

Will Ethanol-Blended Gasoline Affect Groundwater Quality?

Using ethanol instead of MTBE as a gasoline oxygenate could be less harmful to the environment.

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Methyl *tert*-butyl ether (MTBE) contamination in groundwater and surface water in the United States is widespread and currently considered a major threat to drinking water resources (1-3). The fuel additive is therefore being phased out, and it is highly likely that ethanol will replace it. To ensure public safety, possible impacts to groundwater quality resulting from any releases of ethanol-blended gasoline must be understood. Typical scenarios include leaks of ethanol-blended gasoline from underground storage tanks, accidents with railroad cars or tanker trucks, and spills of neat ethanol at distribution terminals.

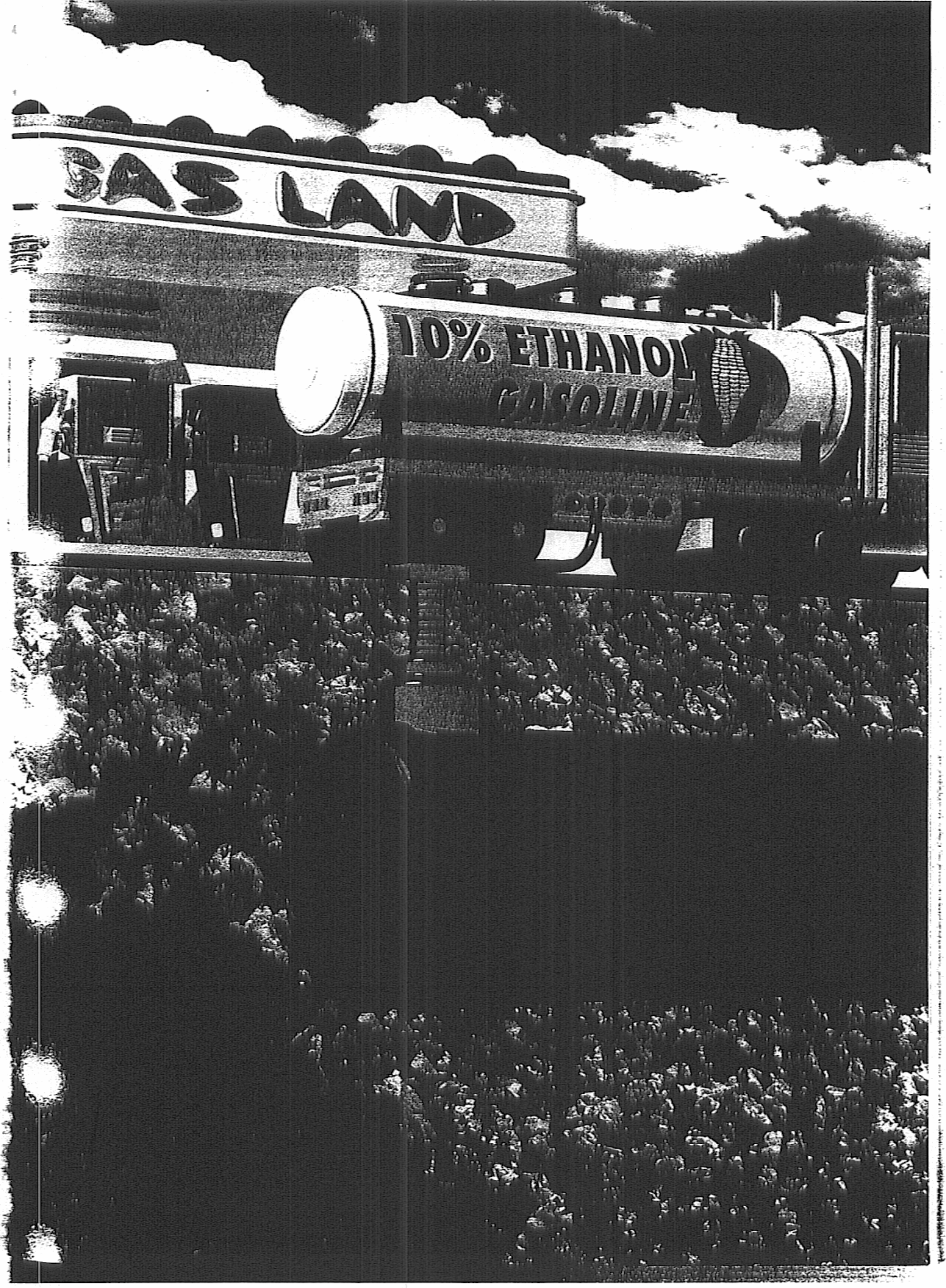
The potential impacts of such releases were the focus of an extensive literature review prepared for the state of California (4) in response to Governor Davis's Executive Order calling for the removal of MTBE from California's gasoline by Dec. 31, 2002 (www.calepa.ca.gov/programs/MTBE/EPCResolution.htm). The study indicates critical environmental fate and transport issues surrounding the use of ethanol-blended gasoline mixtures and serves as a basis for recommending additional research on the environmental fate, which would be necessary for the de-

sign of remediation measures to respond to ethanol-blended gasoline spills.

MTBE was initially added to gasoline to increase octane ratings following the U.S. ban on alkyl lead additives in 1979. Oil refiners decided to comply with the 1990 Clean Air Act Amendments (CAAA) by using MTBE to formulate oxygenated gasoline ("oxyfuel") and reformulated gasoline (RFG) mixtures that contain at least 2.7% and 2% oxygen by weight, respectively (5).

MTBE's potential for groundwater and surface water contamination was not a significant consideration when the decision was made to adopt it as a gasoline oxygenate (5). It is now known, however, that the chemical is a very mobile and persistent contaminant in aqueous systems, because of its high solubility and low biodegradation rates. Consumer complaints of MTBE's pungent turpentine-like odor and taste effectively limit acceptable levels in public drinking water supplies to <5-40 ppb, although there is still significant debate regarding safe levels of MTBE in drinking water.

In its final report, EPA's Blue Ribbon Panel on Oxygenates in Gasoline recommended that the use of MTBE—or any other oxygenate—in the nation's gas-

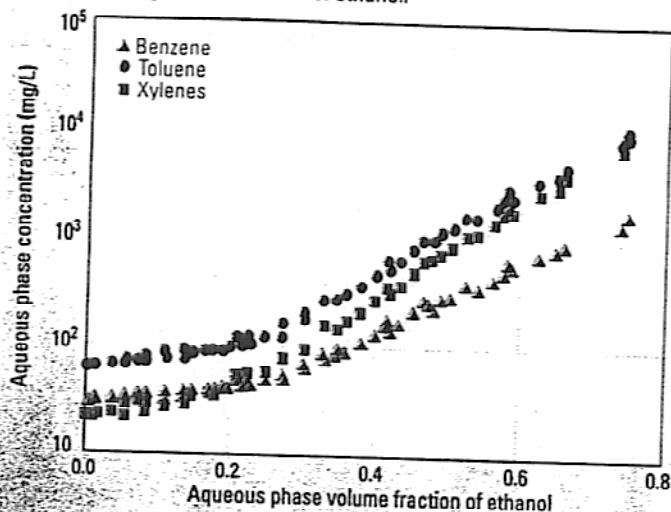


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BTX and ethanol concentrations track logarithmically

Concentrations of BTX in an aqueous phase equilibrated with gasoline show a substantial increase in the effective solubility of these constituents with increasing concentrations of ethanol.



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oline be substantially reduced (6). Seven states have implemented policies to phase out the use of MTBE, and three states limit the concentration of MTBE that can be incorporated into gasoline (www.ethanolrfa.org). The federal government has also proposed a reduction or a ban on the use of MTBE through provisions in the Toxic Substances Control Act (7). To allow for a federal ban on MTBE, EPA has proposed that volatile emissions standards from gasoline be relaxed. This would allow gasoline distributors more flexibility in their use of ethanol as an alternative.

An obvious replacement?

Ethanol is already widely used in oxygenated gasoline. It is used at concentrations of approximately 6–8% (by volume) to comply with the CAAA and frequently at 10% because of the \$0.54/gallon federal excise tax exemption to promote markets for ethanol (5). Ethanol-blended gasoline is available in many Midwestern states and currently accounts for more than 95% of the gasoline sold in the Chicago area (www.ethanolrfa.org/ethanolreport.html). In Brazil, most gasoline contains ethanol.

In separate federal initiatives, ethanol's use as a fuel source is advocated to promote renewable biomass fuels. President Clinton signed an Executive Order in 2000 to accelerate the development and use of biomass fuels, products, and chemicals. The order includes funding for both fiscal years 2001 and 2002 to encourage increased production at affordable prices. Clinton was also joined by the heads of the Agriculture and Energy Departments, EPA, and Senator Richard Lugar (R-IN) in announcing a goal of tripling bioenergy and bioproducts use by 2010.

Significant changes in U.S. infrastructure would be required for large-scale implementation of ethanol as a gasoline additive—whether as an oxygenate or a biomass fuel. The hygroscopic nature of ethanol-blended gasoline prevents its preparation at a refinery and distribution by pipeline (see sidebar on next page (8)). Thus, distribution terminals receive gasoline and ethanol separately to be mixed as it is pumped into a tanker truck for delivery to gasoline stations.

Groundwater quality impacts

There are similarities in the partitioning characteristics of ethanol and MTBE in gasoline (9). The polarity arising from the oxygen atom in ethanol causes it to preferentially partition into water. A similar effect is seen in the polar MTBE molecule, although the solubility of MTBE in water (~4% mass basis) is significantly less than the infinite solubility of ethanol. Like MTBE, ethanol also has a very low tendency to adsorb to mineral surfaces or volatilize from an aqueous phase. The primary difference between ethanol and MTBE is the former's high degree of biodegradability. The *tert*-methyl and ether groups on the MTBE molecule make it difficult to degrade in the subsurface, whereas ethanol is readily degraded under both aerobic and anaerobic conditions and likely will be effectively attenuated under natural conditions.

Although ethanol is unlikely to be a significant groundwater pollutant, there is concern regarding the effects of ethanol on concentrations of other gasoline constituents. Two issues are of most concern. Ethanol in water can create a cosolvent effect, and ethanol biodegradation can deplete the groundwater of nutrients and electron acceptors. Both processes could result in an increase of the concentration of hydrophobic compounds, such as benzene, and thereby increase the distance that these hazardous compounds travel from a spill site before attenuating processes safely reduce their concentrations.

Cosolvency issues

Although compounds in standard-formulation gasoline are relatively immiscible in water, ethanol is completely miscible in both gasoline and water at all concentrations. With a sufficiently large amount of ethanol in a localized subsurface environment, gasoline and water become completely miscible with each other and merge into a single phase (see sidebar). Although this might occur following a spill of neat ethanol into petroleum-contaminated soil at a terminal, ethanol concentrations (<15% by volume in the aqueous phase) in groundwater near the site of an RFG spill are expected to be much lower than the 80% by volume concentrations in the aqueous phase that is required to create a single phase (10, 11).

Aqueous-phase concentrations of ethanol that leach from an RFG or oxyfuel spill could also be high enough to increase the groundwater concentrations of individual chemical species equilibrated with the gasoline. Of most concern are the monoaromatic hydrocarbons, especially the carcinogen benzene. Ethanol also affects equilibrium partitioning relationships by the "cosolvent effect", which is observed

is a reduction of the aqueous-phase polarity of the aqueous phase. High concentrations of polar organic compounds are present.

Heermann and Powers (10) studied the cosolubility effects associated with ethanol in gasoline. Results of batch equilibrium experiments illustrate an approximate logarithmic increase in benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations with increasing ethanol concentrations (see Figure 1). Over the range of the maximum aqueous-phase ethanol volume fractions observed by Corseuil and Fernandes (11) ($\leq 15\%$), benzene, toluene, and xylene concentrations generally increase by approximately 20–60%. The smallest percentage increase was observed for benzene, the least hydrophobic of the BTEX compounds. More hydrophobic compounds in gasoline, such as xylene, will have a greater percentage increase in their aqueous-phase concentrations in the presence of ethanol. These results suggest that it is unlikely that cosolvent-related increases in BTEX concentrations will be significant relative to other processes that affect field-scale concentrations following a spill of ethanol-blended gasoline. Spills of neat ethanol at a bulk terminal, however, could result in very high ethanol concentrations in a localized area and a much more significant—possibly an order of magnitude—increase in BTEX concentrations.

Similar to the cosolvent effects described above, the presence of ethanol in groundwater reduces the extent of sorption of hydrophobic compounds be-

cause of the reduced polarity of the aqueous phase. Although this phenomenon has not been studied for ethanol in gasoline, studies with other cosolvents indicate that the cosolvency effect is less significant for sorption than for solubilization (12, 13). Thus, it appears that ethanol would have little impact on the retardation of BTEX species in an aquifer, at least at the low ethanol concentrations expected for ethanol-blended gasoline spills. The impact of ethanol on more hydrophobic gasoline components is not known at this time.

Biodegradation issues

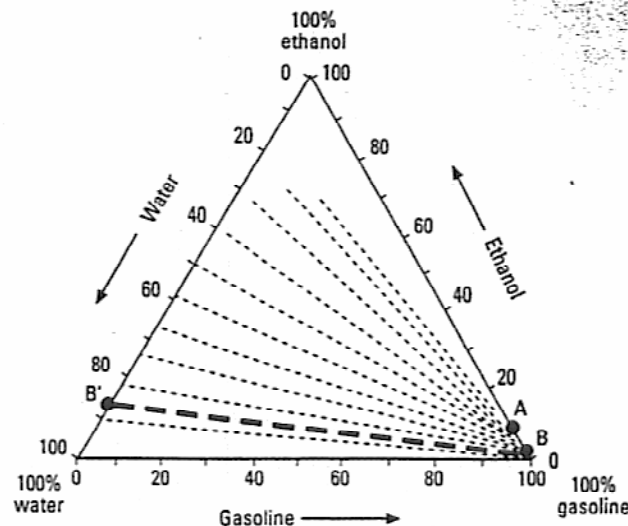
Ethanol can be degraded at a faster rate in both aerobic and anaerobic environments than other gasoline constituents (14, 15). Large concentrations ($>100,000$ mg/L) of ethanol are not biodegradable and are rather toxic to most microorganisms (16). Such high concentrations are unlikely to be encountered at sites contaminated with ethanol-blended gasoline. Thus, ethanol plumes should be degraded by indigenous microbes. Table 1 presents the half-life of ethanol for a variety of redox conditions as determined from laboratory microcosm studies. Conditions in an aquifer (lower microbial concentrations, colder temperatures, depletion of electron acceptors, etc.) could result in longer subsurface half-lives in situ than those depicted in Table 1. Nevertheless, it is expected that ethanol will biodegrade much faster in the subsurface than other gasoline constituents.

The miscibility of gasoline–ethanol–water mixtures

Ethanol-blended gasoline requires unique handling because it tends to separate into two phases when contaminated by water. Ethanol partitioning and the effects of ethanol on solubility can be illustrated on a ternary phase diagram. The shaded region (see figure) indicates the range of water–gasoline–ethanol mass fractions where the three components exist as two separate phases. The unshaded region indicates the composition where these components exist as a single phase. For example, if a gasoline initially contained 10% (by mass) ethanol, its composition would be indicated by point A. If additional water enters the gasoline storage tank or automobile gas tank, the overall composition would change. Several thousand parts per million of water can dissolve into ethanol-blended gasoline. However, if this solubility limit is exceeded and the overall mixture now has mass fractions that are within the shaded area, the gasoline will separate into two phases. A gasoline-rich phase (B) will float on top of a water and ethanol mixture (B'). A significant drop in temperature can also induce phase separation in ethanol-blended gasoline because of the reduced solubility of water and ethanol in gasoline at lower temperatures. This is why separate bulk storage tanks at terminals are needed, and pumping ethanol by pipeline is difficult.

Ternary phase diagram for gasoline–ethanol–water system at 21 °C

The shaded portion of the diagram 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.



Source: Adapted from (5) with permission.

Because of its high oxygen demand, ethanol is likely to be degraded predominantly under anaerobic conditions. None of the products of anaerobic ethanol degradation is toxic, although some metabolites (e.g., butyrate, methane) and changes in inorganic chemical speciation caused by the altered redox potential could have adverse aesthetic impacts. In addition, acetate and other volatile fatty acids could lower pH and inhibit microbial activity if they accumulate at high concentrations in poorly buffered systems. Such effects are likely to be system-specific due to variability in buffering and dilution capacity among contaminated sites.

Biodegradation is often the single most important mechanism attenuating the subsurface migration of gasoline constituents, such as BTEX (17). Therefore, quantifying BTEX biodegradation rates is necessary to predict the net transport of these pollutants from a gasoline spill and to evaluate the potential risks to groundwater resources.

Ethanol is likely to be preferentially degraded by the indigenous microorganisms that would otherwise feed on BTEX



BTEX biodegradation, however, is integrally linked to the biodegradation of ethanol. Ethanol is likely to be preferentially degraded by the indigenous microorganisms that would otherwise feed on BTEX (14, 16). Moreover, with ethanol concentrations expected in the thousands of parts per million, this organic solute could exert a greater biochemical oxygen demand than other soluble components of gasoline. Thus, ethanol is likely to accelerate the de-

pletion of dissolved oxygen and decrease the extent of aerobic BTEX degradation. This is particularly important for the fate of benzene, which is the most toxic of the BTEX constituents (18). When degraded in situ by indigenous microorganisms, benzene can have a half-life that can vary from ~2 days in an aerobic aquifer to >200 days under anaerobic conditions (19). Depending on aquifer chemistry and the rate of natural replenishment of electron acceptors, ethanol could also deplete the electron acceptors and nutrients needed for fully degrading ethanol and BTEX species.

Overall fate of mixtures

Field studies, in conjunction with comprehensive modeling, are needed for evaluating the net impact of cosolvency and biodegradation effects on groundwater quality. Researchers have conducted some modeling studies, but always with significant assumptions about the significance of cosolvency or biodegradation mechanisms (4, 15, 20). For example, many models assume that BTEX biodegradation does not occur in areas where ethanol is present at concentrations above some threshold value.

Nevertheless, the conclusions drawn from various modeling studies suggest that benzene will indeed travel farthest from the site of an ethanol-blended gasoline spill. Predictions generally show that these benzene plumes range from 20 to 150% longer as compared with nonoxygenated gasoline. Variability in predicted plume lengths depends on the modeling study assumptions and the nature of the aquifer and transport properties investigated.

Analysis

Monte Carlo simulations were used to predict a distribution of contaminant plume lengths for three risk scenarios: benzene in groundwater from a standard gasoline spill; benzene in groundwater from an ethanol-blended gasoline spill (5.7% by volume ethanol in the gasoline); and MTBE in groundwater from an MTBE-blended RFG spill. The plume length distributions were then used to estimate the probability that a drinking water well near a spill site would be impacted. Although many simplifying and conservative assumptions were made in this analysis—including that all releases occur simultaneously—the results provide an understanding of the risks of well contamination due to the use of oxygenated gasolines. Figure 2 shows that, relative to risks associated with standard formulation gasoline, there is an increase in the risk that wells will be contaminated by RFG using either MTBE or ethanol as an oxygenate. With ethanol, the risk of contaminating wells decreases after approximately five years. However, the risk continues to grow for MTBE because of the assumption that this chemical is not degraded in the subsurface. The conservative approach used in this analysis, including the low biodegradation rates and assumption that the gasoline source areas are not remediated, results in an overstatement of the risks associated with these additives to gasoline. Nevertheless, the relative trends do favor ethanol when considering risks associated with RFG spills.

More knowledge needed

The California-sponsored study presents extensive knowledge about the fate and impacts of ethanol-blended gasoline in the subsurface, but many physical, chemical, and biological processes affecting concentrations of gasoline constituents are still not adequately understood. Although modeling studies (4, 15, 20) show that assumed biodegradation rates have a significant impact on the predicted increase in benzene plume lengths, currently available research results quantifying these rates are limited in number and scope. Additional studies are clearly needed. Ongoing work at Lawrence Livermore National Laboratory and the University of Iowa should improve our ability to understand and predict how such substrate interactions affect degradation kinetics. Other areas needing research are the rates of ethanol partitioning from a gasoline spill to groundwater and the nature of gasoline pools when ethanol is present or spilled into an existing pool. Experimental, modeling, and field studies would all be appropriate for increasing our understanding of these processes.

The lack of a historical database confounds efforts to understand and predict the impacts of ethanol on groundwater quality. A telephone survey (4) of leaking underground fuel tank regulators in Midwestern states revealed that they know they have had spills of gasoline, but these cannot be tracked, because databases archiving spill histories generally do not differentiate among gasoline types. The lack of any regulatory requirement to test for ethanol also contributes to data scarcity.

For those studying ethanol in gasoline, there are lessons to be learned from MTBE use. The ubiquity of MTBE in the environment was not understood until we started looking for it. Analytical techniques for assessing ethanol concentrations are now available. This analyte, as well as other analytes that indicate the redox state of the aquifer, should be routinely monitored at gasoline-impacted sites, especially in the Midwest and California, where ethanol is already in use. As the federal government and state governments consider legislation to increase the use of ethanol, the potential environmental impacts of various possible fuel oxygenates weighed against anticipated benefits should be a component of these policy decisions.

EPA's Blue Ribbon Panel (6) indicated that life-cycle analysis must be a key element of quantitative assessments used by policy makers for risk and cost-benefit analyses comparing alternative motor vehicle fuels. However, no organization is likely to have sufficient resources to address all the research and assessment required to perform these comparisons before new policies are implemented. Still, given the choice between MTBE and ethanol, and with our current level of understanding, it appears that the groundwater resource impacts associated with the use of ethanol will be less significant and more manageable than those associated with MTBE.

Acknowledgments

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TABLE 1

Ethanol half-life at various redox conditions

The estimated half-life of ethanol varies when it is degraded in aquifer microcosms under different electron acceptor conditions.

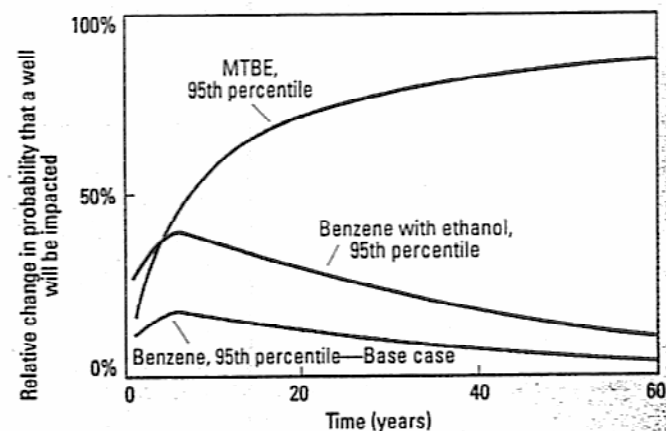
Electron acceptor	Half-life ^a (days)
O ₂	2-3
NO ₃ ⁻	1-3
Fe ³⁺	4
SO ₄ ⁻²	7
CO ₂	6

^aEstimated from laboratory experiments by Corseuil et al. (14).

FIGURE 2

Predicted contaminant plume length

Results of Monte Carlo simulations illustrate relative changes in the probability that a drinking water well will be affected following a spill of nonoxygenated gasoline (base case), ethanol-blended gasoline, and MTBE-blended reformulated gasoline. Analysis details are presented in (4).



Source: Adapted from reference (4).

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