a spill site will affect groundwater concentrations of other constituents from the gasoline—for example, benzene, a known carcinogen.

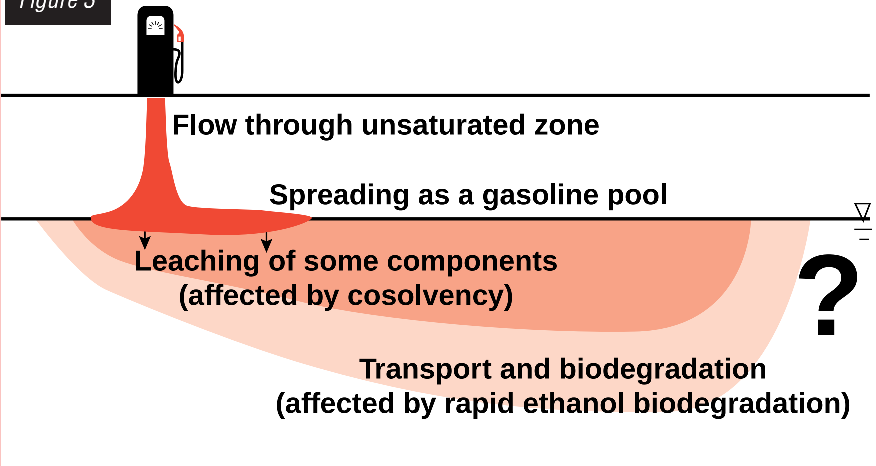
When considering the ultimate risk of any contaminant in the subsurface, we are most interested in potential groundwater concentrations at some receptor point downgradient of a spill site (Figure 3). Numerous processes can affect these concentrations following the spill of a petroleum product. The presence of a hydrophilic compound in the gasoline adds additional processes we have not had to consider previously. Research conducted so far has identified the following important issues:

- Sufficient amounts of ethanol can decrease the interfacial tension of the gasoline, potentially inducing greater lateral spreading of the gasoline within the capillary fringe.
- The presence of ethanol in water can create a cosolvent effect, increasing concentrations of other contaminants.
- All of the oxygen (and other electron acceptors, such as nitrate, iron, and sulfate) and nutrients needed for the biodegradation of benzene can be consumed as ethanol is biodegraded.

Insufficient work has been completed to date to allow us to understand the net effect of the first issue. Both of the other two processes may result in an increase in the concentration of hydrophobic compounds, such as benzene, and an increase in the distance these compounds would travel from a spill site before attenuating processes reduce their concentrations. Note that there are no known field studies of the behavior of ethanol and BTEX (benzene, toluene, ethyl benzene and xylene) from an UST release. Efforts are under way to identify sites where ethanol-blended gasolines have been used and presumably been released from an UST.

■ *continued on page 8*

Figure 3



Predicting groundwater quality and health risks at a downgradient receptor location requires that the net effects of several fate and transport processes be understood. Ethanol in gasoline can potentially increase concentrations of constituents dissolving from the gasoline source and decrease rates of BTEX biodegradation.

■ **Ethanol** *from page 7*

Cosolvency Issues

When mixed with water in the laboratory, ethanol quickly and completely transfers from ethanol-blended RFG into the aqueous phase. Depending on the volume fraction of ethanol in the gasoline and the relative volumes of gasoline and water that are mixed, it is possible that the resulting aqueous-phase concentrations of ethanol will be high enough to increase aqueous-phase concentrations of other hydrophobic compounds such as benzene.

The addition of ethanol to gasoline affects these concentrations by the "cosolvent effect." Cosolvency describes the reduction of the polarity of the aqueous phase when high concentrations of organic compounds, such as alcohols, are present. Essentially, the ethanol molecules add organic material to the aqueous phase, making it more attractive to other organic molecules.

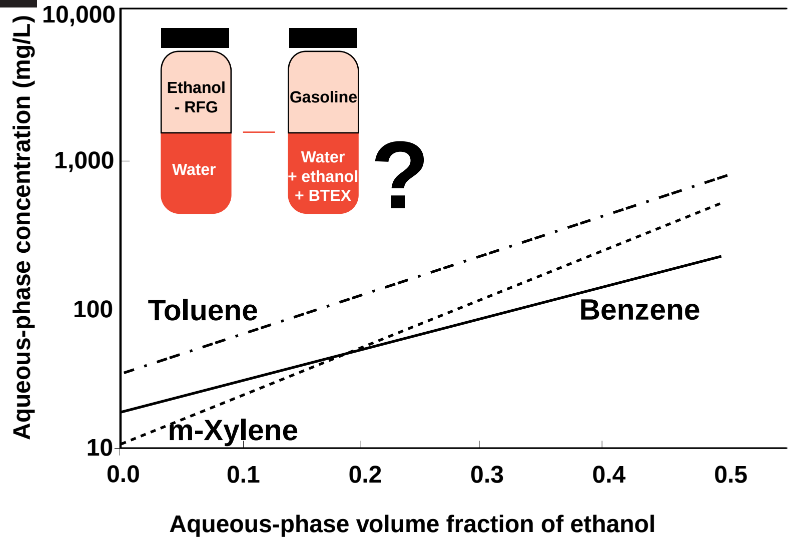
Figure 4 illustrates the approximate logarithmic increase in BTEX concentrations with increasing ethanol concentrations. It has been predicted that the volume fraction of the dissolved ethanol in groundwater systems will be less than or equal to 15 percent (i.e., 150,000 mg/L). At these relatively low ethanol volume fractions, BTEX concentrations in the aqueous phase near a gasoline spill are predicted to increase by approximately 20 to 50 percent.

The smallest percentage increase (smallest slope) was observed for benzene, the least hydrophobic of the BTEX compounds. Therefore, it is unlikely that cosolvent-related increases in BTEX concentrations will be significant at the field scale following spills of ethanol-blended RFG. Spills of neat ethanol at a bulk terminal, however, could result in very high ethanol concentrations in a localized area. This problem could cause a much more significant—possibly an order of magnitude—increase in BTEX concentrations if the soil was previously contaminated with a petroleum product. Field studies are in progress that should help clarify our understanding of cosolubility issues.

Biodegradation Issues

Ethanol can be degraded either aerobically (in the presence of oxygen) or anaerobically (in the absence of oxygen) at faster rates than can other gasoline constituents (e.g., benzene, MTBE). In laboratory studies with microorganisms from a petroleum spill site, ethanol had a half-life of approximately two to three days under aerobic conditions. The half-life was approximately twice as long under anaerobic conditions. Less favorable conditions in an aquifer would likely result in longer half-lives in situ. Nevertheless, it is expected that ethanol will undergo relatively rapid biodegradation in the subsurface. In contrast, MTBE is expected to biodegrade at an appreciably slower rate under most conditions. (Note: MTBE degradation is addressed with caution in light of recent studies that suggest MTBE may not be as recalcitrant as believed. Stay tuned.)

Figure 4



The presence of ethanol can increase concentrations of BTEX species in an aqueous phase equilibrated with ethanol-blended RFG. This drawing of vials illustrates experiments conducted to determine the cosolvency effect. RFG with a range of ethanol concentrations is mixed in a small vial with water. Following mixing to equilibrate, the aqueous-phase concentrations of ethanol and BTEX are analyzed. Results plotted illustrate that contaminant concentrations increase in a generally logarithmic relation with increasing volume fraction of ethanol in the aqueous phase (data from Heermann and Powers, 1999).

Quantifying BTEX biodegradation rates is necessary for predicting the net transport of gasoline constituents from a spill site and, therefore, for predicting potential risks to groundwater resources. These biodegradation rates are integrally linked to the biodegradation of ethanol. Ethanol represents a carbon and energy source that is likely to stimulate the growth of a variety of microbial populations. This effect is great in terms of getting rid of the ethanol in the subsurface, but it comes at a cost: Nutrients and oxygen that are consumed in the biodegradation of ethanol are no longer available to biodegrade BTEX.

This fact is particularly important for benzene, a known carcinogen. When degraded in situ by indigenous microorganisms, the half-life for benzene is considered to be greater than 200 days under anaerobic conditions, compared with its half-life of only 2 days in an aerobic aquifer. These degradation rates have not been confirmed in the presence of ethanol. The consumption of oxygen during the biodegradation of ethanol allows benzene to travel farther with the groundwater than it would from the spill of a nonoxygenated gasoline.

The Fate of Dissolved BTEX-Ethanol Mixtures

Although ethanol has been used in gasoline for a few decades in the Midwest, data quantifying the fate of ethanol in the subsurface and the effect of ethanol on BTEX are generally unavailable. A telephone survey of LUST regulators in these states

How Much Ethanol Is in That Gallon of RFG?

Did you know that no real formal definition exists for how much ethanol you need in gasoline to call it gasohol? It's frequently assumed to be 10 percent, but there is no legal definition. How much of an oxygenate might we expect in a gallon of gasoline? To meet the 2.0 and 2.7 weight percent oxygen requirements of reformulated gasoline (RFG) and oxygenated gasolines (oxyfuel), respectively, requires 10.8 and 14.8 volume percent MTBE. Technically, the use of ethanol in RFG requires only 5.7 percent (7.8 percent for oxyfuel), inasmuch as ethanol has a higher oxygen content than MTBE. In the real world, ethanol is almost always blended into gasoline to 10 percent volume. The reason? MONEY!

There is a federal tax break for the use of ethanol in gasoline—54 cents per gallon of ethanol used. The ethanol tax incentive has three tiers reflecting ethanol/gasoline blends at volumes of 10 percent, 7.7 percent, and 5.7 percent.

The Specifics

The 18.4 cents per gallon federal excise tax on gasoline is used to fund the Federal Highway Trust Fund, the primary source of federal dollars used for road-building projects. The ethanol tax incentive is highest when ethanol is blended at a 10 percent level. When it is blended into gasoline at that level, each gallon of gasoline receives a 5.40 cents exemption from the federal excise tax. (Each gallon of gasoline contains 0.1 gallon of ethanol, so the tax exemption is 0.1 x 54 cents, or 5.4 cents.) For ethanol blended into gasoline at 7.7 percent, each gallon of gasoline receives a 4.16 cents exemption. (In this case, each gallon of gasoline contains 0.077 gallon of ethanol, so the exemption is 0.077 x 54 cents, or 4.16 cents.) For 5.7 percent ethanol/gasoline blends, the exemption is 3.08 cents. (You do the math for this one.)

The actual economic calculus that a gasoline blender would use is fairly complex. To grossly oversimplify things, it is usually most profitable to use the 10 percent blend. It basically means that you can sell your gasoline at the pump for the same price as the nongasohol station across the street but get a 5.4 cents per gallon "rebate" from the federal government. That usually makes more "cents" than blending at 7.7 percent and getting only a 4.16 cent rebate.

A quick check of data from a recent national gasoline survey confirms this assumption. Nationally, the average ethanol concentration in alcohol-blended fuels during the summer of 1999 and the winter of 1999–2000 was about 10.1 percent, with a minimum value of 9.5 percent and a maximum of 11.0 percent.

Several states provide additional subsidies for ethanol produced and used in their own states. The take-home message here is that in the majority of cases, if a gasoline contains ethanol, be it an RFG or oxyfuel, it is probably present at about 10 percent by volume. ■

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revealed that they indeed know that they have had spills of gasohol, but they cannot be tracked because databases archiving spill histories generally do not identify the type of gasoline. The lack of any regulations requiring groundwater to be tested for ethanol content also contributes to the scarcity of data. The paucity of historical data confounds efforts to understand and predict the effects of ethanol on groundwater quality.

We should learn from lessons associated with MTBE—namely, that the ubiquity of MTBE in the environment was not understood until we started to look for it. Analytical techniques for assessing ethanol concentrations are now available. It is time to start adding this analyte to routine monitoring at gasoline-impacted sites, especially in the Midwest, California, and other locations where ethanol is already in use.

At this point, no extensive modeling studies are available to predict the overall fate of ethanol and BTEX in an aquifer following a spill of ethanol-blended RFG. Various researchers have conducted modeling studies but always with limiting assumptions about the significance of cosolvency or biodegradation mechanisms. For example, many of the models assume that BTEX biodegradation does not occur in areas where ethanol is present at concentrations above some threshold value. Regardless of the assumptions employed, the conclusions drawn from the variety of modeling studies suggest that benzene is likely to travel farther from ethanol-blended RFG release sites. Predictions generally show that benzene plumes from ethanol-blended gasoline could be from 20 to 150 percent longer than those from nonoxygenated gasoline.

As states and the federal government ponder the increase in use of ethanol as an oxygenate and a biomass fuel, the potential environmental benefits and costs associated with this oxygenate must be weighed and compared with other economic and social implications. (Ideally, the politics won't overshadow the science.) Conclusions drawn based on the literature review completed for California suggest that the effects on groundwater resources associated with the use of ethanol will be less severe and more manageable than those associated with the use of MTBE. ■

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