HEALTH, ENVIRONMENTAL, AND ECONOMIC IMPACTS OF ADDING ETHANOL TO GASOLINE IN THE NORTHEAST STATES

NEIWPCC
New England Interstate Water
Pollution Control Commission

VOLUME 3

WATER RESOURCES AND ASSOCIATED HEALTH IMPACTS

JULY 2001

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Prepared by the

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HEALTH, ENVIRONMENTAL, AND ECONOMIC IMPACTS OF ADDING ETHANOL TO GASOLINE IN THE NORTHEAST STATES

WATER RESOURCES AND ASSOCIATED HEALTH IMPACTS

EXECUTIVE SUMMARY

BACKGROUND AND SCOPE

Methyl *tertiary*-butyl ether (M*t*BE), is an oxygenate that is widely added to gasoline to comply with the 1990 federal Clean Air Act Amendments (CAAAs). The amendments require all states with ozone pollution problems to implement "reformulated gasoline" (RFG) programs. The RFG program was introduced as part of the CAAAs for the primary purpose of reducing motor vehicle emissions of ozone (smog) precursors (mainly nitrogen oxides and volatile organic contaminants) during summer months and certain toxic pollutants year round. To comply with the program, gasoline must achieve a set of emission performance standards and meet a minimum oxygen requirement of at least 2 percent oxygen by weight. For a variety of reasons, M*t*BE has emerged as the oxygenate of choice for gasoline refiners in most parts of the country and is generally present in RFG at about 11 percent by volume.

While the RFG program has been an important air pollution control and public health protection strategy in the Northeast, from a potable water standpoint, many states have concluded that M*t*BE poses an unacceptable threat to water resources. Because M*t*BE is highly water soluble, and not readily biodegradable, its use in gasoline has resulted in contamination of public and private wells and groundwater resources in New England, as well as surface waters, such as portions of Lake Winnipesaukee, New Hampshire. Due to taste and odor characteristics that affect drinkability and concern about possible acute and chronic health effects, a broad consensus has emerged that the use of M*t*BE in gasoline should be curtailed.

In May 2000, the New England Interstate Water Pollution Control Commission (NEIWPCC) received a request from the New England Governor's Conference (NEGC), Committee on the Environment to assist in evaluating alternatives to M*t*BE. The most likely oxygenate replacement for M*t*BE is ethanol (a.k.a. ethyl or grain alcohol).

Both NEIWPCC and the Northeast States for Coordinated Air Use Management (NESCAUM) were asked to assess the potential public health, environmental, regulatory, and economic impacts of an oxygenate shift. As an organization concerned primarily with water quality issues in the New England states and New York, NEIWPCC was specifically requested to address alternatives with respect to water impacts.

This NEIWPCC and NESCAUM collaborative effort has resulted in a three-volume multimedia assessment of the impacts of the increased use of ethanol in the Northeast. This document is Volume 3 of the coordinated effort with NESCAUM. Volume 2—"Air Quality, Health, and Economic Impacts"—is the NESCAUM document, and Volume 1—"Summary and Recommendations"—is a summary of the two documents.

STATE AND FEDERAL ACTIONS

Gasoline is a toxic and dangerous mix of chemicals, yet it is probably the most ubiquitous manufactured substance in use today, touching the lives of virtually every man, woman, and child in the United States. Indeed, the release of gasoline into water resources is a concern with or without the oxygenates. In the ideal world, we as a society should be aggressively applying our energy and our ingenuity toward eliminating gasoline as an automotive fuel source. At the very least we should seek to significantly curtail gasoline use through conservation efforts and improved automotive fuel performance. In the absence of the ideal world, health and environmental agencies must deal with gasoline—its consequences and its logistical and political complexities.

As new detections of M*t*BE in soil and groundwater continue to occur with increasing frequency, states in the Northeast and elsewhere are viewing M*t*BE with increasing alarm and have been considering or instituting legislative or regulatory actions to ban or reduce its use in gasoline.

At the national level, in 1998, the U.S. Environmental Protection Agency (U.S.EPA) commissioned a Blue Ribbon Panel on M*t*BE and Oxygenates in Gasoline to review the important issues posed by the use of M*t*BE and other oxygenates in gasoline. The panel called for a substantial reduction in the use of M*t*BE as well as action by Congress to remove the current 2 percent oxygenate requirement from the CAAA.

U.S. Senate legislation in the 106th called for, among other things, an M*t*BE ban in four years. So far, the 107th Congress has introduced several bills to ban or control the use of M*t*BE. The goals of the proposed legislation range from banning M*t*BE as a fuel additive to appropriating funds from the Leaking Underground Storage Tank (LUST) Trust Fund to clean up M*t*BE contamination at LUST sites.

As state and federal actions to eliminate or reduce the use of M*t*BE have gained momentum nationwide, the NEGC Committee on the Environment recognized the need for the Northeast states to move quickly to better understand the consequences of replacing M*t*BE with an oxygenate alternative. The states were asked to work as a region to evaluate alternatives to M*t*BE as soon as possible.

AN ETHANOL FOCUS

In response to the NEGC request, NEIWPCC organized an Alternative Fuels Committee made up of staff representatives from state water, health, underground storage tank (UST), and site remediation programs to address tank-related M*t*BE and alternative oxygenate concerns. At a meeting of the Northeast States RFG/M*t*BE Task Force in Boston in May 2000, there was consensus that while there may be a variety of possible alternatives to M*t*BE as a gasoline additive in the Northeast, ethanol will play a major role and will likely be more widely used in this region and throughout the country.

Based on that meeting, NEIWPCC developed a draft outline of an investigation specific to the use of ethanol. The Alternative Fuels Committee proceeded to focus its evaluation on the potential health and environmental impacts of a release of ethanol and ethanol-blended (E-blend) gasoline. Alternative oxygenates other than ethanol were reviewed briefly with an eye toward the possibility of a more thorough evaluation at a future date.

The Alternative Fuels Committee divided into work groups to focus on the key areas of concern associated with ethanol. The summaries below reflect their findings in the following areas of concern: Health Effects, Aquatic Impacts, Storage and Handling, Environmental Impacts, and Other Alternatives.

THE GOALS OF THIS REPORT

The NEIWPCC Alternative Fuels Committee undertook this project with the following goals:

- ▲ Identify available information on ethanol with respect to health effects, aquatic effects, storage and handling issues, environmental impacts associated with ground and surface water resources, and to a lesser extent, alternatives other than ethanol.
- ▲ Ascertain what is known and not known regarding the issues of concern.
- ▲ Prepare a series of summary reports that:
  - Clearly characterize the issues and any associated uncertainties,
  - Present conclusions regarding findings,
  - Make recommendations as to what information is needed to adequately understand and address concerns about ethanol, and
  - Identify, where possible, steps that should be taken to mitigate potential problems if ethanol is widely introduced into the Northeast gasoline supply.

This report represents a multi-state effort. Conclusions, recommendations, and identified uncertainties were reached by consensus.

HEALTH EFFECTS OF ETHANOL

The Health Effects of Ethanol section of this report (Chapter 3) presents a *summary analysis* of ethanol's neurologic and developmental effects, while also considering the evidence for its carcinogenic effects and internal organ (particularly liver) damage. The potential health effects following ingestion of high concentrations of ethanol have been well studied. However, the potential adverse effects associated with repeated exposure to environmentally relevant concentrations are less well understood.

In preparing this analysis, key studies on toxicity of ethanol were identified. However, because of time constraints, a full evaluation of the available data has not been performed. This information is put into a risk context for the drinking water pathway comparative to health risks from M*t*BE.

CONCLUSIONS

The following conclusions are based on health risks associated with exposure to ethanol in cases where drinking water has been contaminated by either pure (neat) ethanol or an ethanol/gasoline blend (E-blend).

- ▲ Low-level ethanol contamination of groundwater (i.e., less than 400 µg/L, a draft Water Comparison Value derived in this chapter) is not expected to substantially alter blood alcohol concentrations or produce a significant health risk. In coming to this conclusion, the potential health risks in sensitive subjects such as pregnant women or those who may have aldehyde dehydrogenase deficiency were also considered.
- ▲ Higher concentrations of ethanol in water may begin to increase health risks but are not expected to materially add to endogenous ethanol concentrations until there is daily exposure to at least 10 mg/L (ppm). Thus, the strong hazard potential of ethanol (production of irreversible fetal effects) is mitigated by the fact that relatively high environmental concentrations would be needed to reach a level of public health concern.

- ▲ The hazard potential for ethanol is greater than for M*t*BE in terms of the types of irreversible damage possible from repeated high-level exposures. In spite of this greater hazard potential, the health protective value for ethanol in drinking water appears to be at least as high, if not higher, than M*t*BE.

- ▲ While this chapter focuses on toxic effects rather than warning properties (i.e., odor and taste), it is noteworthy that the air odor threshold of ethanol (approximately 100 ppm) (TRC, 1988) is three orders of magnitude higher than that of M*t*BE (HEI, 1996). Thus it appears that the warning properties of M*t*BE are stronger, making overexposure to M*t*BE less likely than overexposure to ethanol. It is possible that the secondary effects of an ethanol spill would create anaerobic conditions (i.e., increased color, turbidity, and odor) in groundwater. Thus, in some circumstances, consumer warning could take place in this manner.

UNCERTAINTIES

On the basis of relative toxicity and comparison across possible drinking water guidelines, replacement of M*t*BE with ethanol is not expected to increase the public health risks associated with gasoline spills into groundwater. However, this toxicological assessment does not take into consideration all of the exposure factors that might affect conclusions regarding relative risks. There are several uncertainties that affect the degree of confidence we can have that ethanol will not create significant health risks if spilled into groundwater. As summarized below, these uncertainties are with regard to the degree of ethanol exposure possible, the low-dose effects of ethanol on fetal development, and the possible interactions between ethanol and other chemicals.

- ▲ The risk scenario of greatest potential concern is if a release of neat ethanol (e.g., from an ethanol bulk storage facility) were to contaminate a drinking water supply well. In this case, there is an uncertainty as to whether high levels of ethanol, in the tens to thousands of ppm, could possibly reach a well and not be noticed by water consumers. This would be because of ethanol's poor warning properties (high odor and taste thresholds) (HEI, 1996) and the possibility that other hydrocarbons would not be present in the well to affect taste/odor. In this scenario, a pregnant woman might unknowingly ingest substantial concentrations of ethanol, which for even relatively short periods of time (days to weeks) would lead to potential pregnancy risk concerns. Thus, it is important to determine the likelihood of this critical exposure scenario.

- ▲ In comparison to M*t*BE-blended fuels, the possibility that E-blend fuels can cause depletion of oxygen in groundwater, thus increasing the likelihood that benzene, toluene, ethylbenzene, and xylenes (BTEX) plumes would be longer and have a greater impact on drinking water wells. Any increase in the public's exposure to these chemicals in drinking water should be avoided.

- ▲ The possibility that ethanol can interact with benzene by increasing benzene metabolism in the body to more toxic metabolites is a potential health concern. Ethanol ingestion induces the enzyme, cytochrome P-450-2E1 (Cyp2E1) (Ohnishi, 1977). This same enzyme activates benzene to a series of hematotoxic and carcinogenic metabolites. Alcoholics have higher levels of Cyp2E1 than non-alcoholics, and these levels decrease when they are withdrawn from alcohol (Lucas, 1995; Girre, 1994). While this has been documented in alcoholics who have high chronic exposures, the minimum amount of ethanol ingestion required to increase Cyp2E1 levels is not known. Because the potential exists for coexposure to ethanol and benzene from an E-blend leak into groundwater, it is important to recognize that this potential interaction creates an important uncertainty. Interaction of ethanol with toluene, ethylbenzene, and xylenes has also been reported. (Riihimaki, 1982; Low, 1989).

- The risk assessment relies on the premise of a threshold for fetal effects from maternal ethanol ingestion. While evidence from both human and monkey studies is generally supportive of such a threshold, there may be certain endpoints and subtle neurodevelopmental effects for which a threshold may be difficult to demonstrate (HEI, 1996). This increases the uncertainty regarding low ethanol exposures, especially since the sensitivity of different windows of pregnancy to ethanol is also unknown. Because of these concerns, the American Academy of Pediatrics (AAP, 1999) concludes that the current data do not support the concept of a "safe level" of alcohol consumption by pregnant women, and many obstetricians routinely advise pregnant women to avoid all alcohol during pregnancy.

- This chapter addresses the uncertainty surrounding low-dose ethanol effects during pregnancy by deriving a draft comparative drinking water value that lowers the apparent threshold (as seen in monkey and some human studies) by a 3,000 fold factor. This factor is meant to ensure that the acceptable level of ethanol in drinking water is far below any levels of exposure known to produce fetal effects and to also cover a variety of other uncertainties. While fetal effects are unlikely at ethanol drinking water concentrations below the comparative drinking water value of 400 µg/L, additional low-dose ethanol research in animals and humans is needed to solidify this conclusion.

COMPARATIVE SUMMARY

The tables on pages 6 and 7 provide a comparison of the health effects associated with exposure to M*t*BE and ethanol as they might exist in drinking water. Although it is difficult to make a direct comparison of chemical toxicity values for ethanol and M*t*BE in drinking water, due to a variety of uncertainty factors, it is apparent that ethanol is unlikely to produce any greater health risk than M*t*BE at relatively low concentrations (400 µg/L) in water.

This conclusion is based on a number of factors, the most important of which is that ingestion of low levels of ethanol-contaminated drinking water in this range is unlikely to alter endogenous levels of ethanol in blood. Additional support for this is that ethanol appears to be no more toxic than M*t*BE with respect to acute neurotoxicity or carcinogenicity. However, at high exposures during pregnancy ethanol may present a greater hazard than M*t*BE due to its ability to produce irreversible neurodevelopmental effects. M*t*BE does not appear to produce this type of effect, based on standard teratology testing (Bevan, et al., 1997), although the detailed cellular and behavioral studies conducted with ethanol have not been conducted with M*t*BE.

Overall, the database suggests that ethanol may be associated with a greater hazard potential than M*t*BE at high concentrations (above 5,000-10,000 µg/L) in drinking water. This could be even more likely given that M*t*BE has strong warning properties (i.e., odor and taste) at high concentrations, while ethanol's warning properties are much less conspicuous. Therefore, analysis of ethanol's environmental fate and exposure potential is needed to determine whether ethanol-contaminated groundwater could result in exposure levels to pregnant women that increase the risks for neurodevelopmental effects.

COMPARATIVE EVALUATION OF THE HEALTH EFFECTS OF ETHANOL AND M*t*BE

ETHANOL	**M*t*BE**
400 µg/L water comparison value.	10 µg/L - 70 µg/L (northeast state guideline using various risk assessment methods).
Low dose - CNS stimulation.	Low dose - CNS stimulation.
High dose - CNS depression.	High dose - CNS depression.
Blood level > 500 mg/L - CNS depression.	Blood level 100 mg/L - CNS depression.
Great developmental hazard.	Minimal developmental hazard.
CNS effect in fetus not reversible with frank CNS damage.	No significant fetotoxicity at inhalation doses below 1,000 ppm in mice and rats (approx. 1-2 g/kg/day). (M*t*BE testing did not evaluate late stage CNS developmental effects, a time frame sensitive to ethanol. Additionally, while not teratogenic to rat or rabbit CNS, more subtle neurodevelopmental testing of M*t*BE has not been conducted.)
Greater potential to damage liver.	
Evidence of human carcinogenicity upon chronic exposure. Carcinogenic classification: IARC Group 1 NTP Not listed EPA Not classified	No human data. Carcinogenic classification: IARC Inadequate evidence in humans NTP Not listed EPA Not classified
10 - 15 g/kg/day, elevation of breast tumor in mice.	12 g/kg/day (inhalation) liver tumor in mice Cancer Effect Level (CEL)gavage = 0.25 g/kg/day (rats) $\text{CEL}_{\text{inhalation}}$ = 2.5 g/kg/day (rats).
Few days spiking of ethanol exposure (e.g., from sudden groundwater plume entering drinking water) would have greater public health implications because of developmental effects.	Few days spiking of M*t*BE in drinking water is unlikely to cause developmental effects observed with ethanol.
Sensitive population identified.	No sensitive population identified.

UNCERTAINTY EVALUATIONS

ETHANOL	M*t*BE
High odor threshold. High levels could be consumed unnoticed in drinking water and can be a potential pregnancy concern.	Low odor threshold. Can be detected at low concentrations.
High levels of BTEX could reach potable waters because of oxygen depletion or cosolvency effects.	No oxygen depletion or cosolvency effects with M*t*BE.
Ethanol may increase the metabolism of benzene to carcinogenic metabolites. Such effect has been documented in alcoholics. Ethanol is also known to interact with toluene and xylenes metabolically in humans. This metabolic interaction is important because of the cosolvency effect that ethanol has on BTEX.	
There may be certain endpoints and subtle neurodevelopmental effects for which a threshold may be difficult to demonstrate. There is increased uncertainty regarding low ethanol exposures, especially the sensitivity of different windows of pregnancy to ethanol.	Low potential for lasting neurodevelopmental effects.

RECOMMENDATIONS

Based on the uncertainties listed above, we recommend that further health effects research is needed in the following areas:

- ▲ The health effects of low-level exposure, particularly to expand our understanding of where the threshold lies for neurodevelopmental effects.
- ▲ The toxicokinetics of low-level ethanol exposure (including fetal and maternal blood levels) relative to typical background exposures from the diet and the response of sensitive subpopulations.
- ▲ An assessment of the metabolic interaction between ethanol and other environmental pollutants (e.g., benzene) at environmentally relevant doses.
- ▲ This summary analysis was performed in a limited time frame. A more thorough review of the literature and, perhaps, additional basic research is needed to better substantiate and support these findings.
- ▲ As ethanol will not replace 100 percent of the M*t*BE currently found in RFG, aromatics, olefins, and alkylates are seen as the likely additives that will be used to make up the volume. An assessment of the public health characteristics of these additives is needed before the widespread introduction of ethanol reformulations.

EFFECTS OF ETHANOL ON AQUATIC LIFE

The effects of ethanol on aquatic communities was evaluated to determine if adverse environmental impacts could potentially occur. Based on these evaluations, the following conclusions were drawn.

CONCLUSIONS

- Ethanol is toxic to aquatic life. However, it is 3.7 times less acutely toxic than M*t*BE. Over a longer-term exposure period, toxicity to aquatic life resulting from exposure to ethanol is similar, although somewhat less, than that associated with longer-term exposure to M*t*BE.
- Ethanol is not likely to bioaccumulate or bioconcentrate in the tissues of living organisms. This is due both to its chemical properties and the ability of most organisms to break down and eliminate ethanol from their bodies.
- The breakdown of ethanol in surface waters through biological and chemical processes could potentially result in the consumption of significant quantities of dissolved oxygen in the surface water body. Depending on the conditions in the surface water body and the amount of ethanol introduced, it is possible that sufficient amounts of dissolved oxygen could be consumed to bring about a detrimental affect on aquatic life, such as a fish kill.

ETHANOL STORAGE AND HANDLING

Ethanol storage and handling was reviewed with regard to the life cycle of pure (neat) ethanol and ethanol-gasoline blend (E-blend)—from feedstock production to end user (e.g., automobile, lawnmower). Chemical compatibility of storage components and the environmental impact of producing and transporting ethanol to the Northeast were evaluated. This review included the following issues associated with ethanol storage and handling:

- Ethanol production.
- Bulk storage, blending, and distribution.
- Systems function and materials compatibility issues associated with components of underground storage tanks, piping, dispensing devices, and sealants.
- E-blend end users—automobiles and smaller gasoline-powered recreational and power equipment.

Ethanol, both as a pure product and blended with gasoline, introduces different problems for tank and piping components than M*t*BE-blended gasoline. However, much is known about these problems and their solutions. Concerns associated with storing ethanol and E-blend fuels can be summarized into four categories:

- Compatibility with storage system components.
- Phase separation, causing ethanol to preferentially dissolve in water. This can create water-related problems in storage systems and automobile engines.

- Because ethanol is a solvent, it may loosen rust and other concretions from the interior walls of steel components of storage systems. When this happens, the wear of various storage system components may be accelerated, due to the scouring of internal surfaces with suspended particles, and the operation of gasoline engines may be impaired.
- The electrical conductivity of ethanol and E-blend may lead to corrosion of various metal components and present a potential safety threat during vehicle fueling.

CONCLUSIONS

- The compatibility of underground storage tank (UST) and aboveground storage tank (AST) systems with E-blend fuels is a function of the various fabrication materials that compose a fuel storage system, bearing in mind that materials have evolved over time for the storage of ethanol and E-blend fuels. Each component of the tank system must be checked for compatibility, especially in the case of an existing facility. Particular attention must be given to the design or retrofit of a bulk facility for the storage of neat ethanol. For this reason, the introduction of ethanol into the Northeast gasoline supply will come with the added cost of retrofitting many of the region's tank systems to make them ethanol compatible.
- UST/AST components that are not compatible with E-blend fuels may cause system failures and/or product leaks. Based on the experiences of the New England and New York UST programs (see Chapter 2), it is expected that many owner/operators will not have their facilities voluntarily evaluated for compatibility prior to the introduction of E-blend fuels into their fuel storage systems. At current staff levels, state programs are showing a rate of 4 to 17 years between facility inspections.
- The introduction of ethanol into gasoline will enhance suspension of water and other deposits scoured or cleaned from UST/AST systems. Water and scoured deposits that are not eliminated from UST systems could cause premature failure of the following components: leak monitoring systems (automatic tank gauge (ATG) probes and line leak detectors), submersible pumps, fuel dispensers, piping, hoses, and nozzles and swivels. Gasoline engines could be affected as well.
- Precautions must be taken with the storage of E-blend fuels in single-walled fiberglass tank systems fabricated prior to January 1, 1984, as these tanks may not be compatible with ethanol.
- Questions exist concerning the compatibility of the following tank/dispensing system components and materials with E-blend: lining materials, secondary containment materials, adhesives, glues, sealants, gaskets, and any polymer or elastomer compounds found on dispensing or monitoring devices, such as ATG probes.
- Some component materials associated with dispensers, submersible pumps, and other distribution equipment that come into contact with E-blend gasoline (e.g., cork and Buna-N) may have long-term compatibility problems.
- Ethanol in gasoline may impair the operation of capacitance ATG probes because of increased electrical conductivity to E-blend gasoline.
- Most automotive manufacturers approve the use of E-blend fuels in their newer vehicles. Many non-automotive engine manufacturers now address oxygenated fuels and permit or approve the use of E-blend fuels. However, some older engine models may have components (e.g., swollen carburetor floats) that have exhibited compatibility problems

with ethanol. Many manufacturers, however, provide recommendations for handling and modifying their equipment when E-blend fuel is used.

- ▲ At the present time, there are not sufficient ethanol life cycle analyses available to address issues surrounding the environmental impact of ethanol feedstock production as it pertains to the Northeast.

RECOMMENDATIONS

If E-blend gasoline is to be introduced into the Northeast region, the following steps should be taken to ensure that tank owners and operators are informed and prepared to make the transition with regard to ensuring tank system integrity:

- ▲ To prevent releases due to the degradation of non-compatible materials in UST systems, there should be a program requiring UST owners and operators to obtain certification that their UST system(s) is compatible with E-blend fuels.
- ▲ Develop a guidance document that standardizes a process by which owner/operators or their contractors may assess and certify the compatibility/functionality of their storage tank systems with regard to any component coming into contact with E-blend fuels. The document should inform owner/operators of proper operating procedures for the continuous management of storage tank systems, particularly focusing on the initial conversion of facilities to E-blend fuels and problems associated with ethanol introduction. Such procedures would include replacement of filters, system checks for loosened deposits (e.g., rusts and scales and other loosened deposits), system dewatering, especially at the time of initial conversion, and continuous monitoring of water in the system.
- ▲ Based on the inspection rate at operating facilities, states and/or the federal government should look for ways to increase inspection resources, especially during the transition to E-blend fuels.
- ▲ Conduct more studies on the compatibility of fiberglass-reinforced plastic (FRP) tanks (especially with respect to structural integrity), particularly single-walled FRP tanks fabricated before January 1, 1984 and FRP and flexible piping that haven't been specifically fabricated for E-blends.
- ▲ Educate automobile and power engine equipment owners on the need for checking fuel-compatibility specifications in their owners manuals. E-blends may have some minor impacts on engine operation and may adversely effect some fuel system components, particularly those that depend on lubrication.

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

The life cycle of ethanol-blended (E-blend) gasoline (typically 10 percent ethanol by volume) was examined to identify potential sources of releases for both neat ethanol or E-blend gasoline. Neat ethanol releases can occur at the biomass ethanol plant or anywhere along the transport system to the point where ethanol and gasoline are blended at a gasoline distribution terminal or bulk plant. Shipment is expected to be by rail or marine cargo to the terminal, followed by rail or truck delivery to retail facilities. E-blend gasoline spills can occur from the blending point to gasoline retail facilities (aboveground and underground storage tanks) all the way to the end point of use (e.g., automobile, backyard lawnmowers).

Environmental impacts were evaluated from the standpoint of :

- Neat ethanol and E-blend gasoline releases,
- The potential pathways (i.e., surface runoff, infiltration into soil, groundwater transport) of ethanol/E-blend once released into the environment,
- The behavior (fate and transport) of such releases in the soil, groundwater, and surface water environments and in contrast with M*t*BE,
- Drinking water impacts, and
- The remediation of neat ethanol and E-blend releases into the environment and associated costs in comparison with M*t*BE.

CONCLUSIONS

- The differences between ethanol and M*t*BE with regard to their expected impacts on the subsurface environment are based largely on their initial concentration in the aqueous plume, the very different rates at which they biodegrade, and possibly their residence time in the non-aqueous phase. M*t*BE is relatively recalcitrant to biodegradation and therefore able to migrate a significant distance from the release. Thus it can have a negative impact on groundwater quality for extended periods. Ethanol is rapidly biodegraded, preferentially to the other components of gasoline, however, its behavior in the environment is not well documented. It is expected that a release of neat ethanol will potentially be degraded in periods from several days to one or two years.
- Both ethanol and M*t*BE have a relatively high solubility in water and high mobility in the subsurface. Ethanol, the more soluble, is completely miscible in water (100 percent soluble, compared with 4 to 5 percent for M*t*BE). Once released to the environment, alone or in a gasoline mixture, both ethanol and M*t*BE readily dissolve in rainwater, surface water, and groundwater.
- Three environmental transport properties associated with ethanol are of particular concern:
  - Depletion of oxygen and other nutrients in groundwater due to rapid biodegradation of ethanol that may inhibit the degradation of more toxic components in gasoline (e.g., BTEX) and make the dissolved plume of these components longer.
  - A surface tension effect that takes place when ethanol is in contact with a layer of gasoline on top of the water table. This effect can cause the gasoline to spread laterally.
  - A potential cosolvency effect from a release of neat ethanol or E-blend with high concentrations of ethanol that may make other gasoline constituents (e.g., BTEX) in soil or groundwater more soluble.
- The biodegradation of ethanol in the soil and water environment would first deplete the oxygen and then the anaerobic electron acceptors, potentially preventing or reducing the rate of biodegradation of the benzene, toluene, ethylbenzene, and xylenes (BTEX) constituents in gasoline. This may result in longer BTEX plumes. M*t*BE does not interfere with the natural biodegradation of the other gasoline components, most importantly BTEX.

▲ Lab studies and mathematical models have estimated the potential for E-blend gasoline to cause the toxic BTEX compounds of gasoline to travel from 1.1 up to 2.5 times farther than a standard gasoline blend without ethanol. This may be a serious problem, however, the predicted lengths of the E-blend BTEX plumes will still be shorter than M*t*BE plumes resulting from reformulated gasoline.

▲ Although ethanol degrades rapidly when released to the environment under favorable conditions, if spilled as a neat product where a stabilized zone of petroleum-contaminated soil and groundwater plumes already exist (e.g., oil terminals), it can remobilize the gasoline components and cause lateral spreading of liquid petroleum and 10-fold increases in the concentration of benzene and other aromatic constituents of gasoline (i.e., BTEX). This may cause contamination of groundwater and nearby wells.

▲ Due to the oxygen depletion and cosolvency factors associated with ethanol in groundwater, there is a concern that significant or continuing releases of E-blend (e.g., from a significant undetected UST leak) could result in an extended plume of benzene (and other gasoline components).

▲ Environmental concentrations of ethanol expected as a result of atmospheric deposition through precipitation or from recreational boating activities are unlikely to pose a problem to either human or environmental receptors since these predicted concentrations are below benchmark values derived.

▲ Although environmental benchmarks for the protection of human health are lower than those derived for aquatic life protection, it is likely that impacts to the aquatic community would be observed before human health impacts were detected if high concentrations of ethanol were to reach a surface water body. High concentrations of ethanol could deplete or substantially lower dissolved oxygen content in the surface water within a short period of time, potentially leading to a fish kill from oxygen stress.

▲ Significant spills of ethanol into surface water bodies that have low aeration rates (e.g., ponds, lakes, and large, nonturbulent rivers) can cause massive killings of fish and other aquatic organisms by asphyxiation, the result of oxygen depletion of the water caused by ethanol degradation. For example, in May 2000, a 500,000-gallon release of Wild Turkey bourbon (250,000-gallons ethanol) into the Kentucky River caused the worst fish kill in 50 to 60 years.

▲ Smaller spills of E-blend, such as incidental spillage at gas stations and homeowner spills, are not expected to enhance the migration of benzene. In fact, because of the high biodegradability of ethanol, it is not expected that such small spills will have any significantly different impact on groundwater quality compared with nonoxygenated gasoline. This is in stark contrast to the widespread instances of drinking water contamination with M*t*BE from minor spills of M*t*BE gasoline.

▲ For one-time releases of larger quantities of E-blend gasoline (e.g., a tanker truck accident), the effects of cosolvency are not expected to significantly affect the extent of the resulting plume. In this case, the incident would be known, and as in the case of conventional gas formulation, appropriate and prompt responses, evaluation, and follow-up would be taken.

▲ Much of the technology developed to remediate gasoline and M*t*BE in soil can be expected to work on the remediation of neat ethanol and E-blend gasoline. However these tools have not been tested on environmental releases, so until they are we will not know precisely which methods will work the best and how effective they will be.

- Ethanol plumes should be no more difficult to control hydraulically than M*t*BE plumes.
- Treatment technologies that rely on the physical separation of ethanol from groundwater are not effective. While biodegradation of ethanol in the environment is rapid, removal of ethanol from drinking water once pumped out of a well or reservoir is problematic. Its high solubility makes it virtually impossible to treat using absorptive filters that are effective on private wells for other gasoline contaminants. However, the rapid biodegradation of ethanol makes it unlikely that this oxygenate will affect as many wells as have been affected by M*t*BE unless the concentration of ethanol exceeds the attenuative capacity of the aquifer segment between the source area and the receptor.
- Biological treatment technologies are effective for ethanol contamination, as ethanol is highly biodegradable.
- The expected high concentrations of ethanol in plumes and the resulting high levels of BOD will probably require that treatment systems utilizing in-situ bioremediation technologies have larger capacities over those currently in use.
- The effectiveness of natural attenuation cannot be predicted because there is not enough information regarding the effect of ethanol plumes on the concentrations of terminal electron acceptors or the ability of those plumes to overcome the assimilative capacity of aquifers through which they are traveling prior to impacting a receptor.
- The use of ethanol as a gasoline additive will likely have minimal impact on the technology employed or the costs associated with soil remediation. The impact on groundwater remediation is not yet well understood.
- From the standpoint of soil and water contamination, the ideal gasoline additive for air pollution control should be non-toxic, less water soluble, and more biodegradable than M*t*BE.

UNCERTAINTIES

It is very important to understand that this evaluation is based on predictions from scientific estimations of what will happen to soil and groundwater in the event of a release of E-blend gasoline, and not from field data. The relative impacts of large-volume spills during transport, transfer, and storage are hard to generalize due to the uncertainties in quantifying the effects of ethanol on BTEX plume length, the concentration of terminal electron acceptors, and secondary effects on groundwater quality, such as increased levels of dissolved iron. The following uncertainties have been identified:

- Modeling studies have shown that benzene plume lengths increase if ethanol is in the released gasoline, but these findings have not been confirmed by field studies. Although ethanol gasoline has been in use for years, little information exists on subsurface ethanol plumes, because ethanol concentrations have not been monitored significantly anywhere in the United States.
- It is likely that the overall effect of ethanol is site specific and depends on the release scenario and characteristics, such as site hydrogeology and the nature and amount of electron acceptors and nutrients in the aquifer. The relative environmental impacts expected to result from releases of neat ethanol and E-blend gasoline depend on the release scenarios.

  For example, ethanol would likely have much less impact than M*t*BE in small-volume residential spill scenarios. While gasoline hydrocarbons would stay adsorbed onto soil and volatilize or degrade before ever reaching groundwater, both ethanol and M*t*BE would be carried to the groundwater by infiltrating rainwater. Once in the groundwater, ethanol would rapidly degrade given sufficient nutrients and electron acceptors, whereas M*t*BE would persist and could contaminate drinking water wells. Soluable BTEX could still reach groundwater in this scenario.

▲ To understand the environmental impacts of E-blend gasolines, a thorough understanding of the ethanol life cycle is necessary. Since ethanol has never been extensively distributed in large volumes in the Northeast, the logistics of the life cycle as they would take place in this region are not established.

▲ It is premature to attempt to compare the costs associated with the remediation of groundwater contaminated with ethanol verses M*t*BE. Additional knowledge of and experience with such issues as degradation rates and the effects of soluble iron must be understood.

RECOMMENDATIONS

▲ The use of E-blend gasoline instead of M*t*BE gasoline will result in a significant decrease in well contamination caused by small spills. However, for significant and continuous E-blend gasoline spills, it is premature to predict their effect on well contamination. Field experiments are needed to understand the true extent of the behavior of ethanol in the environment and confirm modeling studies.

For example, a recently published report from Brazil (November, 2000) of the first known controlled release of E-blend gasoline (24 percent ethanol by volume) in a sand aquifer showed the decay rate for ethanol to be 100 times slower than predicted from laboratory studies, meaning that ethanol can exist in the environment 100 times longer than expected. However, we do not know if ethanol would be more persistent than expected in an E-blend of the ethanol concentration associated with the U.S. RFG program—5.7 to 10 percent by volume. The depletion of oxygen and other electron acceptors would likely be much faster and complete with higher concentrations of ethanol.

Therefore, before their widespread introduction to the area, controlled field experiments of neat ethanol and E-blend gasolines must be carried out to determine the precise nature of their impact on the environment and the potential for threats to human health. As these field experiments may take two to three years to produce reliable results, the experiments should be done as soon as possible so that fate and transport principles are better understood with regard to addressing the cleanup of neat ethanol and E-blend gasoline releases. These investigations must include:

- A controlled field study to measure the rate at which ethanol dissolves or separates out of E-blend and is transferred into groundwater.

- A controlled field study to assess the impact of ethanol in gasoline on BTEX plumes in groundwater.

- An analysis of remedial actions and the performance of remedial technologies employed in states that have been using E-blends for the past few decades to answer questions concerning the appropriateness and efficiency of the technologies favored for cleanups in the Northeast.

- An analysis of spill investigations from states that have been using E-blend for the past few decades to answer questions about the fate and transport of ethanol, the effects of ethanol on the biodegradation of BTEX compounds at a field scale, and cosolvency.

  - Field tests of remediation technologies to determine which work and their effectiveness.
  - Research on effective E-blend remediation technologies and their associated costs.
  - Research to provide a feasible approach to point-of-use/point-of-entry treatment of ethanol contaminated drinking water.
  - Evaluation of the potential environmental impacts of an release along the entire ethanol life cycle. Work with the ethanol industry to better determine what the life cycle will look like before distribution activities are initiated.

- If ethanol is adopted as a gasoline oxygenate alternative to M*t*BE, it should be used at the maximum concentration of 5.7 percent to minimize the affects of oxygen depletion and cosolvency, at least until it is determined to have fate and transport characteristics that are manageable. Accordingly, a repeal of the federal tax incentive that results in formulations exceeding the minimum necessary for air pollution benefits should be considered.

- Monitoring for ethanol and terminal electron acceptors should be included as a standard part of the remedial investigations at petroleum release sites. Appropriate test methods and detection limits must be identified.

- A standardized analytical method for the quantification of ethanol in environmental water samples should be adopted. The difficulty in separating ethanol from water in the preparation of samples for analysis has resulted in high detection limits. Consensus on acceptable detection limits is also needed.

- Start testing for ethanol at gasoline releases. The extent of M*t*BE contamination in groundwater was unknown until regulatory agencies started to test for, or require testing of, M*t*BE.

- One characteristic of M*t*BE in gasoline is that it imparts a bad taste and odor to drinking water at levels that are below many state health standards. In this way M*t*BE serves as an early indicator that a well has been contaminated. Ethanol has a much higher taste and odor threshold. However, while ethanol by itself has poor warning properties, experience has shown that due to the strong preference bacteria have for ethanol, a high concentration of ethanol in groundwater would cause groundwater to become anaerobic, increasing color, turbidity, and odors in the water due to anaerobic conditions. If this is the case, the secondary effects of an ethanol spill would likely provide some warning to consumers. Studies should be undertaken to investigate this issue.

- Move away from the 2 percent oxygen mandate focus and create a set of performance standards for gasoline that address both air and water quality concerns. The current requirements for RFG present a set of fuel performance standards to the oil industry for VOCs, NO_x, and toxics that address air quality issues. However, performance standards should also address water quality issues and not create more of a threat to groundwater and drinking water resources than ether-free gasoline. (See NESCAUM's discussion of gasoline formulation in Volume 2.)

- As ethanol will not replace 100 percent of the M*t*BE currently found in RFG, aromatics, olefins, and alkylates are seen as the likely additives that will be used to make up the volume. An assessment of the environmental characteristics of these additives is needed before the widespread introduction of ethanol reformulations.

OTHER ALTERNATIVES TO M*t*BE

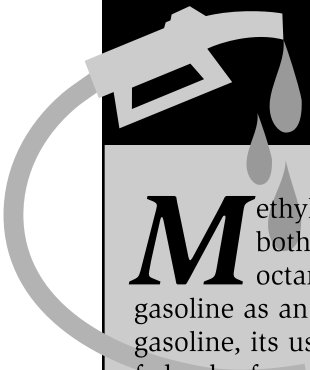
We should continue to seek alternatives to M*t*BE that will ultimately do the best job of protecting both air and water quality. Ethers similar to M*t*BE that could be used as oxygenates include: ethyl *tertiary*-butyl ether (E*t*BE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE). However, because these ethers will likely present the same kinds of impacts on the water environment as M*t*BE because of their similar chemical compositions, they should be considered unacceptable as an oxygenate alternative. Certainly, more data is needed on their expected behavior and health and environmental consequences before any consideration is given to their widespread use.

There are also alternatives to oxygenates that could serve to enhance gasoline octane. These alternatives would only be viable if the current 2 percent oxygen requirement were repealed by Congress. Increasing alkylates in gasoline is a likely solution for making up for the octane and volume that would be lost with the removal of M*t*BE from RFG. Currently, alkylates account for 15 to 30 percent of the finished gasoline pool (Pryor, 2001). These highly branched alkanes have a low water solubility and high volatility, an indication that they would not pose as much a threat to surface and groundwater as M*t*BE. In groundwater they would bond strongly to soil particles and biodegrade very slowly. Currently, there are only limited health effects data available for alkylates.

Toluene is another nonoxygenate alternative to M*t*BE in RFG. The U.S. EPA uses a maximum dontaminant level (MCL) of 1 ppm for toluene in drinking water. There are health effect concerns associated with the compound, but it has not been found to cause cancer. In the case of a spill, it will evaporate from surface waters and leach into groundwater, where biodegradation will occur slowly, but at a rate higher than M*t*BE.

Methylcyclopentadienyl manganese tricarbonyl, or MMT, is a manganese-based oxygen enhancer. Some data suggest that airborne manganese at high doses can cause disabling neurological impairments with symptoms similar to those of Parkinson’s disease. Again, this toxic compound should be considered unacceptable as an oxygenate alternative as it will be years before we could have enough data to understand the health and environmental consequences of its widespread use.

In many ways, the solution to the RFG conundrum will involve tradeoffs. It is important to keep in mind, for example, that the addition of M*t*BE into gasoline decreased the percentage of benzene (a known carcinogen) in gasoline and improved air quality. Any solution will need to strike a delicate balance that meets both air and water quality concerns. Of the possibilities listed above, the alkylates have characteristics that suggest further investigation. However, too little is known about the alternatives discussed above to draw any conclusions as to their viability as M*t*BE alternatives without further study.



CHAPTER 1

INTRODUCTION

Methyl *tertiary*-butyl ether (M*t*BE) is an oxygenate that is widely added to gasoline, both to comply with the 1990 federal Clean Air Act Amendments (CAAAs) and as an octane enhancer. Although M*t*BE has been used (and continues to be used) in gasoline as an octane enhancer since approximately 1979, when lead was phased out of gasoline, its use in the U.S. has increased three-fold in the last decade, primarily because of the federal reformulated gasoline (RFG) program.

The RFG program was introduced as part of the CAAAs for the primary purpose of reducing motor vehicle emissions of ozone (smog) precursors (mainly nitrogen oxides and volatile organic contaminants) during summer months and certain toxic pollutants year round. To comply with the program, gasoline must achieve a set of emission performance standards that include achieving reductions in emissions of nitrous oxides, volatile organic compounds, and toxic compounds, not exceeding a cap on benzene, and meeting a minimum oxygen requirement of at least 2 percent oxygen by weight.

To meet this oxygen mandate, oxygen-containing chemical compounds (oxygenates) must be added to the gasoline formulation. M*t*BE and ethanol (also called ethyl or grain alcohol) are the only two oxygenates currently produced in quantities sufficient to meet the demand created by the RFG program. For a variety of reasons, including its low cost and high-octane characteristics, M*t*BE has emerged as the oxygenate of choice for gasoline refiners in most parts of the country and is generally present in RFG at about 11 percent by volume. Approximately three-quarters of all gasoline currently sold in the Northeast market is RFG—more than one billion gallons of M*t*BE are blended into the region’s gasoline annually.

The CAAA stipulates that RFG must be sold in the nine most polluted ozone non-attainment areas of the country, including metropolitan New York. Other areas of the country that currently use RFG opted into the program for the air quality benefits associated with it. RFG is used statewide in Connecticut, New Jersey, Massachusetts, Rhode Island, and in some areas of New Hampshire and New York. It is not used in Vermont and Maine.

While the RFG program has been an important air pollution control and public health protection strategy in the Northeast, from a potable water standpoint many states have concluded that M*t*BE poses an unacceptable threat to water resources. Because M*t*BE is highly water soluble and not readily biodegradable, its use in gasoline has resulted in contamination of public and private wells and groundwater resources in New England, as well as surface waters, such as portions of Lake Winnipesaukee in New Hampshire. This contamination has come about as a result of gasoline releases from underground storage tank (UST) systems, primarily. Due to taste and odor characteristics that affect drinkability and concern about possible acute and chronic health effects, a broad consensus has emerged that the use of M*t*BE in gasoline should be curtailed.

Because M*t*BE and ethanol are the two oxygenate front-runners, eliminating M*t*BE represents a de facto mandate for ethanol in RFG. Furthermore, because both M*t*BE and ethanol are high-octane compounds, the use of ethanol in gasoline is likely to increase dramatically as M*t*BE is phased out, even without the oxygen requirement.

STATE AND FEDERAL ACTIONS

Gasoline is a toxic and dangerous mix of chemicals, yet it is probably the most ubiquitous manufactured substance in use today, touching the lives of virtually every man, woman, and child in the United States. Indeed, the release of gasoline into water resources is a concern with or without the oxygenates. In the ideal world, we as a society should be aggressively applying our energy and our ingenuity toward eliminating gasoline as an automotive fuel source. At the very least we should seek to significantly curtail gasoline use through conservation efforts and improved automotive fuel performance. In the absence of the ideal world, health and environmental agencies must deal with gasoline—its consequences and its logistical and political complexities. The following is a summary of actions taken by state and federal entities, to date.

Blue Ribbon Panel

As a result of M*t*BE groundwater contamination concerns, in November 1998, the U.S. EPA commissioned a Blue Ribbon Panel on M*t*BE and Oxygenates in Gasoline to review the important issues posed by the use of M*t*BE and other oxygenates in gasoline. On July 27, 1999 the Panel issued recommendations on ways to maintain air quality while protecting water quality from the risks associated with M*t*BE. It concluded that M*t*BE, "due to its persistence and mobility in water, is more likely to contaminate ground and surface water than other components of gasoline." Significantly, the Panel called for a substantial reduction in the use of M*t*BE as well as action by Congress to remove the current 2 percent oxygenate requirement from the CAAA.

States

At the state level, California led the charge in calling for a phaseout of M*t*BE. A number of other states across the country are considering or have already legislated action to ban or reduce the use of M*t*BE in gasoline. In the Northeast, the legislatures in Connecticut, Maine, New York, and Rhode Island have taken the following actions to regulate or ban the use of M*t*BE:

Connecticut - Eliminate M*t*BE in state by October 1, 2003.

Maine - Eliminate M*t*BE in state by January 1, 2003.

New York - Prohibit sale, use, and importation of M*t*BE in state beginning January 1, 2004.

Rhode Island - Urged DEM to look into M*t*BE and determine whether state should regulate or ban it (House resolution 6989).

U.S. EPA

In December 1997, the U.S. Environmental Protection Agency (U.S. EPA) issued a Drinking Water Advisory for M*t*BE, based on taste and odor thresholds, of 20 to 40 ppb. The primary purpose of such an advisory is to provide information to public drinking water suppliers so that they can make more informed decisions about acceptable levels of a contaminant.

EPA intends to propose a secondary standard or National Secondary Drinking Water Regulation (NSDWR) for M*t*BE, based on taste and odor, by late 2001 or early 2002. NSDWRs were established to control contaminants in drinking water that primarily affect the aesthetic qualities relating to public acceptance of drinking water. These secondary levels represent reasonable goals for drinking water quality but are not federally enforceable. Rather, they are intended as guidelines for states. This standard will draw from the existing information presented in the Drinking Water Advisory and analyze additional information to determine an acceptable taste and odor level for M*t*BE. States can adopt this standard.

In March 2000, EPA announced it would begin regulatory action aimed at phasing out the use of M*t*BE in gasoline. Under Section 6 of the federal Toxic Substances Control Act (TSCA), EPA issued what is called an Advance Notice of Proposed Rulemaking to ban M*t*BE from gasoline.

At the same time, EPA called on Congress to amend the Clean Air Act to significantly reduce or eliminate the use of M*t*BE in gasoline in order to protect drinking water. The agency also called on Congress to strengthen the Clean Air Act to guarantee that clean air benefits are preserved. Finally, it called on Congress to replace the 2 percent oxygenate requirement in the Clean Air Act with a renewable fuel annual average content for all gasoline at a level that maintains the current level of renewable fuel (1.2% of the gasoline supply) and allows for sustained growth over the next decade.

Congressional

On September 28, 2000, Senate Bill 2962—legislation sponsored by Committee Chair Bob Smith (NH) to address M*t*BE—was reported out of the Environment and Public Works Committee and placed on the Senate legislative calendar. However, considerable opposition from the oil industry coupled with a stark lack of time before the end of the session made it impossible to move the bill any farther during the 106th Congress. Senate Bill 2962 should be considered a starting point for discussion in the 2001 legislative session.

Senate Bill 2962 called for the following:

- Ban the use of M*t*BE in 4 years;
- Allow the Governor of a state to request a waiver from of the oxygen content requirement for reformulated fuel;
- Create a Clean Alternative Fuel Program to replace the reformulated gasoline oxygen content requirement; the program would include a renewable fuel content requirement that would likely triple the demand for ethanol over the next 10 years;
- Require the U.S. EPA to study the air quality impacts of eliminating the oxygen requirement and provide the agency with the authority to regulate on the basis of those studies to preserve the emissions benefits of the reformulated gasoline.
- Include a cap on the level of aromatics used in reformulated gasoline to prevent air quality backsliding.
- Allow use of Leaking Underground Storage Tank (LUST) Trust funds for remediation of M*t*BE contamination and for conducting inspections at tank sites and authorize appropriation of additional money from the LUST Trust Fund for this purpose.

So far, the 107th Congress has introduced several bills to ban or control the use of M*t*BE. The goals of the proposed legislation range from banning M*t*BE as a fuel additive to appropriating funds from the LUST Trust Fund to clean up M*t*BE contamination at LUST sites.

NEIWPCC'S ROLE

In May 2000, the New England Interstate Water Pollution Control Commission (NEIWPCC) received a request from the New England Governor's Conference (NEGC), Committee on the Environment to assist in evaluating alternatives to M*t*BE. Recognizing the importance for the Northeast states to be in a position of having evaluated potential alternatives to M*t*BE with regard to health effects and potential environmental issues, the committee called for the states to work as a region to find alternatives to M*t*BE as soon as possible.

As noted in the request, NEIWPCC, as the regional water pollution control commission, is "perfectly positioned to ensure that water impacts associated with any alternative(s) to M*t*BE are fully investigated and considered as part of our regional efforts." As part of this request, the NEGC asked the Northeast States for Coordinated Air Use Management (NESCAUM) to undertake a similar evaluation from an air perspective.

This NEIWPCC and NESCAUM collaborative effort has resulted in a three-volume multimedia assessment of the impacts of the increased use of ethanol in the Northeast. This document is Volume 3 of the coordinated effort with NESCAUM. Volume 2 is the NESCAUM document, and Volume 1 is a summary of the two documents. The U.S. EPA's Blue Ribbon Panel recommended that prior to introducing any major new additive to gasoline, a full multimedia assessment (of the effects on air, soil, and water) should be conducted. This effort serves as a major step in fulfilling the spirit of that recommendation.

AN ETHANOL FOCUS

Moves to eliminate or reduce the use of M*t*BE have gained momentum nationwide, and ethanol has emerged as the most likely replacement oxygenate for M*t*BE. At the meeting of the Northeast States RFG/M*t*BE Task Force in Boston in May 2000, there was consensus that while there may be many possible alternatives to the use of M*t*BE as an additive in gasoline in the Northeast, ethanol will play a major role and will likely be more widely used in this region and throughout the country.

Based on the Task Force meeting, NEIWPCC developed a draft outline for conducting an investigation specific to the use of ethanol as an alternative to M*t*BE. To carry out this investigation, NEIWPCC organized an Alternative Fuels Committee, comprised of staff representatives from state water, health, underground storage tank, and site remediation programs, to address tank-related M*t*BE and alternative oxygenate concerns. The Committee proceeded to focus its evaluation on the potential environmental impacts of a release of ethanol and ethanol-blended (E-blend) gasoline. Alternatives to M*t*BE, other than ethanol, were reviewed briefly with an eye toward the possibility of a more thorough evaluation at a future date.

The Committee further divided into work groups to focus on the key areas of concern: Health Effects, Aquatic Impacts, Storage and Handling, Environmental Impacts, and Other Alternatives.

THE ETHANOL ALTERNATIVE

In light of M*t*BE'*s* ever widening impacts on the water environment, it is important that environmentally friendly alternatives be identified. While other alternatives should be evaluated, ethanol is considered to be the most viable near-term alternative to M*t*BE, largely because it is the only oxygenate that might be produced in quantities capable of meeting the demand as an M*t*BE replacement.

Ethanol is a naturally occurring substance that is composed of hydrogen, carbon, and oxygen. It is a small, straight chain molecule (C_2H_5OH), 34.7 percent oxygen by weight, that occurs naturally in animal wastes and as a by-product of natural fermentation processes.

At room temperature, ethanol is a colorless liquid with a sweet odor. It is flammable, volatile, completely soluble in water, readily biodegradable, and does not sorb to sediments or soils. Given its polar, hydrophilic nature, extraction of ethanol from water is extremely difficult. Ethanol does not bioaccumulate in the tissues of living organisms, which have physiological mechanisms that provide for its metabolic breakdown.

While it is best known in association with the production of alcoholic beverages, ethanol is used widely, either pure or denatured, as a solvent and in the production and manufacturing of organic chemicals, cleaning solutions, pharmaceuticals, cosmetics, and many other products.

Ethanol is produced with carbon dioxide from the fermentation of sugars, usually dextrose, converted from starches of grains, a process known as saccharification. When produced as a fuel additive, the alcohol is distilled and dehydrated to increase the ethanol content, and denaturing products are added to make the resulting product unfit for human consumption.

IMPURITIES IN E-BLEND

Ethanol that is blended into fuel products may contain a number of impurities resulting either from the production of ethanol itself or from additives incorporated into ethanol prior to blending with gasoline. Process impurities are dependent upon the methodology used to produce ethanol. The majority of ethanol (approximately 63 percent) (Reeder, 2000) is produced using a wet milling process that separates the starch from the grain prior to fermentation.

Glycerol and fusel oil are the primary impurities associated with wet milling production. Glycerol is removed during subsequent distillation processes and is not likely to be found in the final product. Fusel oil is a complex mixture of up to 50 compounds, mostly amyl alcohols such as 2-methyl-1-butanol and 3-methyl-1-butanol. It also contains acetaldehydes and ethyl acetate in lower concentrations.

Whole grain fermentation is also used to produce ethanol, although to a lesser degree (approximately 35 percent) (Reeder, 2000). Since the non-starch portions of the grain are not separated out prior to fermentation and distillation, additional impurities are introduced into ethanol. When non-starch portions of the plant such as hemicellulose and pectin undergo hydrolysis, methanol and acetic acid are produced in addition to greater amounts of fusel oil. These additional by-products are carried through the distillation process and end up in the final ethanol product.

Chemical additives are also incorporated into ethanol prior to blending into fuel products. These additives include denaturants such as gasoline or gasoline components, which must be added to make the ethanol unfit for human consumption. Denaturants are added to achieve concentrations of 2 percent by volume. A variety of corrosion inhibitors and detergents are also added to make fuel grade ethanol (ASTM). Finally, blending agents such as aromatics, higher aliphatic alcohols, and aromatic alcohols are added to reduce phase-separation tendencies.

Denatured fuel ethanol must contain a minimum of 92.1 percent (by volume) ethanol, including its impurities. Methanol and water cannot comprise more than 0.5 percent and 1 percent, by volume, respectively. The volume percentage for denaturants ranges between 1.96 and 4.76 percent (ASTM).

ETHANOL VERSUS M*t*BE

M*t*BE is a synthetic molecule composed of hydrogen, carbon, and oxygen. It is a larger molecule than ethanol and more highly branched. It is manufactured by reacting isobutylene with a small amount of methanol. At room temperature, it is a colorless liquid and, in contrast with ethanol, has a strong, disagreeable odor. Like ethanol, M*t*BE is flammable, volatile, readily soluble in water, and when dissolved, moves at the same speed as the groundwater. M*t*BE and ethanol do not bioaccumulate in the tissues of living organisms and do not sorb to sediments or soils to any great degree. Unlike ethanol, M*t*BE is not readily biodegradable, and therefore, persists longer in the soil and groundwater compared to other gasoline constituents.

As the federal RFG program took form, M*t*BE became the oxygenate favored by industry because of its low cost, ease of production at refineries, favorable blending characteristics with other fuel components, and lack of phase-separation problems in the presence of water.

ETHANOL-BLEND RFG

Throughout this report, gasoline that has been amended with ethanol will be referred to as “E-blend.” E-blends can meet the requirements of either conventional (non-RFG) gasoline or RFG, which must contain a minimum oxygen content of 2 percent by weight.

Replacing M*t*BE with ethanol will not be straightforward and is likely to result in other changes to the formulation of both RFG and conventional gasoline. Refiners face two main challenges in producing RFG with ethanol instead of M*t*BE. First, the need to lower the volatility of the baseline gasoline to accommodate the addition of ethanol. Even small amounts of ethanol raise the volatility (RVP) of gasoline. To limit evaporative hydrocarbon emissions, the allowable RVP of both conventional gasoline and RFG are effectively constrained. To meet summertime VOC performance standards, refiners will need to use specially formulated, low-RVP base gasoline when blending RFG with ethanol. This is likely to increase the cost of producing the gasoline.

Second, there is the need to make up the octane loss associated with M*t*BE removal. Ethanol has a higher oxygen content than M*t*BE. As a result, RFG need only contain 5.7 percent ethanol (by volume) to meet the minimum 2 percent (by weight) oxygenate requirement. As it is, ethanol is typically blended at a concentration of 10 percent, by volume, because of available tax credits. By comparison, M*t*BE is present at 11 percent by volume in most current RFG formulations. Aromatics, olefins, and alkylates are seen as the likely additives that will be used to make up the difference in volume. (See NESCAUM, Volume 2, for more information about gasoline reformulation.)

The costs associated with switching to ethanol in gasoline in the Northeast have been addressed by NESCAUM. (See NESCAUM, Volume 2.)

It should be noted that some states in the midwest (e.g., Minnesota, Nebraska) have been using high concentration (e.g., 83% ethanol) E-blend fuels for several years. Their experiences should be fully explored. However, according to the results of a recent NEIWPCC survey of all 50 states, very few states monitor for ethanol in groundwater or test for ethanol in gasoline-contaminated lab samples (NEIWPCC, 2000). Thus it seems unlikely that meaningful information on state experiences with ethanol would be available unless specific studies were undertaken.

THE GOALS OF THIS REPORT

The NEIWPCC Alternative Fuels Committee undertook this project with the following goals:

- ▲ Identify available information on ethanol with respect to health effects, aquatic effects, storage and handling issues, environmental impacts associated with ground and surface water resources, and to a lesser extent, alternatives other than ethanol. Chapter 2 provides key information on the status of UST programs in New England and New York.
- ▲ Ascertain what is known and not known regarding the issues of concern.
- ▲ Prepare a series of summary reports that:
  - Clearly characterize the issues and any associated uncertainties,
  - Present conclusions regarding findings,
  - Make recommendations as to what information is needed to adequately understand and address concerns about ethanol, and
  - Identify, where possible, steps that should be taken to mitigate potential problems if ethanol is widely introduced into the Northeast gasoline supply.

This report represents a multi-state effort. Conclusions, recommendations, and identified uncertainties were reached by consensus.

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CHAPTER 2

UNDERGROUND STORAGE TANK PROGRAMS IN NEW ENGLAND AND NEW YORK

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THE SCOPE OF THIS CHAPTER

With the implementation of the federal reformulated gasoline (RFG) program in the 1990s, M*t*BE was added to RFG gasolines to meet the 2 percent (by weight) oxygen requirement. While M*t*BE has been used throughout the U.S. as an octane enhancer in lower concentrations (0 - 11% by volume) in gasoline formulations since 1979, it is now generally present in RFG gasoline at an 11 percent volume. As a result of its higher concentration in gasoline combined with its highly mobile and recalcitrant behavior in soil and groundwater, M*t*BE is now frequently detected in public and private water supplies in the context of gasoline releases, primarily from petroleum storage systems, when other toxics in gasoline (e.g., benzene) are not. For this reason, M*t*BE has ascended into the limelight and has focused attention on state and federal underground storage tank (UST) programs. At issue is the success of regulatory efforts to keep gasoline out of the environment and what, if anything, can be done to enhance these efforts. This chapter provides an overview of state UST regulatory programs in New England and New York.

BACKGROUND

NEIWPCC member states have made great strides in developing regulatory and outreach programs to advance the cause of minimizing the threat of gasoline and other petroleum product releases to the environment. As early as 1984, NEIWPCC and U.S. EPA Region 1 were bringing state environmental agency staff members together to discuss the growing problem of leaking USTs. By the time Congress enacted the Subtitle I RCRA Amendments of 1984, mandating EPA to develop UST regulations to protect human health and the environment, the Northeast states were already moving forward with developing their own programs. For this reason, these states were consulted frequently by U.S. EPA during its rulemaking process.

The federal UST rules were made final in September 1988. In addition to a number of technical and financial responsibility requirements and timetables, the rules established a December 1998 deadline, allowing UST owners up to 10 years to retrofit substandard UST systems or replace them with state-of-the-art systems. With the U.S. EPA rule in place, the states began to refine their rules so that they were “no-less-stringent than” the federal blueprint. The six New England states made applications to EPA for State Program Approval between 1991 and 1995.

PROGRESS

The Northeast states used their option to be more stringent than the federal program as they saw fit. Most adopted requirements for double-walled UST systems as the replacement UST of choice, some required earlier UST upgrade deadlines based on sensitive locations or age-based retirement (20 or 25 years old), most included heating oil used in industrial or large commercial application as a regulated substance, and some had permit programs to ensure that their UST system database was kept as up-to-date as possible.

Table 2.1 UST population and compliance data for New England and New York. (September 2000). (Values presented represent best estimates of state programs.)

	USTs REGISTERED IN 1985	USTs CLOSED SINCE 1985	ACTIVE USTs	% IN COMPLIANCE WITH 1998 DEADLINE (9/2000)
CT	32,225	18,394	13,831	99%
MA	28,047	20,289	12,122	100%
ME	0*	11,620	3,709	99%
NH	9,740	10,163	3,078	99%
NY	Unknown	69,216	32,928	**95%
RI	6,138	6,782	1,795	95%
VT	1,000	4,883	2,442	100%

* The rules that required registration did not come into effect until 1986.

** Based on registration information that is updated every 5 years.

Firm regulatory approaches combined with a huge push on state technical assistance and outreach/warning letters yielded big dividends—a substantial amount of voluntary compliance on the part of the regulated community. As of September 2000, all of the states reported nearly 100 percent compliance with the December 1998 replacement or upgrade requirements. Note, these figures do not reflect operational compliance with leak detection requirements. (See Table 2.1.)

THE UNRESOLVED

In spite of the astounding success in getting the Northeast's fleet of USTs modernized, some key concerns persist that have the potential to affect groundwater. These concerns include abandoned/orphaned USTs, ongoing proper operation and maintenance of USTs, and non-UST-related sources of gasoline releases.

Most states report that they still have a few bare-steel USTs that bankrupt or reluctant owners have yet to remove and assess. Worse yet, scattered about the region are USTs that were abandoned before the 1985 registration/notification deadline and are still in the ground—some might also contain product. These "orphan" tank cases are very difficult to resolve. In many cases, the state will end up pumping out and/or pulling the tanks. Often, these potential sources of contamination go unaddressed until legal action is taken or the property is sold.

Another concern that regulators face is the growing recognition that some UST owners are not properly operating and maintaining their new or upgraded UST systems. Problems with automatic tank gauges (ATGs) in permanent alarm mode, leaking sumps and/or dispensers, spill buckets full of water—to name a few—are all too frequently reported during routine compliance inspections.

There is still a high level of concern regarding the proper performance of routine system maintenance. Regardless of engineering, manufacturing, and installation adequacy, improper maintenance practices can immediately negate all such improvements and place the environment at risk of contamination.

It is clear that the current level of resources in the states may not be sufficient to allow state UST regulators to conduct regular on-site compliance inspections. (See Table 2.2.) States are considering strategies for improving compliance inspection rates, such as ensuring that each facility is visited every year or two or instituting third-party audit programs.

Table 2.2 Frequency of UST facility inspection in New England and New York. (Values presented represent best estimates of state programs.)

	ACTIVE USTs	TOTAL SITES/FACILITIES W/USTs	AVERAGE INSPECTIONS/YEAR	*AVERAGE SITE VISIT VISIT FREQUENCY
CT	13,831	5,160	300	~ 1 / 17 yrs**
MA	11,997	4,766	470	~ 1 / 10 yrs
ME	3,668	1,531	100	~ 1 / 15 yrs
NH	3,078	1,310	225	~ 1 / 6 yrs
NY	32,931	12,179	1,500	~ 1 / 8 yrs
RI	1,809	702	120	~ 1 / 6 yrs
VT	2,442	1,143	300	~ 1 / 3.8 yrs

* UST Sites ÷ Inspections/year = (e.g., 1/5 years).

** Some of these sites include facilities with only small tanks (e.g., 500-1,000 gallons) containing waste oil.

The work of keeping petroleum products out of the environment is far from over. States recognize that more outreach to tank owners and operators, as well as the general public will be required. A few states are considering implementing siting criteria that prohibit or restrict the installation of new USTs in critical groundwater, well head, or private well recharge areas.

Many tank systems that were upgraded according to 1998 deadline standards may still not be "leak proof." Even states that require new tank systems to be double-walled still have single-walled USTs that were installed previous to the adoption of state UST standards. There are still some cathodically protected retrofit and/or lined USTs in operation that are of questionable soundness. (See Table 2.3.) Maine's single-walled tanks must be retired upon expiration of the warranty. New Hampshire has set a retirement date for its remaining single-walled systems (2015).

Table 2.3 New England and New York UST population by containment status. (Values presented represent best estimates of state programs.)

	ACTIVE USTs	SECONDARY CONTAINMENT	SINGLE WALLED	LINED OR CATHODIC PROTECTION (C/P) RETROFIT
CT	13,831	1,428	12,403	0
MA	11,997	6,235	3,037	1,634 (C/P)* 244 (lined)
ME	3,668	2,380	1,231	0**
NH	3,078	2,584	472	22
NY	32,931	19,679	13,252	2,254 (lined)***
RI	1,809	1,050	673	86
VT	2,442	1,936	475	31

* Unknown whether C/P was retrofitted or factory installed.

** Not an option in the state of ME.

*** Do not know the number of tanks retrofitted with C/P.

Although double-walled UST systems provide the best engineering protection from future leaks, there have been documented failures in these systems, as well. (See “A Tank Leak Story” on page 63.)

Finally, even if all of the UST systems in the region never leaked another drop, it is clear from recent studies in Maine and other states that gasoline components such as M*t*BE are released in small quantities in widely varied settings because of careless practices on the part of end users who are fueling or servicing non-automotive engines, such as lawn mowers, recreational vehicles, and outboard motors. (See Chapter 5.) Automobile and tanker truck accidents can be a significant source of contamination. Unless these aspects of modern human behavior can be better controlled, gasoline and its many organic components may be found just about anywhere in our environment.

CHAPTER 3

HEALTH EFFECTS OF ETHANOL

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THE SCOPE OF THIS CHAPTER

This chapter presents a *summary analysis* of ethanol's neurologic and developmental effects, while also considering the evidence for it's carcinogenic effects and internal organ (particularly liver) damage. In preparing this analysis, key studies and reviews describing ethanol toxicity were identified. However, because of time constraints a full evaluation of the available data has not been performed. This summary information is put into a risk context for the drinking water pathway in relation to health risks from M*t*BE.

The use of ethanol in gasoline may lead to exposure of the general public via two main pathways:

- ▲ Inhalation of ethanol vaporized from gasoline (e.g., during refueling) or from unburned ethanol contained in tailpipe exhaust.
- ▲ Exposure to ethanol in tap water as a result of gasoline contamination in groundwater.

The potential health effects following ingestion of high concentrations of ethanol have been well studied. However, the potential adverse effects associated with repeated exposure to environmentally relevant concentrations are less well understood. We will discuss the inhalation pathway briefly in the following section. Our major focus, however, will be directed toward the drinking water pathway. Tables 1 through 5 on pages 42 to 44 summarize information presented in this chapter on the comparative characteristics of M*t*BE and ethanol.

INHALATION OF ETHANOL VAPORS

In 1996, the Health Effects Institute (HEI) reviewed exposure potential and possible health effects associated with ethanol in the atmosphere. That report concluded that there is a safety factor, several orders of magnitude in size, between possible inhalation exposures and ethanol health effects. The National Research Council (NRC, 1996) conducted a follow-up review of various oxygenated fuel issues. This report agreed with the HEI conclusion that ethanol inhalation associated with use in gasoline will not be a public health issue given that such exposure is unlikely to affect endogenous blood ethanol levels.

EXPOSURE TO ETHANOL FROM GASOLINE-CONTAMINATED DRINKING WATER

Previous reports have not addressed potential public health concerns associated with the release of gasoline with ethanol into drinking water. This pathway is important because the amount of ethanol that enters a drinking water well might be a significant source of exposure. Given that there are no federal maximum contaminant levels (MCLs) or state action levels specific for ethanol in drinking water, there is little regulatory basis on which to evaluate this scenario. This exposure evaluation looks at the following critical issues: acute effects (human and animal); subchronic and chronic effects; reproductive effects; developmental effects (human and animal); and cancer (human, animal, and possible mechanisms).

Acute Effects

Human Studies

Acute health effects associated with ethanol have been of greatest concern in the realm of automobile accidents caused by drinking and driving. A blood alcohol level of 500 mg/L (0.05%) has generally been found to be the low-end concentration associated with an increased rate of automobile accidents (HEI, 1996).

Impaired performance on simulated driving tests is frequently used as a sensitivity index of the acute central nervous system (CNS) effects of ethanol. Such testing reveals that a blood alcohol level of 0.05 percent can impair the mean time needed to respond to traffic hazards (West, et al., 1993). Many states use alcohol blood levels of 0.08 or 0.1 percent as their official "driving while impaired" limit. However, there is some evidence that levels as low as 0.012 percent can impair performance under adverse conditions, such as poor lighting (Koelega, 1995). Such highly sensitive vigilance-performance testing has prompted suggestions that the legal blood alcohol limit should be lowered to 0.02 percent (Koelega, 1995).

Overall data from human studies suggest that the threshold for acute neurological effects is in the blood alcohol range of 0.01 to 0.05 percent, depending on the testing conditions. Acute ingestion of 1 g/kg alcohol approximates a 0.1 percent blood alcohol level (HEI, 1996), although this depends on a variety of factors (e.g., how quickly the ethanol is ingested). Based on this relationship, the acute threshold for alcohol effects may be in the range of 0.1 to 0.5 g/kg (corresponding to 0.01 to 0.05 percent blood alcohol)—a dose range that represents the lowest observable adverse effect level (LOAEL) for acute ethanol neurotoxicity in humans.

Animal Studies

Neurological performance tests performed on animals that have received acute doses of ethanol have addressed gross and fine motor effects, memory, and reward (operant/level press) endpoints (HEI, 1996). These studies involved rodents or nonhuman primates; most examined the effects of oral or intraperitoneal (i.p.) exposure, a few looked at the effects of inhaling high concentrations.

In general, these studies have found that ethanol has a biphasic effect on the animals such that endpoints show increased responsiveness at relatively low doses of ethanol and impaired performance at higher doses. For example, rats show increased motor activity and monkeys show increased aggressiveness after receiving oral ethanol doses of 0.1 to 0.5 g/kg. At higher doses, these responses are suppressed and motor incoordination occurs (HEI, 1996). Responses that are based on memory also show a biphasic effect that corresponds to the stimulatory effect of ethanol on the CNS at low doses or early response times after moderate doses—but with CNS depression at higher doses.

Other tests involving rodents, such as schedule-controlled operant behavior and fine motor control, demonstrated effects from ethanol beginning in the 0.25 to 1.0 g/kg dose range. Several operant behavioral studies have involved exposure of rats or mice via inhalation (HEI, 1996). These studies showed that exposure to 20,000 ppm of ethanol and above yielded significant performance decrements, while the lowest dose tested (12,000 ppm) had a borderline effect. It should be noted that rats exposed to 16,000 ppm experienced an alcohol blood level of 0.05 percent, the point at which decrements in human performance have been most clearly documented.

Subchronic and Chronic Effects

Alcoholism is associated with a wide variety of health effects, some stemming directly from the toxic effects of ethanol (and likely its oxidative metabolite acetaldehyde), and some stemming from nutritional deficits that result from the abuse of ethanol. Subchronic and chronic effects associated with alcoholism include the following:

- ▲ Progressive liver dysfunction involving accumulation of fat (hepatic steatosis), alcoholic hepatitis, and cirrhosis can occur with chronic ingestion of 2 g/kg/d (HEI, 1996).
- ▲ Toxic effects on the heart leading to inflammatory and degenerative changes (alcoholic myocarditis).
- ▲ Neurologic degeneration and encephalopathy. The degenerative syndromes in the heart, CNS, and liver have only been documented after long-term, high level exposures. Data describing thresholds for such severe effects or more subtle manifestations are not available.

Blood cellularity changes have also been noted in humans and laboratory animals exposed to ethanol. These changes have involved white cell, neutrophil, and monocyte lineages but have not demonstrated a significant effect on hemoglobin or the red cell content of blood. These effects have been reproduced in mice that have received short-term inhalation exposures of 20 to 38 mg/L ethanol (24 to 48 hour exposure). Peak blood concentrations ranged from 0.14 to 0.56 percent, indicating a moderate to high level of exposure (Malik and Wickramasinghe, 1986).

The consequences of these cellularity changes on immune function have been evaluated in rats with somewhat conflicting results. In one study, oral doses of ethanol sufficient to produce dependency in rats led to functional lymphocyte impairment as determined by lymphocyte proliferative response to B and T-cell mitogens and by altered antibody response to sheep red cells (Jerrells, et al., 1986). However, a follow-up study involving 14-day ethanol administration via inhalation found changes in lymphocyte cell numbers but no change in lymphocyte proliferative ability (Marietta, et al., 1988).

The platelet system also appears to be affected as shown in rats exposed to ethanol to attain a blood concentration of 0.13 percent. This moderate level of exposure caused significant inhibition of platelet aggregation as measured in vitro in a collagen-induced aggregation system (Froines, et al., 1998).

Due to the lack of sufficient dose-response information in the low to moderate exposure range, thresholds for the effect of ethanol on blood cellularity and function have not been identified. Therefore, it is unclear whether such effects are of relevance at the relatively low doses possible from environmental exposure.

Reproductive Effects

Standard two- or three-generation rat reproductive studies have not been conducted with ethanol, so the animal database is deficient in terms of a variety of reproductive endpoints. Isolated studies in humans and rodents, however, support an ethanol-induced genetic effect in germ cells following moderate to high levels of exposure (Froines, et al., 1998).

These findings have identified an association between ethanol exposure and aneuploidy in miscarried pregnancies, chromosomal damage and abnormalities in sperm, and dominant lethal mutations in mice and rats. The mechanism for these genetic effects, which seem to be mediated via male germ cells, has not been elucidated but may involve acetaldehyde as well as ethanol.

A variety of studies have shown that ethanol delays development of the male reproductive tract when prepubertal rats and mice are exposed (Froines, et al., 1998). The Sertoli cell, which supports germ cell division and maturation of spermatocytes, appears to be a primary target (Anderson, et al., 1989). However, studies implicating an ethanol effect on male reproduction do not provide sufficient dose response information as they used a single dose or limited range of doses (moderate to high range) to identify specific effects. While these exploratory studies are not directly useable in quantitative risk assessment, they add to our understanding of the hazard potential from chronic exposure to moderate to high levels of ethanol.

Developmental Effects

Human Studies

High levels of ethanol ingestion during pregnancy have produced fetal alcohol syndrome (FAS), a constellation of physical malformations and neurological effects known to be caused by in utero exposure to ethanol. This syndrome is most clearly linked to binge drinking, which raises the point that, in general, the developmental effects of ethanol are more strongly influenced by dose-rate as opposed to total dose during pregnancy (IOM, 1996; Jacobson and Jacobson, 1995). However, mothers who drink less ethanol per event (i.e., not binge drinking) can still have offspring who are affected by ethanol.

In addition to FAS, a syndrome of more subtle neurological changes termed fetal alcohol effects (FAE) has been documented. These effects include decreased performance on neuropsychological tests, hyperactivity, and lowered intellectual capacity (HEI, 1996; IOM, 1996).

While research on the threshold for fetal alcohol effects in humans is still ongoing, evidence points to an observable threshold (i.e., above this dose effects were observed) of 0.5 ounces/day (approximately one drink per day or 0.20 g/kg/d) for most neurodevelopmental endpoints (Jacobson and Jacobson, 1995; Jacobson, et al., 1996a; Jacobson, et al., 1996b; Jacobson, et al., 1998). This threshold was derived from studies of women over 30 years of age indicating that their offspring may be more sensitive to in utero ethanol exposure than the offspring of women under 30 years of age (Jacobson, et al., 1996a).

While several studies in humans support such an observable threshold, data for certain neurodevelopmental endpoints (e.g., Bayley Scales - Mental Development Index) suggest effects at the lowest analyzed ethanol drinking rate (ethanol ingestion rates in the range of 0.0014 to 0.25 ounces per day), which are below the observable threshold for other effects (0.5 ounces per day or approximately 1 drink per day or 0.20 g/kg/d) (Jacobson and Jacobson, 1994). However, the effect seen on the Bayley Scales - Mental Development Index at the lowest analyzed drinking rate was only present when one measure of performance (comparison of group means) was used. The reduction was not seen when a second measure of performance (percent poor responders) was used. Typically, the most robust effects are independent of the measure used to assess the performance. This inconsistency in the conclusion that the reduced performance was caused by ethanol is less certain than if both measures of performance were significantly reduced.

The daily ethanol dose is 0.2 g/kg/d or a daily intake of 1 drink per day (i.e., 0.5 ounces of pure ethanol/day). It is calculated as follows: 1 drink contains about 0.5 fluid ounces (14.9 ml) of pure ethanol, 14.9 ml of ethanol weighs about 11.8 grams given a density of 0.789 g/ml); 11.8 grams/60 kg of body weight = 0.20 g/kg/d.

Although the daily dose of 0.20 g/kg/d represents a dose at which most neurobehavioral effects would not be observed, given the uncertainty in specifying it as an observable threshold for all of ethanol’s fetal effects, including the performance on Bayley Scales - Mental Development Index, it appears prudent to consider 0.20 g/kg/d as the human LOAEL. This is supported by the animal evidence cited below in which the LOAEL for subtle neurodevelopmental effects (i.e., cognitive function, motor development) in monkeys was similar (0.25 g/kg/d).

Animal Studies

FAS and more subtle neurological effects can also be produced in animals receiving in utero exposure to ethanol. Prenatal exposure in rats and mice at doses of 2-3 g/kg/d have produced effects on a variety of neurobehavioral endpoints in offspring, although lower doses were not tested (HEI, 1996).

In rodents, the neonatal period corresponds to roughly the third trimester of human brain development. Thus the growth spurt in CNS development can be tested postnatally in rodents (HEI, 1996). Biochemical and morphological studies of brain tissue from rodents exposed prenatally failed to find evidence of effects on several parameters, but postnatal exposure to approximately 2 g/kg/d yielded evidence of stunted brain growth.

Monkeys have a CNS development profile that is similar to humans. When ethanol was administered to monkeys at different stages of pregnancy, clear effects were seen in offspring cognitive function and motor development at 1 to 3 g/kg/d; some features of FAS were apparent (HEI, 1996). Slight effects may have occurred in monkeys at maternal doses as low as 0.25 g/kg/d.

The animal studies support the finding from human studies that the drinking pattern (e.g., binge drinking) can be a greater influence on fetal development than the total dose over the course of pregnancy. The studies suggest that the early period of CNS development (6-8 weeks gestation in monkeys) may be the most sensitive period for neurodevelopmental effects from alcohol. However, ethanol's developmental studies are insufficient for a clear determination of which gestational periods represent the greatest vulnerability for neurodevelopmental effects.

Cancer

Human Studies

Epidemiology studies of various designs have consistently shown a correlation between the drinking of alcoholic beverages and cancers of the oral cavity, pharynx, larynx, esophagus, and liver. There is some evidence for other types of cancers (i.e., stomach, colon, rectum, pancreas, breast, lung) (IARC, 1988).

While alcoholic beverages are generally a mixture of ingredients, it is the ethanol content of these beverages that is most implicated in the cancer outcomes that have been found (IARC, 1988; HEI, 1996). The International Agency for Research on Cancer (IARC) termed the cancer evidence for alcoholic beverages to be *sufficient* for humans, placing alcoholic beverages in the Group I (carcinogenic to humans) category. However, the National Toxicity Program's Ninth Report on Carcinogens (NTP, 2000) has not listed ethanol as a carcinogen. Furthermore, U.S. EPA has not classified ethanol as to its carcinogenicity.

Animal Studies

IARC has classified the animal evidence regarding ethanol carcinogenicity as inadequate. This finding is based on the limitations present in several studies in which ethanol failed to elicit a tumor response from long-term exposure in rodents (IARC, 1988).

A recent study in rats on an ethanol-spiked liquid diet generally failed to show evidence for increased tumors, although the breast tumor data were equivocal (Holmberg and Ekstrom, 1995). Another study, this one in mice dosed at higher levels in drinking water (approximately 10-15 g/kg/d), yielded a clear increase in tumors of breast tissue. This dose level was also associated with extensive hepatic fibrosis (Watabiki, et al., 2000).

Ethanol has been shown to accentuate the carcinogenic effects of several nitrosamines and vinyl chloride. This effect may be related to ethanol's ability to induce a form of liver metabolism (CYP2EI) known to be essential in the activation of these carcinogens (Ohnishi, 1977).

Possible Cancer Mechanisms

While alcoholic beverages have been linked consistently to a variety of human cancers, there is only limited supporting evidence from animal studies, possibly because of limitations in study design in many of the studies conducted. The evidence that ethanol can enhance the carcinogenicity of other compounds suggests a promotional effect that may be based on chronic irritation of tissue at portals of entry and tissue damage. In humans who are drinking alcoholic beverages, this effect would most likely result from a high level of exposure at the oral cavity through the liver.

Genetic toxicity studies have shown mixed results with ethanol—some in vivo studies of chromosomal damage have exhibited effects while others did not. Results of in vitro studies in mammalian, bacterial, and fungal cells were mostly negative. This database is more supportive of a promotional mechanism for ethanol, but it does not rule out the possibility that under certain circumstances, ethanol may affect deoxyribonucleic acid (DNA) in a way that could lead to mutation and cancer.

Consistent with this scenario is the fact that the major oxidative metabolite from ethanol in liver and other tissues is acetaldehyde. Acetaldehyde is genotoxic and carcinogenic in animal tests. Thus, the rate of acetaldehyde formation and removal in the various genotoxicity test systems used with ethanol may have governed the degree to which a positive response was seen.

Overall Cancer Assessment

Ethanol should be considered to be a potential human carcinogen based on available epidemiology data, limited animal data suggesting a promotional effect, and mechanistic considerations. However, there is little basis for dose response assessment or development of a unit risk value for the cancer endpoint. Where this has been attempted (Richard Wilson report to CalEPA, 2000), there are considerable uncertainties in terms of how to conduct the dose response modeling and whether the underlying database can support such a calculation. For example, the study relied upon in the Wilson assessment (Holmberg and Ekstrom, 1995) showed only marginal breast cancer effects which were not statistically significant. This analysis yielded a cancer potency factor roughly 10 fold below that calculated by others for M*t*BE. This suggests that if the rat breast cancer finding is a suitable point of departure for dose-response modeling, this would translate to a relatively low cancer potency.

Given the possibility that ethanol acts primarily via promotional mechanisms and that in this analysis a comparison is being made with similarly derived M*t*BE values (for which a cancer uncertainty factor approach has been used in a number of cases), it is appropriate to consider a 10-fold uncertainty factor in ethanol risk assessments to account for potential carcinogenic effects.

RISK IMPLICATIONS: ESTIMATING A COMPARATIVE VALUE FOR ETHANOL EXPOSURE

We are not aware of any drinking water guidelines that are specific to ethanol. However, based on the toxicity profile described in this chapter, we can put the risks associated with ethanol exposure from water ingestion into a dose-response context to calculate a comparative daily exposure level and an associated drinking water concentration.

This exercise is not an attempt to set an ethanol drinking water MCL or action level, it is simply a means for comparing M*t*BE (for which there are drinking water guidelines) and ethanol dose-response assessments. This risk-based value may also provide some perspective on instances where ethanol has been detected in groundwater.

If there is a need to formally develop drinking water, groundwater, or surface water criteria for ethanol in the future, risk-based approaches such as those presented in this document, or others, may be used by different state or federal agencies. Additionally, some states may choose to utilize general contaminant guidelines to evaluate ethanol contamination. For example, New York State currently has a general drinking water standard of 50 µg/L for chemicals, including ethanol, that are classified as unspecified organic compounds under state regulations. Such general guidelines may be retained depending on the data for a chemical-specific, risk-based evaluation.

Given the extensive study that has been done of ethanol exposure in humans, the current assessment relies primarily on human rather than animal data. Ethanol effects in humans cover a wide spectrum—acute neurological effects ranging from arousal/excitation at relatively low doses to central nervous system (CNS) depression at higher doses; developmental effects ranging from subtle cognitive and learning deficits at lower doses to fetal alcohol syndrome (FAS), which involves cranial malformations and brain damage; liver damage; blood cellularity changes; and increased cancer incidence, particularly at the portals of entry (oral cavity, g.i. tract, liver). With the possible exception of cancer, the effects seen in humans are also readily reproduced in animals. The dose response is similar across species where direct comparisons are possible.

The effects of greatest concern at relatively low doses appear to be neurodevelopmental deficits, given the potential for such effects to affect learning and to be essentially irreversible. The apparent threshold maternal dose for this developmental effect is in the range of 0.20 g/kg/d, based upon evidence in both humans and monkeys. Other LOAELs are in this range or slightly lower (e.g., 0.1 to 0.5 g/kg/d for reversible stimulation of CNS in animals; 0.1 to 0.5 g/kg/d for subtle acute neurological effects in humans).

Application of Uncertainty Factors

The developmental observable threshold of 0.20g/kg/d can be viewed as a no observable adverse effect level (NOAEL) for some effects and perhaps a LOAEL for other effects. Given this uncertainty in identifying a NOAEL for all of ethanol's effects, it is prudent to divide the apparent threshold level of 0.20 g/kg/d by 10 fold to be sure of not overestimating the NOAEL. This estimated NOAEL for all effects (0.02 g/kg/d or 0.05 ounces ethanol per day) is in the range of the lightest drinking group (0.0014 to 0.25 ounces per day), where the possibility exists that subtle effects were seen (Jacobson and Jacobson, 1994).

In addition, ethanol's in utero effects in both animals and humans have been more closely associated with binge drinking (e.g., 7 drinks on Saturday night, none the rest of the week, average is 1 drink/day) than more routine drinking (e.g., 1 drink per day on each day of the week, average is also 1 drink per day). Because blood ethanol levels increased with the number of drinks per event, these observations suggest that at least some of ethanol effects on development are associated with peak blood ethanol levels and not average blood levels.

Deriving a NOAEL on a pro-rated or average daily dose basis is conservative, because the averaged daily exposure will not produce the type of blood ethanol spikes that cause the greatest neurodevelopmental risk. This is consistent with the drinking water contamination scenario in which binge (or spiking) exposure to ethanol is unlikely. Therefore, setting the NOAEL 10 fold below the observable human threshold for a number of endpoints and in the range of some borderline findings is reasonable, given that this is being applied to an exposure scenario (drinking water) that does not involve risky (binge drinking) behavior. Application of additional uncertainty factors (as follows) further ensures that the Water Comparison Value is at an exposure level that is well below that which has been associated with effects in animals or humans.

Further division of this NOAEL by an uncertainty factor to account for inter-individual differences is appropriate even though this analysis covered studies of what might be the most at risk population (women over 30 years) and looked at alcohol interactions with other environmental factors (e.g., tobacco smoke). A full 10-fold inter-individual uncertainty factor is prudent given the pharmacokinetic differences known for ethanol in the population (genetic polymorphism for aldehyde dehydrogenase, see section below), and the fact that epidemiology studies have not evaluated very large cohorts of exposed women.

A three-fold uncertainty factor is necessary because of data gaps in the ethanol dose-response database. While it is assumed that fetal exposure will produce the most sensitive response to ethanol, appropriate dose-response studies for the other major effects of ethanol (e.g., hepatic, reproductive, hematopoeitic) are lacking. A 3-fold uncertainty factor addresses the possibility that an endpoint other than neurodevelopment would drive the risk assessment if the proper studies were available.

One additional uncertainty factor of 10 fold is prudent because of the potential cancer risk presented by ethanol. This is a common default approach used in the past by the U.S. EPA Office of Drinking Water and numerous states for carcinogens that have equivocal test data in animals, that are not clear genotoxicants, for which no unit risk factor exists, and for which promotional effects may be the primary cancer mechanism. Ethanol fits this profile.

It is worth noting that it would be ideal to perform a more quantitative cancer assessment, and U.S. EPA's draft cancer risk assessment guidelines provide other approaches (e.g., margin of exposure approach, alternative low dose modeling). However, for the purposes of this assessment, the use of a 10-fold uncertainty factor for ethanol cancer risk is appropriate, given that a comparison is being made with M*t*BE, for which this uncertainty factor approach has also been used in various drinking water criteria to address cancer risk.

The above considerations yield a cumulative uncertainty factor of 3,000 fold for deriving a comparative drinking water value for ethanol in drinking water.

Estimation of a Comparative Drinking Water Value

It is important to restate that the goal of this document is not to establish a formal drinking water action level or MCL for ethanol. Rather, the current goal is to provide a reasonable estimate of a value in drinking water to allow a comparison with drinking water guidelines for M*t*BE.

The cumulative uncertainty factor described above is 3,000 fold (10x for LOAEL to NOAEL, 10x for interindividual differences, 3x for database insufficiencies, 10x for cancer potential). This yields an acceptable exposure dose of 0.067 mg/kg/d (200 mg/kg/d divided by 3,000).

The drinking water concentration that corresponds to this daily exposure dose is 2.0 mg/L (0.067 mg/kg * 60 kg pregnant woman divided by 2 liters/day). Applying the standard Relative Source Contribution factor of 0.2 (a default factor that ensures that no more than 20 percent of total ethanol exposure can come from drinking water) would lower the acceptable water concentration by a 5-fold factor to 0.4 mg/L, or 400 µg/L.

This concentration of ethanol in drinking water is unlikely to significantly increase blood ethanol concentrations from their endogenous level of approximately 10 mg/L (0.001%) (range of baseline concentrations varies from 0.3 to 27 mg/L across subjects) (HEI, 1996). This is because the daily dose associated with 400 µg/L ethanol in water is only 0.013 mg/kg/d (0.4 mg/L * 2 l/d * 1/60 kg bwt.), which is approximately 20,000 times smaller than the ethanol dose from one alcoholic drink a day and approximately 70-fold lower than the prorated daily dose associated with one drink during the course of a pregnancy.

This daily exposure level would be expected to produce a blood ethanol concentration of only 0.019 mg/L (1.9E-06%), which is based on the assumption of a well-mixed one compartment model with an ethanol volume of distribution of 0.7 L/kg (HEI, 1996). The calculation is simply: 0.013 mg/kg/d ÷ 0.7 L/kg = 0.019 mg/L. This blood concentration is well below naturally occurring endogenous levels (0.3 to 27 mg/L). If the total daily ethanol dose was ingested gradually over the course of the day, the effect on blood concentrations would be even smaller.

Assuming a linear relationship between dose and blood level, drinking water concentrations would need to be at least 10 times higher than the draft Water Comparison Value (or 4 mg/L) to elevate ethanol blood levels into the endogenous baseline range. Since the total daily ethanol dose from drinking water is likely to be ingested gradually over the course of the day rather than in one or two bolus doses, the effect on blood concentrations would be even smaller. Given this exposure pattern and the range of endogenous levels, it would appear that drinking water concentrations of 10 mg/L or higher would be needed to cause a measurable increase in baseline blood ethanol concentrations.

While blood ethanol is not a direct indicator of fetal exposure, it is a useful biomonitor for assessing fetal risks. This is because maternal blood levels rapidly equilibrate with fetal blood and elimination from the fetus appears to be governed by the maternal clearance rate (Clarke et al., 1986; Clarke, et al., 1987). Further, a variety of studies have related maternal peak concentrations of ethanol to fetal outcomes, showing that this biomarker is relevant to the developmental endpoints of concern. Data showing that ethanol may be slower to clear from amniotic fluid than maternal blood suggest that fetal exposure may be prolonged (Brien, et al., 1983; Clarke et al., 1986; Clarke, et al., 1987). However, accumulation of ethanol in amniotic fluid is in part an excretory pathway from the fetal circulation (Clarke, et al., 1987).

Given that maternal and fetal blood concentrations are similar over time in animal models, even when amniotic fluid levels become elevated (Clarke et al., 1986), the importance of amniotic fluid ethanol is uncertain. Further, the utility of amniotic fluid as a biomarker of ethanol's fetal effects has not been evaluated. Therefore, this report uses the traditional biomarker, maternal ethanol blood concentrations, to evaluate the potential effect of ethanol drinking water ingestion on fetal risk.

COMPARISON OF ETHANOL AND M*t*BE HEALTH RISKS

The spectrum of health effects caused by M*t*BE is somewhat similar to ethanol in terms of both chemicals causing acute CNS stimulation (low-dose effect) or CNS depression (high-dose effect) and possible cancer effects. M*t*BE may have a greater potency to induce acute CNS depression relative to ethanol. The evidence for this is that blood M*t*BE concentrations of approximately 100 mg/L in rats are associated with sedative effects in both inhalation and gavage studies (Rao and Ginsberg, 1997).

In contrast, ethanol does not appear to cause CNS depression in rodents below a blood concentration of approximately 500 mg/L (0.05%). However, ethanol is a clear developmental hazard, while M*t*BE is not likely to be of concern in this regard. Further, CNS effects of ethanol in the fetus can be irreversible with frank CNS damage. In contrast, M*t*BE, although neurotoxic, has shown no evidence of CNS damage with all neurologic effects appearing to be reversible. This finding includes animal developmental studies in which high M*t*BE exposures have failed to produce significant neurotoxicity in offspring.

Ethanol also appears to have a greater potential to damage the liver from chronic exposure, and the evidence for cancer effects relevant to humans is clearer with ethanol. Some states have used the M*t*BE animal cancer evidence to construct drinking water or surface water protection criteria for M*t*BE based upon low-dose-linear modeling (e.g., NY, NH, CA). In these cases, the M*t*BE criteria are in the range of 10 µg/L to 13 µg/L. However, based on ethanol's irreversible developmental effects, it appears that the hazard potential of ethanol is of greater overall concern than M*t*BE.

The cancer comparison between M*t*BE and ethanol is not straightforward, because the ethanol evidence is primarily in humans while the M*t*BE evidence is in animals. The only clearly positive animal bioassay with ethanol found breast tumor elevation in mice at a very high dose, 10 to 15 g/kg/d. Similarly for M*t*BE, a daily dose of approximately 12 g/kg/d via inhalation was required to elicit tumors in mice, in this case of the liver (Burleigh-Flayer, et al., 1992).

While these comparisons would appear to indicate a similar cancer effect level across chemicals, the extrapolation is made more complex by the different dose routes and strains of mice involved in these studies. Further, M*t*BE has somewhat lower cancer effect levels (CELs) in rats (gavage rats - CEL = 0.25 g/kg/d - Belpoggi, et al., 1995; inhalation rats - CEL = 2.5 g/kg/d - Chun, et al., 1992). As stated earlier, the preliminary cancer potency estimate developed by Richard Wilson for CalEPA would put ethanol's potency at roughly one-tenth of that estimated for M*t*BE. However, the unit risk values for both M*t*BE and ethanol contain considerable uncertainty.

Thus, both chemicals appear to require high level chronic administration to elicit tumors in laboratory animals, and both may be acting via nongenotoxic mechanisms (although both form aldehyde metabolites that are genotoxic). While there are some similarities in the cancer effects profile between these chemicals, the human evidence of ethanol carcinogenicity tends to put ethanol into a higher hazard classification for cancer concerns than M*t*BE.

The conclusion reached from dose-response assessment is somewhat different in that the derived Water Comparison Value for ethanol might be about 6 fold greater than the level currently set for M*t*BE in Connecticut, for example, that uses a standard of 70 µg/L. Other New England states have derived risk-based surface water, drinking water, or groundwater values for M*t*BE that range from 10 to 13 µg/L.

Too much should not be made of this difference, however, given that there are more human data for ethanol than for M*t*BE, so the overall uncertainty factor (UF) is not as large for ethanol as it is for M*t*BE (ethanol - 3,000x total UF; M*t*BE - 10,000x total UF). Thus though ethanol represents a greater potential hazard from ongoing high level exposure, it appears that the acceptable exposure level in drinking water can be in the same range or even higher than the level set in Connecticut for M*t*BE.

The importance of dose rate to the in utero effects of ethanol and the suggestion of critical windows of ethanol exposure make it important to not average the exposure dose over the course of pregnancy (i.e., allowing peaks and valleys in exposure) but instead to maintain exposure below a critical health protective level on each day of pregnancy.

This dose rate consideration makes ethanol exposure different from M*t*BE in that a few days of spiking ethanol exposure (e.g., from a sudden groundwater plume entering drinking water) would have greater public health implications than if the pollutant were M*t*BE. This is because M*t*BE is not a significant developmental hazard, and any adverse effects from a sudden high level exposure would be more likely to be reversible.

Sensitive Subpopulations

Certain individuals are more sensitive to ethanol because they have deficient activity of the key detoxification enzyme aldehyde dehydrogenase (Froines, et al., 1998). The genetic polymorphism underlying this defect has been traced to a mutant allele in the aldehyde dehydrogenase gene. This trait is most prevalent in Asian populations, of which 50 to 80 percent of the people are affected, in contrast with Europeans and North Americans, of which 5 to 10 percent of the people are affected (Froines, et al, 1998).

The consequence of this deficiency is a flushing syndrome that stems from a buildup of the ethanol metabolite, acetaldehyde, in blood. Acetaldehyde peak blood levels in individuals with the mutant allele are more than 10 times higher than normal subjects after an acute ethanol dose. Given that at least some of the fetal and carcinogenic effects of ethanol may be mediated by acetaldehyde, this genetic polymorphism has significant risk implications (i.e., those with deficient aldehyde dehydrogenase activity may be at higher risk).

In addition, ethanol ingestion can provoke asthma symptoms in Asian asthmatics, possibly as a result of the bronchoconstrictive effects of acetaldehyde (Froines, et al, 1998). The 10-fold uncertainty factor used above for inter-individual variability is intended to account for the aldehyde dehydrogenase genetic polymorphism.

An especially sensitive subpopulation has not been identified for M*t*BE, although a number of individuals have reported in the past that they are sensitive to inhaling oxygenated fuel vapors (or combustion byproducts). The cause of such complaints (e.g., M*t*BE in oxygenated fuel or other environmental or host factors) has not been confirmed.

CONSIDERATION OF EXPOSURE TO BREAKDOWN PRODUCTS IN AIR AND WATER

The blending of ethanol into gasoline is expected to increase exhaust emissions of acetaldehyde, which results from the incomplete oxidation of ethanol. The combined exhaust and evaporative emission of acetaldehyde from cars is reported to increase by 59 percent when ethanol-containing gasoline (10 percent ethanol by volume) is used (HEI, 1996).

Acetaldehyde is acutely irritating, toxic to respiratory tissues, and mutagenic and carcinogenic (Froines, et al, 1998). As described elsewhere, it is also formed in vivo from ethanol metabolism and may significantly contribute to the effects caused by ethanol exposure.

An exactly analogous situation arises with M*t*BE and formaldehyde—M*t*BE is converted to formaldehyde during the combustion of M*t*BE-blended fuel, and M*t*BE is converted to formaldehyde by liver metabolism. The switch from M*t*BE to ethanol may thus involve a decrease in formaldehyde exposure but an increase in acetaldehyde exposure.

A decrease in formaldehyde exposure may have beneficial public health implications, because acetaldehyde is approximately 800 times less irritating than formaldehyde in mouse RD_{50} studies (Bos, et al, 1992), and because the cancer unit risk for formaldehyde on EPA's Integrated Risk Information Service (IRIS) is 6-fold higher than the unit risk for acetaldehyde (www.epa.gov/iris). However, without knowing how much of an increase in acetaldehyde ambient concentrations is possible from use of ethanol in gasoline, it is not possible to determine whether the switch in oxygenate will change public health risks due to combustion byproducts.

It should be noted that the in vivo metabolic formation of acetaldehyde from ethanol may not be as efficiently eliminated as formaldehyde formed metabolically from M*t*BE. This is because endogenous formaldehyde is readily removed by a variety of dehydrogenases or can combine with tetrahydrofolate and enter intermediary metabolism via the 1 carbon pool (ATSDR, 1999). In contrast, acetaldehyde requires the enzyme aldehyde dehydrogenase, which may be deficient in certain members of the public.

Ethanol may form acetic acid as a partial breakdown product in water. In high concentrations, acetic acid is highly irritating to mucosal surfaces in the gastrointestinal and respiratory tract (HSDB-2000). However, acetic acid is readily tolerated at concentrations of 4 to 10 percent, the level at which it exists in vinegar. It has a relatively low order of acute toxicity and an oral LD_{50} of 3.5 g/kg in rats. While the toxicology database on acetic acid is very limited, it is not expected to be a public health concern at the relatively low (ppm to ppb) levels possible in groundwater contaminated by ethanol.

UNCERTAINTY ANALYSIS

Review of ethanol health risks needs to include a discussion of the major uncertainties in the risk assessment. Useful dose-response data are available in humans consuming ethanol, and this information has been incorporated into a screening-level assessment of what might be a reasonable range for an ethanol drinking water guideline.

This screening level assessment incorporated a large degree of uncertainty (total uncertainty factor of 3,000 fold) because: (a) the ethanol database still contains substantial data gaps; (b) different individuals will respond with varying sensitivity to ethanol, with the full range of this sensitivity not known; (c) the threshold for ethanol effects on key systems and functions has not been precisely defined; and (d) the public health relevance of ethanol's carcinogenic effects at high doses are uncertain for low-dose or short-term exposures.

There is additional uncertainty when comparing the ethanol screening-level drinking water level described in this chapter to M*t*BE water guidelines that already exist. This is because there are a variety of different M*t*BE guideline levels in different states, and each of these values have their own set of uncertainties and assumptions. Thus, neither the ethanol nor M*t*BE guideline levels discussed in this chapter represent precise health benchmarks. Rather, they represent prudent public health values that define levels below which adverse effects are unlikely, while recognizing the many uncertainties inherent in the risk assessment of these chemicals.

It can be said that comparing one uncertain value against another uncertain value leads to an uncertain comparison. However, the utility of our approach is that both chemicals, ethanol and M*t*BE, were put through a similar drinking water risk assessment process (ethanol in this chapter, M*t*BE in previous assessments). This similarity in approach for the two chemicals makes the comparisons made in this chapter useful. The finding that the screening-level ethanol drinking water value is at least as high if not higher than the M*t*BE value suggests that even considering all the uncertainties, it is unlikely ethanol will create a greater health risk than M*t*BE at relatively low concentrations in groundwater (below 400 µg/L).

There are, however, several uncertainties that affect the degree of confidence we can have that ethanol will not create significant health risks if spilled into groundwater. As summarized below, these uncertainties are with regard to the degree of ethanol exposure possible, the low-dose effects of ethanol on fetal development, and the possible interactions between ethanol and other chemicals.

- The risk scenario of greatest potential concern is if a release of neat ethanol (e.g., from an ethanol bulk storage facility) were to contaminate a drinking water supply well. In this case, there is an uncertainty as to whether high levels of ethanol, in the tens to thousands of ppm, could possibly reach a well and not be noticed by water consumers. This would be because of ethanol's poor warning properties (high odor and taste thresholds) (HEI, 1996) and the possibility that other hydrocarbons would not be present in the well to affect taste/odor. In this scenario, a pregnant woman might unknowingly ingest substantial concentrations of ethanol, which for even relatively short periods of time (days to weeks) would lead to potential pregnancy risk concerns. Thus, it is important to determine the likelihood of this critical exposure scenario.

- In comparison to M*t*BE-blended fuels, the possibility that E-blend fuels can cause depletion of oxygen in groundwater, thus increasing the likelihood that benzene, toluene, ethylbenzene, and xylenes (BTEX) plumes would be longer and have a greater impact on drinking water wells. Any increase in the public's exposure to these chemicals in drinking water should be avoided.

- The possibility that ethanol can interact with benzene by increasing benzene metabolism in the body to more toxic metabolites is a potential health concern. Ethanol ingestion induces the enzyme, cytochrome P-450-2E1 (Cyp2E1) (Ohnishi, 1977). This same enzyme activates benzene to a series of hematotoxic and carcinogenic metabolites. Alcoholics have higher levels of Cyp2E1 than non-alcoholics, and these levels decrease when they are withdrawn from alcohol (Lucas, 1995; Girre, 1994). While this has been documented in alcoholics who have high chronic exposures, the minimum amount of ethanol ingestion required to increase Cyp2E1 levels is not known. Because the potential exists for coexposure to ethanol and benzene from an E-blend leak into groundwater, it is important to recognize that this potential interaction creates an important uncertainty. Interaction of ethanol with toluene, ethylbenzene, and xylenes has also been reported (Riihimaki, 1982; Low, 1989).

- The risk assessment relies on the premise of a threshold for fetal effects from maternal ethanol ingestion. While evidence from both human and monkey studies is generally supportive of such a threshold, there may be certain endpoints and subtle neurodevelopmental effects for which a threshold may be difficult to demonstrate (HEI, 1996). This increases the uncertainty regarding low ethanol exposures, especially since the sensitivity of different windows of pregnancy to ethanol is also unknown. Because of these concerns, the American Academy of Pediatrics (AAP, 1999) concludes that the current data do not support the concept of a "safe level" of alcohol consumption by pregnant women, and many obstetricians routinely advise pregnant women to avoid all alcohol during pregnancy.

- This chapter addresses the uncertainty surrounding low-dose ethanol effects during pregnancy by deriving a draft comparative drinking water value that lowers the apparent threshold (as seen in monkey and some human studies) by a 3,000 fold factor. This factor is meant to ensure that the acceptable level of ethanol in drinking water is far below any levels of exposure known to produce fetal effects and to also cover a variety of other uncertainties. While fetal effects are unlikely at ethanol drinking water concentrations below the comparative drinking water value of 400 µg/L, additional low-dose ethanol research in animals and humans is needed to solidify this conclusion.

These uncertainties are important considerations when assessing the risks associated with adding ethanol to gasoline.

COMPARATIVE SUMMARY

The tables on pages 42 to 44 summarize the following information presented in this chapter:

- Comparative evaluation of the health effects of ethanol and M*t*BE (Table 3.1).

- Toxicity of ethanol at various concentrations in the blood of animals (Table 3.2).

- Relative blood levels of alcohol associated with different types and severities of effects, including the baseline concentrations of ethanol in the blood of the general population (Table 3.3). This table also contains a calculated concentration of ethanol in blood associated with ingestion of drinking water containing ethanol at the water guideline concentration developed in Chapter 4 of this report.

- Comparative evaluation of the breakdown products of ethanol and M*t*BE in air and water (Table 3.4).

- Evaluation of the major uncertainties associated with each chemical (Table 3.5).

Table 3.1 Comparative evaluation of the health effects of ethanol and M*t*BE.

ETHANOL	M*t*BE
400 µg/L water comparison value.	10 µg/L - 70 µg/L (northeast state guideline using various risk assessment methods).
Low dose - CNS stimulation.	Low dose - CNS stimulation.
High dose - CNS depression.	High dose - CNS depression.
Blood level > 500 mg/L - CNS depression.	Blood level 100 mg/L - CNS depression.
Great developmental hazard.	Minimal developmental hazard.
CNS effect in fetus not reversible with frank CNS damage.	No significant fetotoxicity at inhalation doses below 1,000 ppm in mice and rats (approx. 1-2 g/kg/day). (M*t*BE testing did not evaluate late stage CNS developmental effects, a time frame sensitive to ethanol. Additionally, while not teratogenic to rat or rabbit CNS, more subtle neurodevelopmental testing of M*t*BE has not been conducted.)
Greater potential to damage liver.	
Evidence of human carcinogenicity upon chronic exposure. Carcinogenic classification: IARC Group 1 NTP Not listed EPA Not classified	No human data. Carcinogenic classification: IARC Inadequate evidence in humans NTP Not listed EPA Not classified
10 - 15 g/kg/day, elevation of breast tumor in mice.	12 g/kg/day (inhalation) liver tumor in mice Cancer Effect Level (CEL)gavage = 0.25 g/kg/day (rats) $\text{CEL}_{\text{inhalation}}$ = 2.5 g/kg/day (rats).
Few days spiking of ethanol exposure (e.g., from sudden groundwater plume entering drinking water) would have greater public health implications because of developmental effects.	Few days spiking of M*t*BE in drinking water is unlikely to cause developmental effects observed with ethanol.
Sensitive population identified.	No sensitive population identified.

Table 3.2 Toxicity of ethanol in animals.

TEST SYSTEM	BLOOD LEVELS (mg/L)	OBSERVED EFFECTS
Mice	1,400 - 5,600 (moderate to high level)	Blood celullarity changes
Rat	1,300	Inhibition of platelet aggregation
Not specified	Moderate to high level	Genetic effect on germ cell
Rat	Moderate to high level	Delays in the development of the male reproductive tract

Table 3.3 Blood levels of ethanol and observed effects, legal limits, and screening water level.

BLOOD LEVELS OF ETHANOL (mg/L)	OBSERVED EFFECTS IN HUMANS, LEGAL LIMITS IN BLOOD AND BASELINE VALUES	REMARKS
100 - 500	Thresholds for acute neurological effects in humans.	
500	Increased rates of automobile accidents.	About 38,000 times the estimated protective water level.
800 - 1000	Legal limit for driving.	About 6,000 - 76,000 times the estimated protective water level.
120	Evidence of impaired performance in humans.	About 9,000 times the estimated protective water level.
200	Impaired performance in humans and newly recommended legal limit for driving.	About 15,000 times the estimated protective water level.
200*	Blood level associated with **developmental effects; benchmark dose selected*** to derive water screening level associated with this blood level of ethanol is **0.2 g/kg/day.***	
0.3 - 27	Baseline concentrations across subjects.	
0.013	Blood level associated with the water comparison value of **400 µg/L.***	

* Basis for draft water comparative value.

Table 3.4 Comparative evaluation of the breakdown products of ethanol and M*t*BE in air and water.

ETHANOL	M*t*BE
Blending of ethanol will increase the exhaust emission of acetaldehyde (59%). Acetaldehyde is irritant, mutagenic, and carcinogenic.	One of the breakdown products of M*t*BE is formaldehyde. Formaldehyde is 800 times more irritating than acetaldehyde and its unit risk value is six times higher than acetaldehyde.
Acetaldehyde is less readily removed from body. Removal is enzyme (aldehyde dehydrogenase) dependent which is lacking in certain population.	Formaldehyde is more readily removed from the body than acetaldehyde.

Table 3.5 Uncertainty evaluations.

ETHANOL	M*t*BE
High odor threshold. High levels could be consumed unnoticed in drinking water and can be a potential pregnancy concern.	Low odor threshold. Can be detected at low concentrations.
High levels of BTEX could reach potable waters because of oxygen depletion or cosolvency effects.	No oxygen depletion or cosolvency effects with M*t*BE.
Ethanol may increase the metabolism of benzene to carcinogenic metabolites. Such effect has been documented in alcoholics. Ethanol is also known to interact with toluene and xylenes metabolically in humans. This metabolic interaction is important because of the cosolvency effect that ethanol has on BTEX.	
There may be certain endpoints and subtle neurodevelopmental effects for which a threshold may be difficult to demonstrate. There is increased uncertainty regarding low ethanol exposures, especially the sensitivity of different windows of pregnancy to ethanol.	Low potential for lasting neurodevelopmental effects.

The previous tables provide a comparison of the health effects associated with exposure to M*t*BE and ethanol as they might exist in drinking water. Although it is difficult to make a direct comparison of chemical toxicity values for ethanol and M*t*BE in drinking water due to a variety of uncertainty factors, it is apparent that ethanol is unlikely to produce any greater health risk than M*t*BE at relatively low concentrations (400 µg/L) in water.

This conclusion is based on a number of factors, the most important of which is that ingestion of low levels of ethanol-contaminated drinking water in this range is unlikely to alter endogenous levels of ethanol in blood. Additional support for this is that, as shown in Table 3.1, ethanol appears to be no more toxic than M*t*BE with respect to acute neurotoxicity or carcinogenicity. However, at high exposures during pregnancy ethanol may present a greater hazard than M*t*BE due to its ability to produce irreversible neurodevelopmental effects. M*t*BE does not appear to produce this type of effect, based on standard teratology testing (Bevan, et al., 1997), although the detailed cellular and behavioral studies conducted with ethanol have not been conducted with M*t*BE.

Overall, the database suggests that ethanol may be associated with a greater hazard potential than M*t*BE at high concentrations (above 5,000-10,000 µg/L) in drinking water. This could be even more likely given that M*t*BE has strong warning properties (i.e., odor, taste) at high concentrations, while ethanol's warning properties are much less conspicuous. Therefore, analysis of ethanol's environmental fate and exposure potential is needed to determine whether ethanol-contaminated groundwater could result in exposure levels to pregnant women that increase the risks for neurodevelopmental effects.

HEALTH EFFECTS OF ETHANOL

CONCLUSIONS

This health effects analysis leads to the following conclusions regarding health risks associated with exposure to ethanol in cases where drinking water has been contaminated by neat ethanol or E-blend gasoline:

- ▲ Low-level ethanol contamination of groundwater (i.e., less than 400 µg/L, a draft Water Comparison Value derived in this chapter) is not expected to substantially alter blood alcohol concentrations or produce a significant health risk. In coming to this conclusion, the potential health risks in sensitive subjects such as pregnant women or those who may have aldehyde dehydrogenase deficiency were also considered.
- ▲ Higher concentrations of ethanol in water may begin to increase health risks but are not expected to materially add to endogenous ethanol concentrations until there is daily exposure to at least 10 mg/L (ppm). Thus, the strong hazard potential of ethanol (production of irreversible fetal effects) is mitigated by the fact that relatively high environmental concentrations would be needed to reach a level of public health concern.
- ▲ The hazard potential for ethanol is greater than for MtBE in terms of the types of irreversible damage possible from repeated high level exposures. In spite of this greater hazard potential, the comparative value for ethanol in drinking water appears to be at least as high, if not higher, than M*t*BE.
- ▲ While this chapter focuses on toxic effects rather than warning properties (i.e., odor, taste when present in water), it is noteworthy that the air odor threshold of ethanol (approx. 100 ppm) (TRC, 1988) is three orders of magnitude higher than that of M*t*BE (HEI, 1996). Thus it appears that the warning properties of M*t*BE are stronger, making overexposure to M*t*BE less likely than overexposure to ethanol. Discussion in Chapter 6 (page 112) suggests that the secondary effects of an ethanol spill would create anaerobic conditions (i.e., increased color, turbidity, and odor) in groundwater. Thus, in some circumstances, consumer warning could take place in this manner.

HEALTH EFFECTS OF ETHANOL

RECOMMENDATIONS

Based on the uncertainties listed above, we recommend that further health effects research is needed in the following areas:

- ▲ The health effects of low-level exposure, particularly to expand our understanding of where the threshold lies for neurodevelopmental effects.
- ▲ The toxicokinetics of low-level ethanol exposure (including fetal and maternal blood levels) relative to typical background exposures from the diet and the response of sensitive subpopulations.
- ▲ An assessment of the metabolic interaction between ethanol and other environmental pollutants (e.g., benzene) at environmentally relevant doses.
- ▲ This summary analysis was performed in a limited time frame. A more thorough review of the literature and, perhaps, additional basic research is needed to better substantiate and support these findings.
- ▲ As ethanol will not replace 100 percent of the M*t*BE currently found in RFG, aromatics, olefins, and alkylates are seen as the likely additives that will be used to make up the volume. An assessment of the public health characteristics of these additives is needed before the widespread introduction of ethanol reformulations.

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CHAPTER 4

EFFECTS OF ETHANOL ON AQUATIC LIFE

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THE SCOPE OF THIS CHAPTER

The effect of ethanol on aquatic communities was evaluated to determine if adverse environmental impacts could potentially occur. This chapter addresses possible impacts with respect to acute and chronic toxicity, water quality criteria, bioconcentration and bioaccumulation, and oxygen depletion.

ACUTE VERSUS CHRONIC TOXICITY

Toxicity to aquatic life must be considered in any situation where a chemical enters a waterbody. Toxicity is typically evaluated using two broad measures: acute and chronic responses. A substance that is acutely toxic will kill or otherwise impair exposed organisms following a brief exposure period. Chronic toxicity results from a longer-term exposure.

Acute toxicity is evaluated through laboratory tests in which organisms are exposed to known quantities of a toxicant—ethanol in this case. Mortality is observed over a period of time, typically 48 to 96 hours, and a LC50 value is calculated. The LC50 value is the concentration of the substance that kills 50 percent of the test organisms within the time frame of the test.

In the case of chronic toxicity, a longer exposure to the toxicant may lead to the death of the organism or impairments, such as a reduced ability to grow or reproduce. Chronic toxicity is measured under controlled laboratory exposures, and the concentration that produces the lowest or no observable adverse effect is reported as the test outcome. For the purposes of this study, the potential toxicity of ethanol to aquatic organisms was evaluated by reviewing toxicity values for ethanol obtained from U.S. EPA's ECOTOX database (USEPA, 2000). The full ECOTOX report is provided in the Chapter 4 Appendix A.

Water quality criteria are often developed from aquatic toxicity information to estimate a discrete concentration of a substance that will result in either acute or chronic toxicity to aquatic organisms. Detailed procedures and rigorous data requirements for developing water quality criteria have been established in EPA guidance.

WATER QUALITY CRITERIA

Currently, acute and chronic water quality criteria for the protection of aquatic life have not been developed for ethanol. U.S. EPA's ECOTOX database, which contains toxicity information for environmental receptors (e.g., plants, fish), contained insufficient toxicity data to fulfill the requirements for developing such criteria. However, EPA has developed guidance for developing water quality benchmarks in the absence of sufficient information to derive a criterion. This guidance is contained in the *Final Water Quality Guidance for the Great Lakes System* (USEPA, 1995) and is referred to as Tier II procedures.

Using these Tier II procedures, there was sufficient information to derive acute and chronic water quality benchmarks for aquatic life. The procedures parallel those used for developing water quality criteria. However, they incorporate certain application factors and assumptions to compensate for data gaps.

Acceptable acute toxicity information was available for aquatic invertebrates (daphnia species), rainbow trout, and the fathead minnow. Based on the available data and using the Tier II procedures, the following acute and chronic water quality benchmarks for ethanol were calculated. The criteria calculations are contained in Chapter 4 Appendix B.

Water Quality Benchmarks for Ethanol

Acute	564 mg/L
Chronic	63 mg/L

These values indicate that an ethanol concentration of 564 mg/L in the water column is likely to cause acute toxicity to aquatic life. Similarly, an ethanol concentration of 63 mg/L in the water column is likely to cause chronic toxicity.

EPA is currently developing water quality criteria for M*t*BE (Gostomski, 2000). The draft aquatic life water quality criteria are:

Draft Water Quality Criteria for M*t*BE

Acute	151 mg/L
Chronic	51 mg/L

A comparison of the ethanol and M*t*BE water quality values shows that both the acute and chronic values for M*t*BE are lower than those for ethanol. A lower value indicates greater toxicity. Therefore, based on these water quality benchmarks, we can generally conclude that M*t*BE is more toxic to aquatic life than ethanol. In acute exposures, ethanol is approximately 3.7 times less toxic than M*t*BE. For chronic exposures, toxicity of both ethanol and M*t*BE is similar. However, ethanol is slightly less chronically toxic than M*t*BE.

BIOCONCENTRATION AND BIOACCUMULATION

The ability of a substance to enter into and remain in the tissues of living organisms through either bioconcentration or bioaccumulation is an additional concern when considering potential impacts to aquatic life and the environment. Bioconcentration and bioaccumulation can be estimated from a substance's affinity for fatty tissues, approximated through the octanol water partition coefficient (K_{ow}) for the substance.

Octanol is an organic chemical that mimics the properties of fatty substances. If a beaker with both octanol and water is prepared, the two chemicals will not mix; rather, they will exist in two phases within the beaker. When the substance of interest is introduced into this beaker, it will distribute itself between the two phases.

Substances that preferentially enter the octanol phase tend to bioaccumulate. This preference is reflected in a high value for the K_{ow} for that substance. Both ethanol and M*t*BE have low K_{ow} values (8.71 and 0.50 for M*t*BE and ethanol, respectively) (Layton and Daniels, 1999), indicating that they are not likely to enter into and remain in fatty tissues of living organisms.

For ethanol, this finding is further supported by the fact that there are metabolic pathways designed to break down the compound. The high rate of metabolism of ethanol coupled with the low K_{ow} value provide strong support that ethanol will not bioconcentrate or bioaccumulate.

OXYGEN DEPLETION

In addition to direct toxic impacts to aquatic life, the ability of a substance to affect instream oxygen concentrations is also of concern in an aquatic environment. Aquatic organisms rely on these dissolved oxygen (DO) concentrations for survival. For example, at a water temperature of 25°C, a stream might contain 8 mg/L of dissolved oxygen. Based on chemical stoichiometry, it can be estimated that [one molecule] 46 grams of ethanol will remove [3 molecules] 96 grams of oxygen from the stream.

$C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_20$

Molecular Weight of Ethanol (C_2H_6O) = 46 grams

Molecular Weight of Oxygen Molecule (O_2) = 32 grams

3 x 32 = 96 grams oxygen removed

Ethanol, however, is rapidly biodegraded by microbes that are present in the water column, a process that also requires oxygen. This oxygen requirement can be expressed as biochemical oxygen demand (BOD). The BOD value combined with an estimate of the rate of biodegradation can be used as input to the Streeter-Phelps (Thomann and Mueller, 1987) water quality model to estimate the amount of ethanol required to use up the dissolved oxygen in a stream.

The Streeter-Phelps model considers both the ability of a substance to be biodegraded and the physical aspects of the waterbody with regard to the effective breakdown of the substance. The primary physical consideration is the reaeration rate for the stream, a value that approximates how much oxygen is taken up into a stream. This value is based on stream morphology and flow characteristics, such as depth and flow rate.

By selecting typical values for the various stream parameters, models for small, average, and large rivers can be constructed. It is assumed that the maximum amount of oxygen that will be dissolved in the water is 8 mg/L. It is also assumed that in the typical waterbody, 7 mg/L is actually dissolved in the water column.

The models for each stream scenario can be run, varying the BOD inputs, to determine the amount of BOD required to remove 7 mg/L of dissolved oxygen from the stream. The amount of ethanol needed to achieve these BOD values can be back calculated from the BOD concentration. The model and associated assumptions (Mauger, 2000) used in the model are as follows:

Streeter-Phelps Equations

D	Total Deficit:	8 mg/L		
Do	Initial Deficit	1 mg/L		
K1	BOD Decay Rate	1.3/d		
K2	Reaeration Rate		Small Stream	15/d
			Average River	7.5/d
			Large River	2/d
BOD	Ultimate BOD (instream after mixing)			
X	Distance Downstream			
V	Stream Velocity		Small Stream	0.5
			Average River	0.75
			Large River	1

1. Xc = Critical distance downstream where lowest dissolved oxygen concentration occurs
   $Xc = v / (K2-K1) * \ln ((K2/K1) * (1 - (Do * (K2-K1) / (K1 * BOD)))$
2. Dc = Worst case dissolved oxygen deficit
   $Dc = (K1/K2) * BOD * e \wedge (-K1 * (x/v))$

The BOD decay rate was obtained from a review of current literature as discussed in Volume 4, Chapter 5 of the Lawrence Livermore National Laboratory report (Layton and Daniels, 1999) on ethanol. The BOD(20) for ethanol is 1.8 grams oxygen consumed per gram of ethanol (Verschueren, 1983). The BOD associated with instream ethanol concentrations equal to the acute and chronic water quality benchmarks was calculated by dividing the ethanol concentration by the BOD(20) value. The model was run using these assumptions, and the associated deficits for dissolved oxygen were calculated.

The model output for these scenarios indicate that the oxygen demand needed to biodegrade these benchmark levels of ethanol far exceeds the amount of oxygen present in the stream, even under fully saturated conditions. Therefore, the depletion of oxygen from the stream will be a more critical determinant of impact on aquatic life than direct toxicity to aquatic organisms.

To determine what levels of BOD would deplete 7 mg/L of oxygen in the stream and result in a lethal, hypoxic condition, the models were run again with varying instream BOD concentrations. The results were as follows:

Instream Ethanol Concentrations Capable of Depleting Instream DO

Small Stream	56 mg/L
Average River	32 mg/L
Large River	13 mg/L

Note, the model predicts that when instream BOD concentrations are held constant across the three waterbody sizes, a lower concentration of ethanol is needed in a larger river to deplete instream DO than in a smaller river. This is because lower reaeration rates are typically exhibited by larger waterbodies.

Under this scenario of holding instream BOD concentrations equal, different volumes of ethanol are needed for each river to achieve the same instream BOD concentrations. However, if the volume of ethanol, rather than the instream BOD concentration, were held constant across the three different sized waterbodies, it is likely that the larger water bodies would experience a reduced impact on instream dissolved oxygen concentrations relative to the smaller streams because of the greater dilution afforded by the larger water bodies.

The results of the BOD analyses using the Streeter-Phelps model demonstrate that oxygen depletion is a significant concern in any situation where elevated concentrations of ethanol enter a stream. Fish kills, for example, have been documented in incidents of large releases of grain alcohols to water bodies, generally the result of anoxia produced from high biochemical oxygen demands associated with bacterial utilization of the alcohols. Acute or chronic toxicity of grain alcohols on smaller organisms is less well documented, but can be inferred.

It is important to note that impact to aquatic organisms due to hypoxia will occur before oxygen is completely removed from the water column. In most cases, impacts due to oxygen deficit occur at dissolved oxygen concentrations below 5 mg/L (USEPA, 1976).

HEALTH EFFECTS OF ETHANOL ON AQUATIC LIFE

CONCLUSIONS

This evaluation has led to the following conclusions regarding the effects of ethanol on aquatic life:

- Ethanol is toxic to aquatic life. However, it is 3.7 times less acutely toxic than M*t*BE. Over a longer-term exposure period, toxicity to aquatic life resulting from exposure to ethanol is similar, although somewhat less, than that associated with longer-term exposure to M*t*BE.
- Ethanol is not likely to bioaccumulate or bioconcentrate in the tissues of living organisms. This is due both to its chemical properties and the ability of most organisms to breakdown and eliminate ethanol from their bodies.
- The breakdown of ethanol in surface waters through biological and chemical processes could potentially result in the consumption of significant quantities of dissolved oxygen in the surface water body. Depending on the conditions in the surface water body and the amount of ethanol introduced, it is possible that sufficient amounts of dissolved oxygen could be consumed to bring about a detrimental affect on aquatic life, potentially leading to a fish kill.

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CHAPTER 5

ETHANOL STORAGE AND HANDLING

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THE SCOPE OF THIS CHAPTER

There are a number of issues relating to the production, storage, and handling of neat ethanol (denatured ethanol that is neither mixed nor diluted) and ethanol-blend (E-blend) gasoline mixtures for use in New England and New York that can be addressed in terms of the E-blend life cycle. (See Figure 5.1 on page 56.) Using this life cycle, we can travel along the route that ethanol/E-blend would typically take to its ultimate end user and discuss the major points associated with the chemical compatibility of storage components and the environmental impact of producing and transporting ethanol to the Northeast.

Because ethanol cannot be added to gasoline until it is ready for delivery to an E-blend storage tank, additional facilities will ultimately be needed in the Northeast to store neat ethanol before it is mixed with gasoline for delivery to the local gas station. The product storage and distribution system, be it tanker truck, rail car, marine tanker, bulk terminal, or gasoline storage tank, must be able to safely deliver gasoline to the customer and prevent fuel releases.

In this chapter we will discuss the specific fuel storage compatibility issues relating to tanks, piping, dispensing devices, and sealants. We will conclude by discussing issues associated with the end users—automobiles and smaller gasoline-powered recreational and power equipment.

PRODUCING ETHANOL

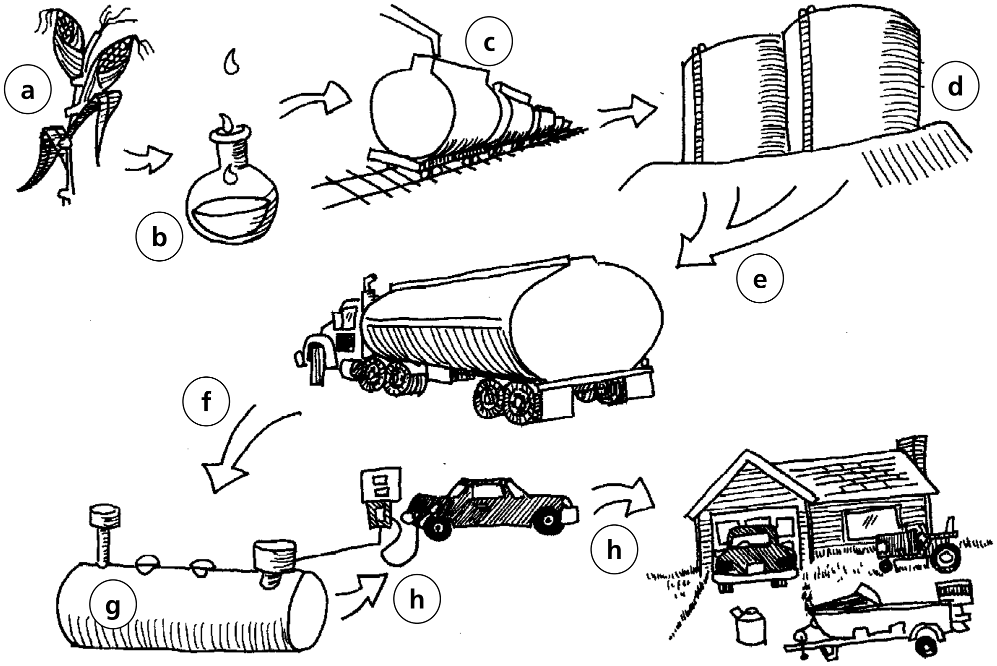
Today, ethanol is typically produced by processing starch extracted from corn kernels and, to a lesser degree, other starch crops, such as sorghum, wheat, and potatoes. Corn-based ethanol production produces approximately 2.5 gallons of ethanol from one bushel of corn (Reformulated Fuels Association, 2000).

The ethanol production process is often referred to as a zero-waste and value-added process, inasmuch as there are a number of coproducts or marketable goods that are created to fully utilize the corn input. Coproducts of ethanol production include carbon dioxide, used for carbonated beverages or flash freezing of meat, and distillers grains, used for high quality livestock feed.

Currently, the ethanol market utilizes approximately seven percent of the nation's corn crop, involving more than 900,000 farmers who are members of ethanol production cooperatives (Reformulated Fuels Association, 2000).

Because of feedstock costs, ethanol is very costly to produce from corn and other starch crops. In the absence of non-corn feedstocks, such as sorghum, the expected increase in ethanol demand due to the use of ethanol in oxygenated fuel will drive corn prices up even more. The ethanol market is currently assisted by a partial rebate of the federal excise tax on motor fuels, making it artificially competitive with other additives.

Figure 5.1 Ethanol and E-blend gasoline life cycle. The cycle begins with (a) biomass production and moves on to (b) ethanol production/distillation; (c) rail, barge, or truck transport to bulk storage; (d) neat ethanol bulk storage; (e) ethanol/gasoline blending; (f) delivery to an E-blend storage tank, (g) storage in an E-blend storage tank, and finally, (h) transfer to end users.



Two types of processes are used to produce ethanol from corn: dry milling and wet milling.

- The *dry milling* process begins with the grinding of corn into a fine powder meal, which is then put through a liquification process where it is combined with water and alpha-amylase, an enzyme. The resulting liquefied starch is turned into fermentable sugars through the addition of the enzyme gluco-amylase. Yeast is added to the sugars to cause fermentation. The fermented product, ethanol, is then distilled. During this process, the residual product is separated from the ethanol and used to produce other coproducts. Any remaining water is removed from the ethanol through a dehydration process. The alcohol is then denatured with gasoline or other chemicals to make it unfit for human consumption.
- *Wet milling* differs from dry milling in that it utilizes a chemical process rather than a grinding process to break down the corn kernels.

MEETING INCREASED DEMAND

Because of trends that indicate a growth in the demand for ethanol as an alternative fuel and the potential for using ethanol to replace M*t*BE as the gasoline oxygenate of choice, considerable resources are already being directed at the development of new competitively priced biomass feedstocks for the manufacture of ethanol. The current demand for ethanol in the Northeast is about 31 million gallons per year. An estimated 684 million gallons per year would be needed in the region to meet the total demand for oxygenated fuel (NESCAUM, 1999). However, the current U.S. production capacity of ethanol is not enough to meet the total demand for oxygenated fuels. Furthermore, transporting ethanol to the Northeast from the midwest would significantly increase its costs (Womach, 2000).

Given these cost considerations, regional biomass ethanol production would benefit the east and west coasts of the United States. Demand could be met through the utilization of local feedstock and cellulosic feedstock technology, allowing non-corn producing areas of the country to produce ethanol for local use. Biomass ethanol plants in the Northeast could utilize feedstocks such as forestry and municipal wastes to meet the regional demand. In New York, plans are underway for the development of a facility to produce ethanol from trash and solid waste (NYS Assoc. of Service Stations & Repair Shops, 2000). Increased demand could also be met through international imports from other countries (e.g., Brazil) (Womach, 2000).

Ethanol can be produced from cellulosic matter such as “herbaceous and woody plants, agricultural (corn stalks) and forestry residues, and a large portion of many municipal solid waste and industrial waste streams” (U.S. Department of Energy, 2000). To produce ethanol from cellulosic biomass such as corn stalks, the cellulose and hemicellulose that make up the plant cell walls must be broken down into simple sugars. The simple sugars are then fermented to make ethanol. The breakdown of cellulose is an expensive step because this material cannot be liquefied like starch—a focus of current research. Businesses and organizations in the United States, including the Department of Energy’s Biofuels Program, are funding the development of technologies to efficiently and economically use cellulosic matter for ethanol production.

The prospect of developing an ethanol biomass industry in the Northeast brings with it some important questions regarding the impact of feedstock production on the environment:

- Will an increase in ethanol demand mean an increase in the acreage of land dedicated to feedstock production?
- The dedication of increased acreage to the production of ethanol feedstocks would mean an increase in the use of fertilizers, herbicides, and pesticides. How will this potential increase affect groundwater and surface water quality? Would impacts differ depending on the feedstock under production?
- Is the energy value of pure ethanol greater than the energy consumed in the production of ethanol? The Renewable Fuels Association maintains that the production of ethanol from corn and other feedstocks uses less energy than it generates (Renewable Fuels Association, 2000).

At the present time, there are not sufficient ethanol life cycle analyses available to address issues surrounding the environmental impact of ethanol feedstock production as it pertains to the Northeast. (See the NESCAUM Volume 2 report for more discussion on ethanol production.)

GENERAL CONCERNS WITH THE USE OF NEAT ETHANOL AND E-BLENDS IN STORAGE TANK SYSTEMS AND GASOLINE ENGINES

The following four major concerns are associated with the use of neat ethanol and ethanol blends in storage tank systems and gasoline engines: compatibility, phase separation, solvency, and conductivity. Discussions presented throughout this chapter, for the most part, center on how these concerns affect the various components of storage tank systems and gasoline engines. Recommendations are provided at the end of this chapter as to how these concerns can be addressed if ethanol is used as a regional fuel oxygenate.

- **Compatibility** Many components of storage tank systems and gasoline engines are composed of plastic-like materials, such as polymers, elastomers, and thermoplastics. The potential for ethanol diffusion through, and gradual deterioration of, the materials used to contain neat ethanol or E-blend gasoline can be predicted. As a solvent, ethanol may be drawn into polymers, causing them to swell and soften resulting in a weakening of the polymer structure. Also, ethanol extracts plasticizers and thus reduces the flexibility and toughness of the polymers (i.e., causing brittleness).

- **Phase separation** Substances will mix with each other based on their polarity. Water is considered to be polar. Ethanol is a little less polar than water but is much more polar than gasoline. (Gasoline is considered to be non-polar.) Ethanol mixes completely with water but also dissolves fairly well in gasoline. Water and gasoline do not mix very well. However, when smaller amounts of water are found in tanks containing E-blend gasoline, the water will be drawn into the blend due to the polar nature of ethanol. As the amount of water increases, at some point it will overwhelm the capacity of the ethanol to keep the water dissolved in the E-blend gasoline. In this case, the ethanol will be drawn into water layers because ethanol will preferentially dissolve in water due to its similar polarity (Stahler, 2001). There are two major concerns associated with this occurrence: (1) an engine cannot run on a mixture of ethanol and water; and (2) the ethanol and water blend at the bottom of a fuel tank, be it a bulk aboveground tank, retail UST, or vehicle tank, can lead to corrosion of metals.

- **Solvency** Because it is a solvent, ethanol may loosen rust and other concretions from the interior walls of steel components of a storage system (e.g., tanks and piping). Also significant is the propensity for ethanol to loosen other deposits in the fuel system of gasoline engines. By loosening rust and other deposits, ethanol may accelerate the wear of various storage system components by scouring internal surfaces with suspended particles and interfere with the operation of gasoline engines.

- **Conductivity** Ethanol and E-blend are electrically conductive and may lead to corrosion of various metal components. Conductivity could also be a safety issue during vehicle fueling.

BULK STORAGE, BLENDING, AND DISTRIBUTION

Neat ethanol is not blended with gasoline at the refinery because it tends to separate from the gasoline or absorb water during transport. Also, given that ethanol is a solvent, it has a propensity to clean the storage systems of any sludge or dirt by pulling them into solution, creating the potential problem of contaminating E-blend gasoline if it is blended with gasoline early in the distribution process. For these reasons, neat ethanol must be blended with the gasoline at the last point in the distribution network—the bulk terminal—just prior to delivery to the service station.

Whereas M*t*BE is easily produced and blended with gasoline at the refinery, ethanol needs special treatment. It must be transported as neat ethanol inside clean containers and through clean pipes until it is finally blended with gasoline at the loading rack as it goes into the tanker truck.

Ethanol is typically delivered to the bulk terminal by way of tanker truck or railcar. This activity can be equated to 10 to 20 truck deliveries per day of ethanol (50,000 to 150,000 gallons) to supply a terminal with enough ethanol to produce an E-blend gasoline at a 10 percent volume. These estimates are based on a terminal with a throughput of half a million to 1 million gallons of gasoline per day. At this time, commercial pipeline transport of ethanol-blended fuels is not generally considered plausible due to water contamination concerns.

Bulk Terminal Storage

Bulk terminals must have a dedicated tank for storing ethanol that is clean of all potential contaminants, especially water, and dedicated piping for deliveries made to the tank. There must also be dedicated lines for delivering the ethanol both to the loading rack and into the tanker truck. Therefore, neat ethanol bulk storage systems must be designed or retrofitted specifically for this purpose.

Tanks and piping systems at bulk terminals are typically aboveground and constructed of steel. Steel is used because of fire safety concerns (neat ethanol has a flashpoint of 55°F). If an aboveground tank is involved in a fire, a properly constructed steel tank will not release product into the fire. If the tank is constructed of plastic, it will melt, releasing the product into the fire. Because ethanol is flammable, and burns with a virtually invisible flame, such a fire would be especially hazardous.

Tanks may have a liner installed to cover the bottom and the first 18 inches of the tank shell to help control corrosion caused by water at the bottom of the tank. Such a liner would be of similar construction to the type used for underground tanks. (For more information on compatibility issues with epoxy liner materials see the discussion on linings under “Effects of E-Blend Gasoline on Underground Storage Tank Systems.”)

Tanks at bulk terminals are generally surrounded by a secondary containment system, typically in the form of a dike or a remote impoundment. Secondary containment systems can be constructed of a variety of materials including concrete, naturally occurring or bentonite clay, geosynthetic clay liners, or lined asphalt. However, sometimes these containment areas are constructed of native materials that can be very permeable.

Containment systems around the tank and loading rack may not be compatible with ethanol. This could be especially true of clay liners, where spilled ethanol may dry out the liner, thus directly effecting the permeability of the liner and allowing cracks to develop. In particular, ethanol concentrations above 50 percent cause serious degradation to clay liners (Petrov, 1997), allowing spills of the ethanol and other petroleum products to be released into the environment.

Ethanol is extremely volatile, evaporating from gasoline into air five times more readily than M*t*BE. (See NESCAUM, Volume 2 for a discussion of volatility.) However, ethanol vapors are more dense than air and settle (EPA420-R-99-021, 1999; University of Wisconsin UST Technology Update, 2000). To minimize vapor loss, the American Petroleum Institute (API) recommends that ethanol or high concentration E-blend gasoline be stored in a tank with a fixed roof and an internal floating cover or a small cone roof tank without a floating cover, provided compliance with air quality standards is not compromised. API cautions that external floating roofs are not acceptable for ethanol storage because of risks that water may contact product. Also, where tank design allows, a 16-ounce pressure, 1-ounce vacuum pressure-vacuum vent made for ethanol service should be installed (American Petroleum Institute, 1985). Retrofitting such tanks would be costly.

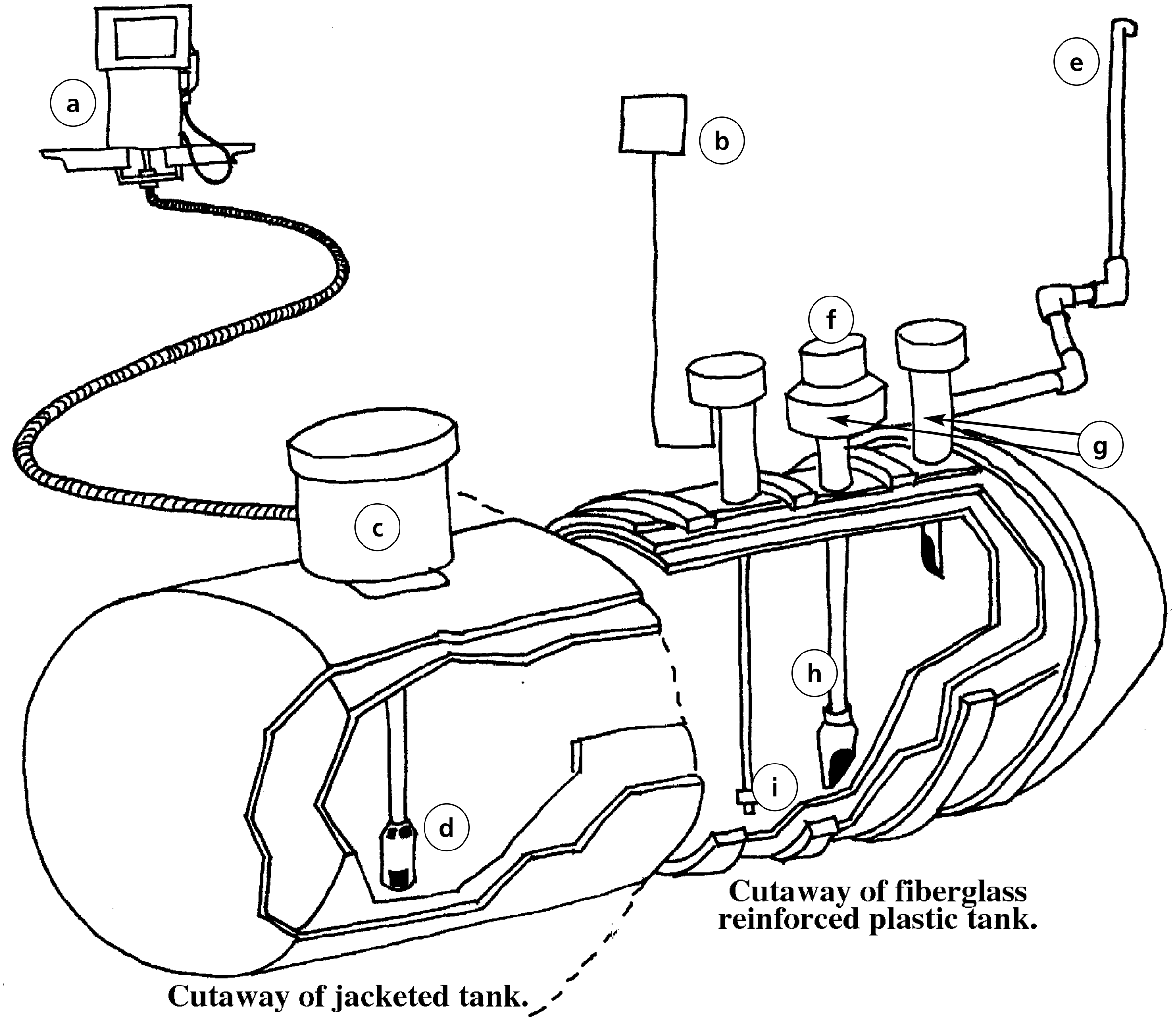
Blending

Ethanol can be blended with gasoline using an in-line blender, an in-tank recirculation method, or in-truck blending—a method that usually results in incomplete blending. If in-truck blending is performed, gasoline should be added to the tank truck first so that vapors in the compartment exceed the upper flammability limit and therefore become too rich to ignite (American Petroleum Institute, 1985).

EFFECTS OF E-BLEND GASOLINE ON UNDERGROUND STORAGE TANK SYSTEMS

Once ethanol has been blended with gasoline (at about 10 percent ethanol by volume) and delivered to an underground storage tank (UST) or an aboveground storage tank (AST), the potential effects of the E-blend on the integrity of the gasoline containment system become a concern. Thus it is essential that the components of the storage system be evaluated with respect to potential problem areas. In this report the storage system is examined within the framework of two broad categories: the tank and the delivery system (e.g., piping, bushings, water pastes, and filters). (See Figure 5.2.) This discussion focuses on USTs, although most of the considerations apply to ASTs as well.

Figure 5.2 An underground storage tank (UST) system with (a) dispenser, piping, tank, and tank components. Components: (b) ATG leak detection console, (c) submersible pump manifold containment sump, (d) submersible pump, (e) vent pipe, (f) spill bucket, (g) location of overfill devices, (h) drop tube, (i) ATG probe. This diagram incorporates two types of tank examples: a jacketed tank (left) and a fiberglass reinforced plastic (FRP) tank (right).

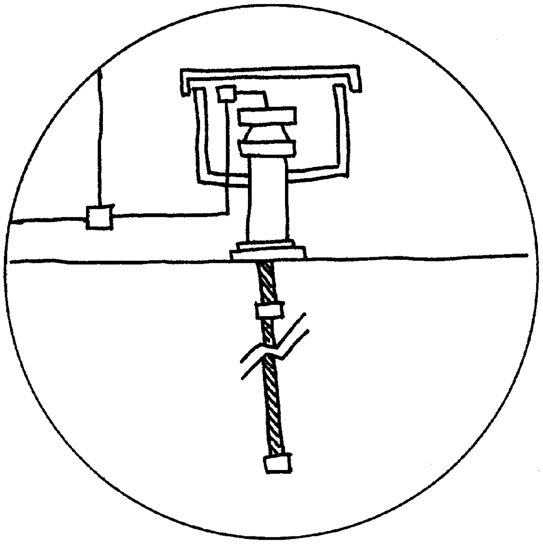


UST System Components

To most people, the gasoline used to fuel their vehicles comes from a small island of gas pumps—many never even give a thought to the fact the fuel is stored in tanks. In fact, most retail gasoline is stored in underground storage tanks that are connected to a delivery system that is composed of numerous important components. A modern UST system consists of the tank, piping, pump system, dispenser, nozzle, vapor recovery system, and dispenser sump. Fuel pumping systems operate by either suction or pressure technologies. The pressure system is the most common and delivers product from the tank through the piping to the dispenser by means of a submersible pump located at the bottom of the storage tank. (See Figures 5.2 and 5.5.)

In addition to these more obvious components, UST systems are required to have environmental protection devices that include the following:

Figure 5.3 Automatic tank gauge (ATG) leak detection device with in-tank sensor to measure fuel level.



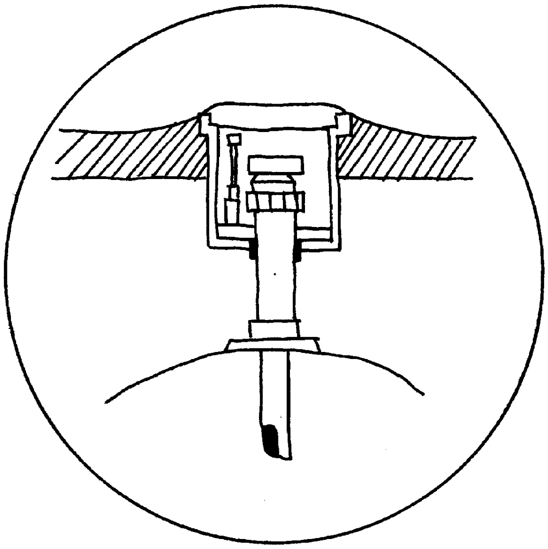
- ▲ **Leak detection** technologies designed to alert tank owners or operators about loss of product from tank or piping into the environment. Such systems include double-walled tanks and piping with monitors in between the walls or sophisticated, liquid level measurement devices called automatic tank gauges (ATGs). (See Figure 5.3.) Other allowable leak detection methods that are not built into the UST include groundwater monitoring, vapor monitoring, statistical inventory reconciliation, and inventory methods.

- ▲ **Corrosion protection** to ensure that tank and piping integrity is not compromised because of corrosion. Corrosion protection requirements can be met through the use of cathodic protection systems designed to protect the external part of the steel tank wall from the corrosion process; internal lining of steel tanks that will protect the internal part of the tank wall from the corrosion process; steel tanks clad with non-corrodible materials, such as fiberglass; tanks constructed of non-corrosive materials, such as fiberglass-reinforced plastic (FRP) tanks; or steel tanks jacketed with an FRP or plastic shell that forms the secondary containment.

- ▲ **Overfill prevention devices** that stop the flow of product being delivered into the UST or signal that the tank is close to full. (See Figure 5.4.)

- ▲ **Spill prevention** containers (spill buckets) that are designed to catch drips when the delivery truck hose is disconnected. (See Figure 5.4.)

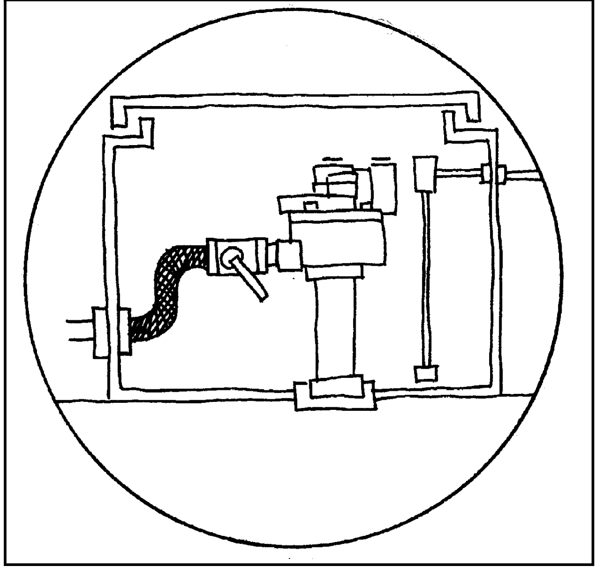
Figure 5.4 Spill bucket and overfill device located at UST fill port.



Prior to federal UST requirements, bare steel tanks were commonly used to store gasoline. These tanks would corrode over time and become the sources of gasoline releases into the environment. An even greater percentage of releases stemmed from piping failure, typically caused by corrosion and loose fittings at the joints. Piping has evolved from galvanized steel piping to cathodically protected steel to FRP piping with glued joints. In the last 10 years, flexible piping has done away with the offending joints. These systems have connections only at the tank, where the piping and submersible pump meet, and the dispenser. These connections are surrounded by containment sumps, where leaks in the system can be monitored. (See Figure 5.5.)

With protection from corrosion, leak detection, and spill and overfill prevention, one would think that USTs couldn't possibly leak (or if they do have a leak, that it would be found and fixed very quickly), but the bottom line is that tank systems are not foolproof. They require some amount of routine

Figure 5.5 A submersible pump manifold in a containment sump, where piping and electrical connections are housed.



operational maintenance. (See "A Tank Leak Story" on page 63). Add to this the fact that all tank systems are made liquid-tight by means of gaskets, seals, and sealants that represent potential chinks in the containment system armor.

TANKS

Underground storage tanks are constructed of one of two primary containment materials that would come into direct contact with stored gasoline: steel or fiberglass-reinforced plastic (FRP). Jacketed steel tanks, composed of a polymer secondary containment around the primary steel tank, may come into contact with product both inside the steel tank and in the interstitial spaces between primary and secondary containment. The following is a discussion of potential ethanol-related concerns for each type of tank.

Steel

Steel USTs have been shown to be satisfactory for storing 100 percent ethanol and E-blend gasoline (Archer Daniels Midland Co., 1998). Steel tanks have been used to store alcohols for more than 50 years without documented compatibility problems. Although ethanol has been shown to "scour" rust and scale from internal metal walls of containment structures, internal deterioration of the tank structure is considered insignificant during the regulatory life of the UST structure.

It is important to keep in mind, however, that because it is a solvent, ethanol will loosen rust and other deposits from the interior walls of steel tanks and piping. Furthermore, the suspension of water within the E-blend, perhaps caused by the hydrophilic nature of ethyl alcohol, may enhance rusting and/or galvanic corrosion in those portions of the UST system directly in contact with product. Also significant is the propensity for ethanol to loosen other deposits. Over time, conventional gasoline leaves deposits of varnish-like residues in UST components. By loosening these deposits, ethanol may accelerate wear of various components by scouring internal surfaces with suspended particles.

Neat ethanol has a flash point of 55°F (13°C) and enough electrical conductivity to prevent accumulation of static charges that are large enough to be sources of ignition. Presumably, by enhancing the conductivity of gasoline, ethanol concentrations could have an effect on the corrosion of UST metals within an UST system as a consequence of conducting and distributing static charges from successive deliveries. Such impacts are likely to be negligible, except perhaps at locations where conditions for galvanic corrosion already exist (e.g., dissimilar metals, holidays, stressed metals).

Given the hydrophilic nature of ethanol, the presence of ethanol in gasolines may cause incidental waters from the bottoms of tanks to go into suspension, possibly enhancing what is otherwise presumed to be a negligible potential for corrosion. (Corrosion from EtOH, MeOH, t-BuOH, M*t*BE and their mixtures in oxygenated fuels in the presence of water can be inhibited by solutions of an alkenyl or alkyl succinic acid polymer or its anhydride in an aromatic hydrocarbon solvent [Garrecht, Knepper, and Dear, 1992]).

The U.S. Department of Energy has issued recommendations that double-walled, low-carbon, cold-finished steel tanks are serviceable for storage of neat or high-concentration ethanol-blended fuel (E85), although butt-welded tanks are preferable. Plated-metal tanks should not be used.

A TANK LEAK STORY

The following story, excerpted from an article by David McCaskill in NEIWPCC's UST newsletter, *L.U.S.T.Line* (1999) is an example of how things can go wrong at an UST facility, even when everything seems right. The story is about a March 1999 release of 4,000 gallons of gasoline from a state-of-the-art double-walled UST system in Maine. Thankfully, the gasoline station was located in an area served by town water, so groundwater contamination was not so much an issue as public safety.

The big question in this incident was: how did 4,000 gallons slip through the multiple defenses of this very model of a modern storage system? As with many such cases, the answer was tracked to a combination of cascading equipment failure combined with faulty follow-up.

This UST system consisted of double-walled fiberglass tanks and pressurized double-walled piping. In this type of piping system, the product is moved from the tank to the dispenser and nozzles by a submersible pump inside the tank. The product is sucked out of the tank by the pump to a manifold that sits on top of the tank, where it is then pushed up through the piping. In this installation, the submersible pump manifold, which contains electrical connections to the motor and plumbing to the piping, is housed in the containment sump so that any leaks from the pump or piping can be contained and monitored. The sump itself is attached to the tank opening via a pressure plate and rubber gaskets.

This type of piping system is monitored for leaks using two methods. One is a line leak detector—a device used to monitor for catastrophic piping leaks (i.e., three gallon per hour or more) and located, in most cases, in a port on the submersible pump manifold. The line leak detector will only detect three gallon per hour leaks down-stream of where it is installed.

The other method detects smaller leaks using leak detection sensors that are located near the bottom of the containment sump. Most of these probes are micro float switches which, when immersed in liquid, make an electrical contact, sending an alarm to a control box.

On March 10, 1999, a contractor was called to the Maine site to investigate a customer complaint about a low-flow condition at the dispenser nozzle. Gasoline was found dribbling out of the pump manifold, and about one-half gallon had pooled in the bottom of the sump. The pump manifold was opened and fibers from an ingested sorbant pad were found to be restricting the flow. A failed gasket was replaced, and product was removed from the sump.

On March 11, the gasoline gurgled out of a storm drain, and state and local investigators arrived.

On March 12, the contractor was called back to the site to test the product line for the unleaded tank, which was found to be tight. However, when the containment sump was tested by filling it with water, all the water leaked out. Further investigation found that the gasket at the bottom of the sump was torn and had allowed product to leak out.

A Maine DEP review of the electronic alarm history for the facility showed that sump alarms were on December 21, 1998, January 1 , 1999, and March 3, 1999. The owner stated that the first two alarms were the result of water infiltration through the sump covers during a storm event (rain). Each time the alarm sounded, the manager had removed about two inches of water from the sumps. The owner stated that the manager was not aware that the March alarm had occurred.

A review of the inventory showed a loss of around 4,000 gallons of gasoline from March 3 to March 11.

What could have been done to prevent this problem? It boils down to maintenance and vigilance. The system, as a whole—pump, line leak detector, containment sump—failed to do its job, and someone didn't respond to the sump probe alarm (or at least not appropriately).

This UST system was literally screaming for help, but unfortunately the operator probably thought that it was crying "water in the sump" wolf. The clues to this catastrophe were all there, but no one person heeded them all or knew what they all meant. Someone needed to understand the system as a whole so that it would be possible to step back and put all the pieces of the puzzle together.

- ▲ **Steel Tank Linings** Older epoxy linings used to line steel USTs, both inside and out, have been found to soften when exposed to E-blend (10 percent ethanol by volume) (Downstream Alternatives, Inc., 2000; Archer Daniels Midland Co., 2000). Although many general-purpose lining formulations were devised after 1980 to be compatible with E-blends, internally lined steel tanks may not be suitable for storage of ethanol or E-blend gasoline, given that general purpose lining materials installed in the past have softened when exposed to ethanol vapors (American Petroleum Institute, 1985). New epoxy compounds (e.g., Bridgeport GA-27-P) may be suitable for UST lining in those states that allow lining for other than preventative maintenance.

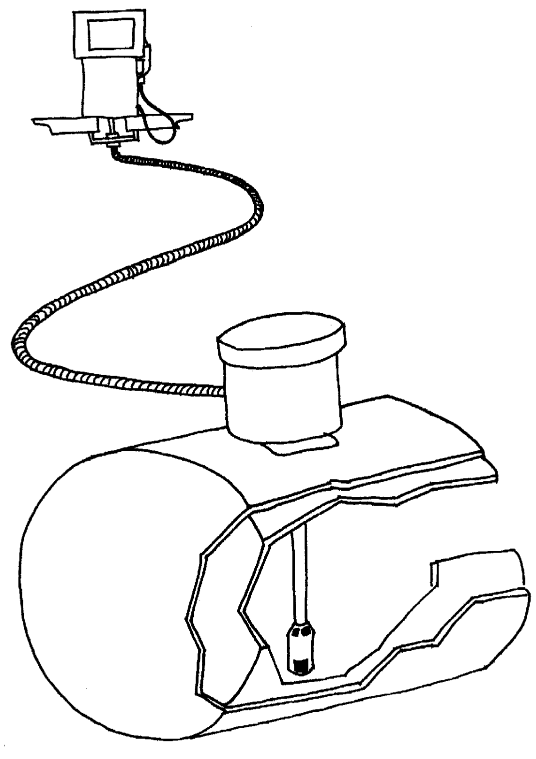
Jacketed and Clad Steel Tanks

While the primary tanks of jacketed and clad tanks are constructed of steel, the secondary containment system or external coating is constructed of FRP, high-density polyethylene (HDPE), or urethane. (See Figure 5.6.) Jacket materials showed no signs of blistering, softening, cracking, or other damage-impairing performance in measurements of flexural strength, tensile strength, and Izod (blunt) impact (Geyer, 1996). For information on concerns associated with FRP see below.

If E-blend gasoline were to leak into the interstitial spaces, causing the E-blend to come into contact with an HDPE secondary containment system, the warranty of the HDPE allows for only a short exposure. The E-blend must be promptly cleaned out so that the HDPE will not be damaged (Copenhaver, January 23, 2001).

Total Containment, a manufacturer of jacketed tanks and flexible piping systems, maintains that, "Leaks should be cleaned up in 72 hours. Parts can still be used after they are cleaned, and inspected. The tank's jacket will not be compromised after exposure" (Copenhaver, February 2001). Warranties for Total Containment tanks have been invalidated for exposures to gasoline-contaminated soils for prolonged periods. An incident of jacket failure has been documented under similar circumstances. For information about other jacketed tank brands and other claddings, contact their manufacturer. In cases of bad management practices, recurrent spill/overfills, and residual contamination, there is the potential for deterioration/compromise of the various jacket coatings.

Figure 5.6 Section of a jacketed UST with a steel primary tank and an FRP or high-density polyethylene outer jacket.



Fiberglass-Reinforced Plastic (FRP)

FRP tanks and piping have been tested for fuel compatibility since 1965. (See Figure 5.2.) In 1983, Underwriters Laboratories, Inc. (UL) updated its materials compatibility testing protocol to recognize E-blend fuels in the marketplace. Since 1983, some manufacturers of FRP tank and primary piping containment systems have UL-listed certain products for alcohol-based fuels and storage of 100 percent ethyl alcohol and methyl alcohol. No comparable standard exists for steel or lined steel tanks and piping (Downstream Alternatives, 2000).

Published experimental data are deficient. However, some reports and protocols established by industry suggest that FRP components and epoxy linings that do not have special alcohol-resistant modifications to their resin matrices may be unsatisfactory for the storage of 100 percent ethanol and methanol. Storage of E-blends may pose compatibility problems when ethanol concentrations exceed certain percentages (Archer Daniels Midland Co., 1998).

Two studies suggest that E-blend gasolines that do not exceed 10 percent volume ethanol may pose little or no threat to the retention properties (e.g., flexural strength, hardness) of FRP tanks. Those two studies were conducted by the ARCO Chemical Company and L.J. Broutman & Associates in a study for the Steel Tank Institute. However, far more testing is necessary before industry should attempt to extrapolate these results to the entire realm of anticipated conditions.

ARCO tested Owens Corning FRP laminates in six test fuels (base fuel ARCOclear unleaded, 10 percent volume ethanol, 10 percent volume OXINOL 50 blending component, 16 percent volume ARCONOL GTBA, 5 percent volume methanol, 5.5 percent volume OXINOL 50 blending component). The fiberglass samples were submerged in these test fuels for one, three, and six months and then tested for flexural strength, flexural modulus, and hardness, using the Barcol hardness test method. The findings of this 1982 ARCO study indicated that there were no significant changes in weight or thickness of the fiberglass samples, suggesting that retention properties were maintained in all six fuels (ARCO Chemical Company, 1982).

The L.J. Broutman & Associates study tested three FRP tanks: a 10,000 gallon capacity tank not fabricated or UL-listed for storage of ethanol blends, a 550 gallon capacity tank fabricated and UL-listed for the storage of ethanol blends up to 10 percent ethanol, and a 550 gallon capacity tank fabricated and UL-listed for storage of up to 100 percent ethanol. This study, which submerged tank panels into various gasoline/ethanol mixtures for exposure times up to 15,000 hours, indicated that structural property changes including strength and stiffness of the fiberglass were measurable but not significant.

During these tests, weight gains were observed in the range of 2 to 10 percent due to the absorption of ethanol by the FRP samples not fabricated for the storage of ethanol. In those samples, flexural stiffness retention was estimated to be reduced by 30 percent from a predicted 30 year exposure to 10 percent E- blend. (The same samples lost 75 percent of their stiffness when exposed to methanol blends.) The L.J. Broutman & Associates study concluded that “gasohol storage may lead to an increased frequency of buckling failures in tanks that were not designed to store these oxygenated fuels” (Hofer and Skaper, 1985).

Following the widespread introduction of E-blend gasolines in the late 1970s, both Xerxes and Owens-Corning (OC), the two primary manufacturers of FRP tanks in the United States at the time, modified their FRP matrices to address concerns about alcohol compatibility with their UST products. “Beginning in 1982, the UL # 1316 test protocol was expanded to include the immersion and physical testing of fiberglass tank samples in higher concentrations of ethanol-gasoline test liquids.” (Curran and Mittermaier, 2000.)

The Xerxes 1993 limited warranty for UL-listed FRP USTs was rendered invalid for the storage of E-blend gasoline exceeding 10 percent ethanol by volume. For older tanks, the storage of E-blends was not recommended. The warranty for Xerxes UST components was also voided for storage of gasoline with M*t*BE in exceedance of 10 percent by volume (Xerxes Corporation Warranty, effective 5/15/93). The 1996 warranty for Owens-Corning Fiberglas Corporation UST components was voided for exceedances of the same ethanol/methanol criteria as Xerxes Corporation (Owens-Corning Fiberglas Corporation, 1996).

In December 1981, OC completed UL listing and introduced a 30-year warranty on its standard FRP UST for 10 percent ethanol-blended fuel. For those tanks, the use of E-blends over 10 percent or use of *any* methanol blends in the standard OC FRP UST would void the manufacturer’s warranty and the UL listing for the tank. For methanol blends or E-blends exceeding 10 percent, an optional vinylester resin system was UL-listed and made available as an OC option. (Methanol can also be present in gasoline as a result of incomplete reaction in the manufacture of M*t*BE.)

On April 14, 1995, Owens-Corning issued a letter to its tank customers advising its clientele that OC tanks made prior to January 1981 were not warranted for *any* alcohol or alcohol-blended fuels, nor were these tanks tested and listed by UL for such fuel storage. Storage of ethanol and E-blends would thus void both the OC warranty and the UL listing for these tanks In the same letter, OC advised its customers that tanks made between July 1984 and June 1990 were unwarrantied and unlisted following use or storage of E-blends over 10 percent and methanol blends over 4.75 percent (Owens-Corning letter to OC Tank Customers, April 14, 1995).

On May 8, 2000, Owens-Corning issued a letter stating that "Owens-Corning knows of no technical reason why properly installed pre-1981 tanks should not perform equally as well as post-1981 tanks when used to store fuels containing 10 percent ethanol" (Owens-Corning, 2000). This same letter made it clear that Owens-Corning was not extending or broadening the original warranty for these tanks.

In a phone conversation, a representative of a major petroleum marketer described tests that were conducted on an older single-walled fiberglass tank in which E-blend fuel had been stored for five years. The tests showed Barcol hardness readings of zero from the interior surface to a point roughly halfway through the laminant. Subsequent tests on the inner layers of the fiberglass showed a Barcol reading of eight, where the standard for a new tank should be around 40 prior to exposure to any fuel and around 30 after such exposure.

Neither Owens-Corning nor other major oil companies that were contacted during this ethanol study have indicated that they have had any problems with the storage of E-blend fuels, nor have they conducted any tests on removed tanks. Clearly, more studies on the long-term structural integrity of FRP tanks that have stored E-blend gasolines are required. This testing must be conducted on tanks that have actually been in service.

The U.S. Department of Energy recommends that FRP tanks storing neat or high concentrations of ethanol be lined with chemical-grade rubber to prevent the fuel from contacting the fiberglass (U.S. Department of Energy, Argonne National Laboratory, 1996). However, we are not aware of any chemical-grade rubber suitable for this type of application.

LEAK DETECTION DEVICES

Leak detection devices are composed of various materials—metals, polymers, and elastomers—that may not be compatible with E-blend fuels and could therefore malfunction, allowing leaks to go undetected or, depending on their location in the system, allow a leak to occur.

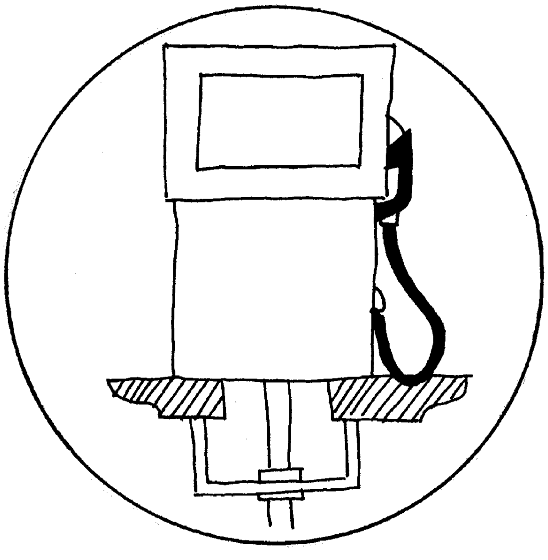
Automatic tank gauge systems that have capacitance probes will not work with E-blend fuels, because these fuels are conductive, and capacitance probes must be used in a nonconductive product. For magnetostrictive tank probes, the fuel float must be changed for both chemical compatibility with ethanol and the change in specific gravities between the E-blend and the previous fuel (i.e., RFG or conventional) stored in the tank.

DELIVERY SYSTEM COMPONENTS

Ethanol is a smaller molecule than M*t*BE and other oxygenates added to RFG since January 1, 1995. Thus, as with some types of FRP and epoxy coatings, the potential for ethanol diffusion through and gradual deterioration of other materials used to contain neat ethanol or E-blend gasoline is predictable. As a solvent, ethanol may be drawn into polymers, causing them to swell and soften, resulting in weakening of the polymer structure. Also, ethanol can extract plasticizers, thereby reducing the flexibility and toughness of the polymers (i.e., causing brittleness).

A number of recommendations and protocols used by E-blend and petroleum industries point to compatibility concerns involving E-blend fuels and auxiliary UST system components.

Figure 5.7 UST gasoline dispenser, nozzle, and dispenser sump.

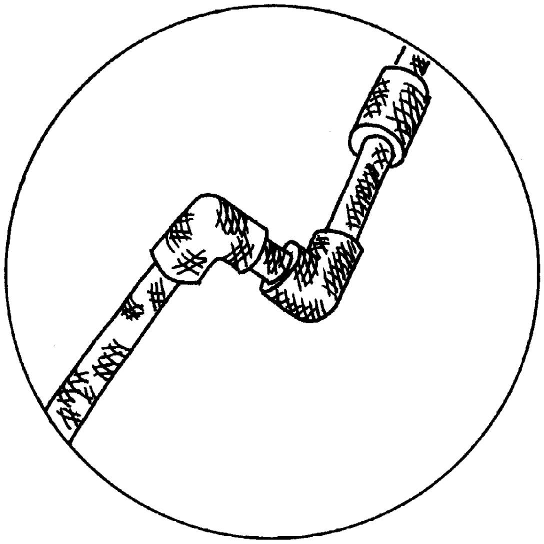


Dispenser

The dispenser is the most visible and universally recognizable UST system component. (See Figure 5.2.) It houses the gasoline metering device and plumbing connections and their various gaskets and seals, all of which are susceptible to leaks if the system is not properly maintained and if they are not compatible with a fuel and its additives. To address possible leaks in the dispenser area, new double-walled UST systems are typically installed with dispenser sumps that contain spills and drips. Leak detection can also be added.

Piping

Figure 5.8 FRP piping with glued connections.

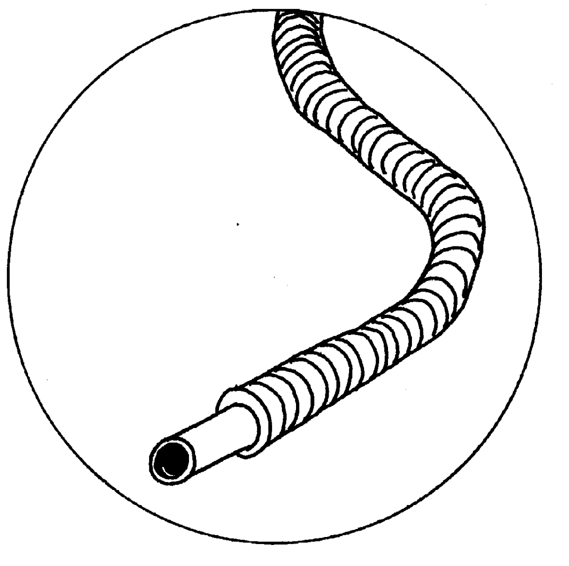


- **Fiberglass-Reinforced Plastic (FRP)** At this time there is insufficient data to draw conclusions on the compatibility of FRP piping with E-blend fuels. It should be noted that fiberglass piping is glued, and there are some questions about the compatibility of old adhesives with E-blend fuels. (See Figure 5.8.) While it appears that such piping may have little trouble handling 10 percent ethanol blends, there is currently no way to easily assess whether the adhesive was mixed and cured properly. If it was not, the adhesive may be quite vulnerable to chemical attack by ethanol.

- **Flexible** Because of its flexibility and lack of joints, flexible piping has become widely used in tank system installations, although there have been some problems with first generation flexible piping (e.g., biological degradation, defective fittings). (See Figure 5.9.) Primary flexible fuel piping systems consist of multilayered thermoplastics. In terms of permeation, whereby molecules in their gaseous form diffuse through the piping walls, alcohols have been problematic with regard to the integrity of thermoplastics. For the most part, newer flexible piping systems have been redesigned to meet E-blend permeation criteria, however older systems may not be sufficiently impervious.

  Total Containment, a manufacturer of jacketed tanks and flexible piping systems, has indicated that their first generation flexible pipe (PP 1500) is not included in the warranty for use with alcohol. “If using an E10 system with our PP1500, the piping will have to be retracted and replaced. Our alcohol-rated piping systems will hold up for the life of the piping system (30 years). Owners do not need to replace the piping system after 10 years when using alcohol-rated pipe" (Copenhaver, February 2001). UL is in the process of strengthening its requirements for flexible piping permeation.

Figure 5.9 Flexible piping. Popular with installers because it has no joints, just connections at the dispenser and tank.



Elastomers (refer to Table 5.1)

Materials not recommended for use with ethanol and E-blends include the following elastomers: Buna-N (seals only), neoprene (seals only), and urethane rubber (ADM 1998; Downstream Alternatives, 2000). Expanded polyurethane and Buna-N underwent even greater attack in the presence of methanol fuel (Foulkes, Kalia, and Kirk, 1980).

For rubbers swollen by gasoline-methanol mixtures, the results of which may be proportionately applicable to ethanol, tensile strength and elongation may be related to swell volume by simple linear relationships and appear to obey equilibrium stress-strain relationships (Abu-Isa, 1983).

Polymers (refer to Table 5.1)

Certain polymers are not recommended for contact with ethanol at E-blend concentrations. These include, but are not limited to, polyurethane and recently applied alcohol-based pipe dope, particularly when not fully cured. Shellac, especially shellac used as an adhesive in fuel treatment and dispensing equipment (e.g., filters), will deteriorate with exposure to E-blends.

Cork (refer to Table 5.1)

Because of its propensity to shrink and shrivel, cork appears to be unsuitable for use with ethanol, methanol, and E-blends (Archer Daniels Midland Co., 1998).

Bushings (refer to Table 5.1)

Although rarely submerged, bushings (located where there are fittings into the tank or another system component) are exposed to splashing of E-blends. Non-metallic containments (e.g., jackets) constructed over primary steel tanks and integral piping are even less likely to be exposed to ethanol. Nylon bushings showed no signs of blistering, softening, cracking, or other damage-impairing performance in measurements of flexural strength, tensile strength, and Izod (blunt) impact (Geyer, 1996). Importantly, these conclusions were based on a retention of only 50 percent of original physical property values after immersion in various strength alcohol blends of methanol and ethanol, and methanol or ethanol mixed with reference fuels. However, creep and stress cracking of polymers may be accentuated by exposure to E-blend fuels due to the known phenomenon of plasticizer extraction (Marshall, 2001).

Metals

While unsubstantiated, it is possible that ethanol could enhance the conductivity of gasoline in a manner that might effect corrosion of metal components of USTs (e.g., conducting static charges from repeated fill-ups throughout an automobile's fuel system). Increased fuel conductivity may also result in increased internal galvanic corrosion of steel tanks and components.

Suspended Deposits

Besides plugging and clogging conventional filters and strainers, E-blend could be responsible for more rapid deterioration of meters, seals, and gaskets than occurred prior to its introduction (Getty Petroleum, 2000).

Filters

Given that ethanol is hydrophilic and therefore absorbs moisture, an advantage derived from blending ethanol with gasoline—that of preventing gas-line freezing in cold weather—is offset by the possible disadvantage of entrapped water in fuel filters (especially at pumps, but presumably in automobiles, as well), a consequence of increased moisture in the fuel (Renewable Fuels Associates, 2000; Getty Petroleum, 2000). As a result of water retention, fuel filters can clog and malfunction, creating the need for frequent replacement. To combat this problem, during periods of E-blend distribution, Getty Petroleum has adopted a policy of converting to filters that are specifically designed for stripping water from gasoline.

Water Pastes

A converse problem to that of water retention by E-blends is the tendency for free water to extract significant amounts of ethanol from blended gasolines. To complicate this problem, the usual water-detection pastes that are used as part of standard inventory control and leak detection, are ineffective in the presence of most alcohols (although some pastes are marketed that do function in the presence of alcohol). If a water/ethanol tank bottom mixture exists, it should be pumped immediately. Note that it is highly flammable (Getty Petroleum, 2000).

POTENTIAL EFFECTS OF METHANOL

Methanol has historically been used to denature ethanol at a maximum blended concentration of 5 percent. When the ethanol is then blended with gasoline the methanol concentration is reduced to approximately half of 1 percent. Recent communications suggest that methanol is no longer used to denature ethanol.

Although correlations have been found between corrosion of metals and exposures to methanol, steel and weld immersion tests in methanol blends and reference fuels with 4 percent water showed measurable corrosion only in the fuel/water media tests. Corrosion was limited to the immersed portion of the steel and not the air/exposed portions of the samples—comparable to ullage in an underground tank (Geyer, 1996). The conclusion drawn from this limited body of research with respect to the integrity of steel USTs and large-scale usage of methanol is that it is measurably corrosive to thickly gauged steel components in the presence of water. No published data are available from which a conclusion can be drawn that ethanol is as corrosive as methanol.

The Xerxes 1993 limited warranty for UL-listed FRP USTs was rendered invalid for the storage of E-blends exceeding 4.75 percent methanol for gasoline and Oxinol-50 (methanol and GTBA mixture) blends; and exceeding 5 percent methanol for Dupont EPA waiver (gasoline with methanol and a minimum of 2.5 percent cosolvent) blends.

Corrosiveness testing of 15 percent methanol by volume gasoline blends on conventional materials used for fuel dispensing and automotive fuel storage/fuel delivery systems has shown that the presence of water, salt, and air dramatically increases corrosiveness of methyl gasohol. Aluminum was unaffected, but copper, brass, AISI 1181 [76362-83-9], AISI 1008 [11103-16-5], Zsn, and terneplate all showed signs of corrosion (Foulkes, Kalia, and Kirk, 1980). Conductivity measurements also showed that the presence of water and salt in methanol fuels (the introduction of which could occur in winter conditions) causes galvanic corrosion. That these results could be applicable to ethanol and other alcohol fuel additives, albeit to a lesser degree, is a reasonable hypothesis.

Table 5.1 Gasoline storage and handling equipment to be considered for ethanol compatibility and permeability.

Adapted from Curran and Mittermaier, 2000.

The following lists in this table do not necessarily indicate that components and materials are incompatible with E-blend fuels. As previously discussed, some materials listed (e.g., Buna-N and cork) may react with ethanol over time in a manner that reduces their integrity, perhaps significantly. Failure of components and materials that come into contact with the fuel can cause external product leakage and/or equipment failure. Therefore the compatibility of these components and materials with E-blend fuels must be verified.

Dispenser Components

Failure of the following component materials that commonly come into contact with fuel can cause external leakage:

- Aluminum tubing in fuel paths
- Black steel pipe risers and ground joint unions
- Buna-N in "0" rings and lathe-cut gaskets
- Cast iron in meter bodies and fluid paths
- Copper in air eliminator floats
- Hard-formed plastic in air eliminator floats
- Copper tubing in fuel paths
- Cork/Buna-N in flat gaskets
- Die cast aluminum in meter bodies and fluid paths
- Graphite rope in suction pump shaft seals
- Fluorocarbons in "0" rings and lathe-cut gaskets

Failure of the following component materials that come into contact with fuel can cause malfunction of fuel storage and distribution equipment:

- Carbon bearings and meter valves
- Cast iron suction pumping units
- Leather meter piston cups (old meters)
- Rulon and graphited Teflon meter piston cups and shaft seals

Submersible Pumps

Failure of the following component materials that come into contact with fuel can cause external leakage:

- Anodized aluminum pump and motor shells and wiring conduit
- Buna-N "0" rings and lathe-cut gaskets
- Viton "0" rings and lathe-cut gaskets
- Cast iron flow manifolds and electrical enclosures
- Epoxy wiring seals
- Fluorocarbon "0" rings and check-valve poppets

Failure of the following component materials that come into contact with fuel can cause a malfunction:

- Acetal plastic pump impellers and housings
- Black iron fuel piping in the tank
- Carbon motor pump thrust bearings
- Stainless steel motor shells and motor/pump shafts

Table 5.1 (continued) Gasoline storage and handling equipment to be considered for ethanol compatibility and permeability.
Adapted from Curran and Mittermaier, 2000.

Monitoring Systems

The following component materials that come into contact with fuel are used for tank gauges:

- Aluminum for electrical conduit
- Epoxy to encapsulate electrical parts
- Glass in capacitance and buoyancy-type probes
- Nitrophyl in magnostrictive floats
- Nylon for electrical insulation
- PVC jacketed cable for wiring at the top of the probe
- Type 316 stainless steel for magnostrictive shells

Hoses

Failure of the following component materials may cause a fuel leak or a vapor return blockage:

- Epichlorohydrin in the inner fuel-containing walls
- Neoprene in the external cover of the hose
- Nitrile in the inner fluid-containing walls
- Nitrile/PVC in the external cover of the hose
- Nylon used for containing vapor
- Thermoplastics used for containing vapor
- Nozzles and Swivels

Failure of the following component materials that come into contact with fuel can cause external leakage:

- Buna-N valve poppets and seals
- Die-cast aluminum swivel fuel-carrying parts
- Fluorocarbons in valve poppets and seals
- Sand-cast aluminum in fuel-carrying parts
- Super fluorocarbon valve poppets and seals

Failure of the following component materials that come into contact with fuel can cause equipment malfunction:

- Buna-N valve poppets
- Nickel plating in seal and bearing surfaces
- Stainless steel operating shafts
- Fluorocarbons in valve poppets

THE END USERS

Automotive Gasoline Engines

Industry research conducted by Downstream Alternatives, Inc. shows that all major automobile manufacturers have approved the use of 10 percent E-blends. (See Table 5.2.) However, gasoline tank and fuel system compatibility with E-blend is a concern in pre-1980 vehicle models. E-blend fuels can increase moisture-related metal corrosion in automobile fuel systems because of ethanol's propensity to increase gasoline moisture content.

In one study (Temple and Sidhu, 1992), pitting was found in carburetor components subject to three to four years of E-blend use, suggesting that the useful lives of automobile components designed for use with hydrocarbon fuels could be reduced with the continuous use of alcohol blends.

E-blend fuels can also have an impact on elastomer components in automobile fuels systems, as ethanol has been shown to cause swelling in elastomers. According to Downstream Alternatives (1996), "swelling can be severe with methanol, but relatively insignificant with other alcohols."

Comingling of E-blends and straight gasoline in automobile fuel tanks may result in increases of both vapor pressure and evaporative emissions. (This phenomenon will lead to more fugitive emissions, particularly at gasoline stations where there are no vapor recovery systems.)

Ford (1988) and Chrysler (1987) warranties are not affected by E-blends. Mercedes Benz has warranted its automobiles (date unknown) for E-blends with less than or equal to 10 percent ethanol or less than or equal to 3 percent methanol. However, mixtures of ethanol and methanol are not permitted under Mercedes Benz warranties (American Petroleum Institute, 1985).

Small Non-Automotive Engines

Small non-automotive engines include motorcycles, recreational equipment (e.g., snowmobiles, ATVs), marine engines, and lawn/garden equipment, such as lawn mowers, string trimmers (e.g., weed whackers), blowers, and chain saws. The use of E-blend fuels in non-automotive engines raises concerns about the potential for corrosion of certain engine components as well as several separate issues that are specific to these types of engines.

There are distinct operational and use characteristics associated with small non-automotive engines that must be taken into account when considering potential impacts of ethanol and E-blends:

- ▲ These engines are often used on a seasonal basis (e.g., snowmobiles, lawn mowers). This seasonal use necessitates lengthy storage periods.
- ▲ Because of the inexpensive nature of some of this equipment (e.g., lawnmower, weedwacker), it is often not cared for according to the manufacturer's recommendations, especially during storage periods.
- ▲ The environment in which small engines such as marine motors and snowmobiles are used is often quite extreme (e.g., water, extreme cold).
- ▲ Small engine components are typically made of very light weight materials (for ease of handling), which necessitates the use of a variety of metals, plastics, and elastomer components that may differ greatly from the materials used in automobiles.

All of these operational/use characteristics have an effect on the compatibility of small non-automotive engines with ethanol and E-blends.

Downstream Alternatives, Inc., a leading fuel industry consulting firm, has taken a comprehensive look at these issues and has surveyed manufacturers of small non-automotive engines about their positions on the use of oxygenated fuels, including ethanol.

The firm has found that questions of compatibility associated with ethanol use in these engines center on the following issues:

- Materials compatibility
- Phase Separation
- Lubricity
- Enleanment
- Over-Blends

The following is a summary of their findings.

- **Material compatibility** As with automobiles, metals, plastics, and elastomer components of the engine and fuel system in non-automotive engines are of concern with regard to use with E-blends.

  In a controlled test conducted by the Valvoline Oil Company in 1989, it was found that "ethanol performed comparably to the control fuel in both hardness and volume change" (Downstream Alternatives, Inc., 1994) in two-stroke cycle engines, when compared to the control fuel without ethanol.

  A 1987 U.S. Coast Guard report on the use of E-blends indicated that certain fuel hoses could be prone to permeation by ethanol and should be upgraded. Since the early 1980s non-automotive engine manufacturers have upgraded their materials and are now "largely unaffected by proper oxygenated fuel formulations" (Downstream Alternatives, Inc., 1994).

  Although Sears products, as of October 30, 1987, are capable of operating with 10 percent E-blend, Sears customers demanded compatibility modifications for E-blends after it was learned that Onan carburetor floats swelled when used with such products. Concurrently, Tecumseh and Briggs and Stratton have improved their products and carburation components so that they are compatible with E-blends.

- **Phase separation** Phase separation, a function of ethanol's affinity for water, is a major concern for manufacturers. Because ethanol attracts moisture and because water separates out of gasoline, the ethanol and water can separate from the gasoline and settle at the bottom of the fuel tank. There are two major concerns associated with this occurrence: (1) an engine cannot run on a mixture of ethanol and water; and (2) the ethanol and water blend at the bottom of the fuel tank can lead to corrosion of metals.

  Phase separation can become a problem because of the nature of small non-automotive engines. Lawn mowers, for example, are often stored for long periods of time. As a result, there is more opportunity for moisture to find its way into the fuel storage system through atmospheric absorption. If a mower is stored with a half empty tank, the moisture absorption rate can increase.

  Manufacturers recommend that mowers be prepared for storage either by draining the fuel systems completely or by storing them full of gasoline. Some manufacturers also suggest treating the fuel with a fuel stabilizer during periods of storage. Marine engines need particular care because they are used in the water environment, which increases the potential for moisture in the fuel system.

▲ **Engine lubricity** Concerns about the impact of E-blend fuels on engine lubricity have also been raised. Several manufacturers have expressed concern, but the limited data available suggest that ethanol is not expected to have a negative impact on lubricity. The Valvoline Oil Company's 1989 *Report on Ethanol/Gasoline in Two-Stroke Cycle Engines* found that E-blend fuels "provided slightly better lubricity" (Downstream Alternatives, 1994) than the control fuel without ethanol.

However, there are indications that ethanol-water phases in the distribution system or fuel tanks can "compete with the engine lubricating oil for bonding to the metal engine parts" (Curran and Mittermaier, 2000). The Society of Automotive Engineers has repeatedly documented enhanced upper cylinder wear in engines operating on ethanol fuels. Loss of lubricity and the formation of acids, due to the partial oxidation of ethanols, are thought to be responsible (Marshall, 2001).

▲ **Enleanment and over-blends** The addition of oxygen into a fuel can result in a leaner air/fuel ratio. This is specifically an issue for small non-automotive engines because they are not equipped with systems that can automatically adapt fuel flow. Enleanment has not been shown to be a problem with most small engine equipment. Marine engines and snowmobiles, however, can encounter negative effects from a change in the air/fuel ratio.

Because they are operated in extreme temperature environments, snowmobiles require a rich air/fuel ratio, and marine engines operate at wide-open throttle for extended periods. In these situations manufacturer recommendations may include engine adjustments.

A 1994 Tech Exchange document from the Yamaha Motor Corporation to its customers and dealers concerning outboard motors notes that "oxygenated fuels have a very slight leaning affect on the fuel mixture. This will not cause any problems with the performance of the Yamaha outboards. At times, the leaner mixture may cause the idle to be slightly rougher than normal. If this occurs, richen the pilot screw 1/4 turn." (Yamaha Motor Corporation, 1994)

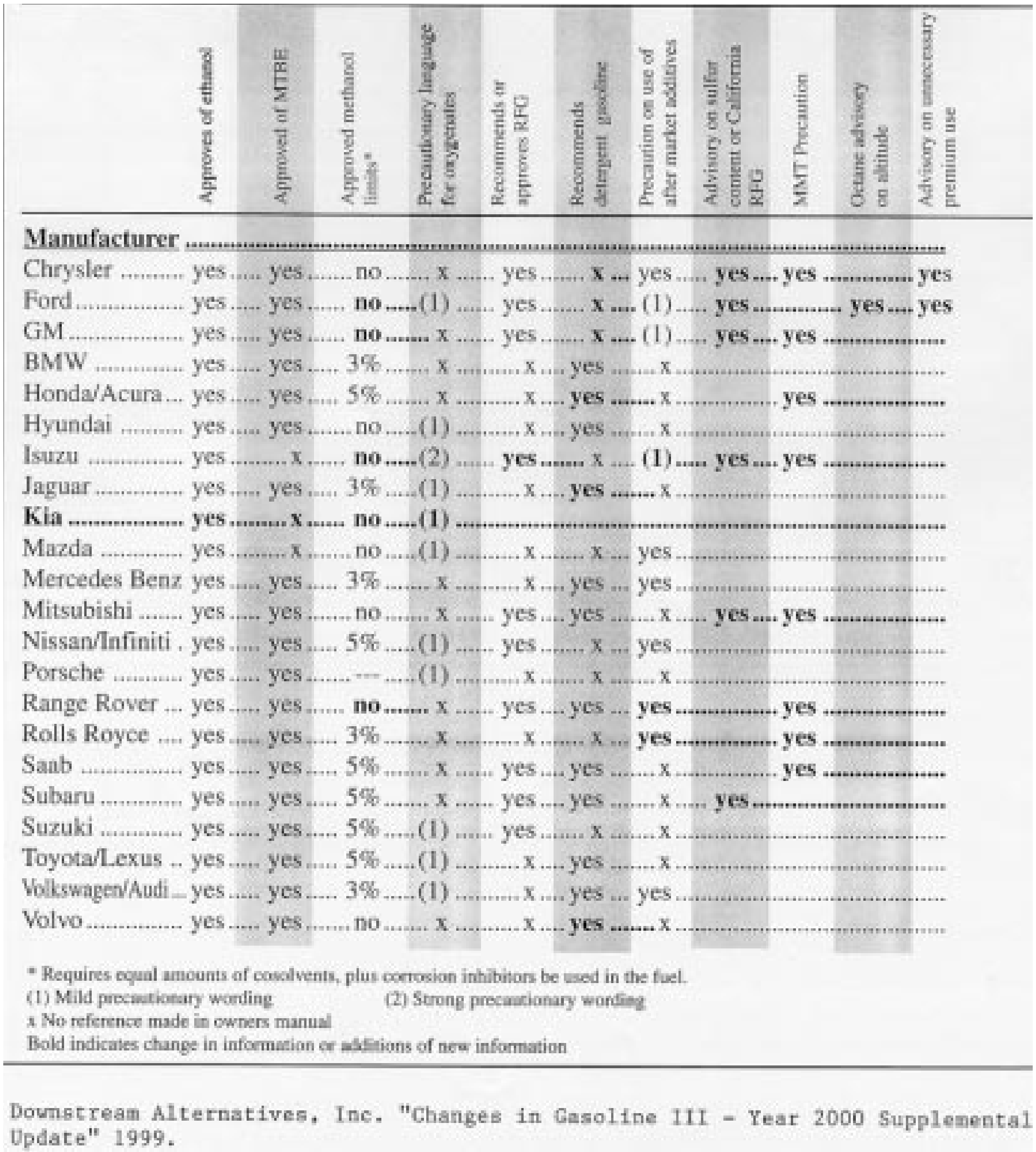
Gasoline standard specifications do not consider gasoline use in small engines, hence manufacturers are left to their own devices to decide whether fuel formulations are approvable for use. In the early 1980s, when ethanol use was still limited, small engine manufacturers did not have the data to decide whether use of these blended fuels would be compatible with their engines/components. Few manufacturers had the economic wherewithal to test their products with E-blend fuels. As a result, they simply suggested that such fuel not be used in their engines.

However, changes to gasoline formulations were taking place, and oxygenate use became more and more commonplace. By the late 1980s, most small non-automotive engine manufacturers had changed their fuel recommendations to allow the use of 10 percent blended ethanol. They didn't necessarily promote its use, but they suggested certain precautions for using their products with E-blends.

A 1999 review of manufacturers fuel recommendations by Downstream Alternatives indicates that many manufacturers now address oxygenated fuel use and permit or approve the use of ethanol. Many of these manufacturers, however, provide recommendations for handling and modifying their equipment when E-blend fuels are used. Owners of small non-automotive engines should consult their owner's manual. If E-blends are not mentioned, they should contact the manufacturer or an authorized dealer.

Kawasaki Motor Corporation makes the following recommendations for its power equipment: “gasoline containing up to 10 percent ethanol also known as ‘gasohol’ is approved for use. Avoid using blends of unleaded gasoline and methanol whenever possible, and never use ‘gasohol’ containing more than 5 percent methanol. Fuel system damage and performance problems may result” (Downstream Alternatives, Inc., 1999). Kawasaki Motor Corporation also indicates that their power equipment should never be stored with E-blend and that the owner should drain the fuel system according to instructions in the owner’s manual.

Table 5.2 Auto manufacturers fuel recommendations recap (based on 1999 model year owners manual).



Manufacturer	Approves of ethanol	Approved of MTBE	Approved methanol limits*	Precautionary language for oxygenates	Recommends or approves RFG	Recommends detergent gasoline	Precaution on use of after market additives	Advisory on sulfur content or California RFG	MMT Precaution	Octane advisory on altitude	Advisory on unnecessary premium use
Chrysler	yes	yes	no	x	yes	**x**	yes	**yes**	**yes**		**yes**
Ford	yes	yes	**no**	(1)	yes	**x**	(1)	**yes**		**yes**	**yes**
GM	yes	yes	**no**	x	yes	**x**	(1)	**yes**	**yes**		
BMW	yes	yes	3%	x	x	yes	x				
Honda/Acura	yes	yes	5%	x	x	**yes**	x		**yes**		
Hyundai	yes	yes	no	(1)	x	yes	x				
Isuzu	yes	x	**no**	(2)	**yes**	x	(1)	**yes**	**yes**		
Jaguar	yes	yes	3%	(1)	x	**yes**	x				
Kia	**yes**	**x**	**no**	**(1)**							
Mazda	yes	x	no	(1)	x	x	yes				
Mercedes Benz	yes	yes	3%	x	x	yes	yes				
Mitsubishi	yes	yes	no	x	yes	yes	x	**yes**	**yes**		
Nissan/Infiniti	yes	yes	5%	(1)	yes	x	yes				
Porsche	yes	yes	---	(1)	x	x	x				
Range Rover	yes	yes	**no**	x	yes	yes	**yes**		**yes**		
Rolls Royce	yes	yes	3%	x	x	x	**yes**		**yes**		
Saab	yes	yes	5%	x	yes	yes	x		**yes**		
Subaru	yes	yes	5%	x	yes	yes	x	**yes**			
Suzuki	yes	yes	5%	(1)	yes	x	x				
Toyota/Lexus	yes	yes	5%	(1)	x	yes	x				
Volkswagen/Audi	yes	yes	3%	(1)	x	yes	yes				
Volvo	yes	yes	no	x	x	**yes**	x				

* Requires equal amounts of cosolvents, plus corrosion inhibitors be used in the fuel.
(1) Mild precautionary wording (2) Strong precautionary wording
x No reference made in owners manual
Bold indicates change in information or additions of new information

Downstream Alternatives, Inc. "Changes in Gasoline III - Year 2000 Supplemental Update" 1999.

ETHANOL STORAGE AND HANDLING

CONCLUSIONS

The compatibility of UST/AST systems with E-blend fuels is a function of the various fabrication materials that compose a fuel storage system, bearing in mind that materials have evolved over time for the storage of ethanol and E-blend fuels. Each component of the system must be checked for compatibility, especially in the case of an existing facility. Particular attention must be given to the design or retrofit of a bulk facility for the storage of neat ethanol. For this reason, the introduction of ethanol into the Northeast gasoline supply will come with the added cost of retrofitting many of the region's tank systems to make them ethanol compatible.

UST/AST components that are incompatible with E-blend fuels may lead to system failures and/or product leaks. Based on the experiences of the New England and New York UST programs, it is expected that many owner/operators will not have their facilities evaluated for compatibility prior to the introduction of E-blend fuels into their fuel storage systems. At current staffing levels, state programs are experiencing a rate of 4 to 17 years between facility inspections.

The introduction of ethanol into gasoline will enhance suspension of water and other deposits scoured or cleaned from UST/AST systems. Water and scoured deposits that are not eliminated from UST systems could result in the following premature component failures: leak monitoring systems (ATG probes and line leak detectors), submersible pumps, fuel dispensers, piping, hoses, nozzles and swivels. Gasoline engines could be affected as well.

Precautions must be taken when storing E-blend fuels in single-walled fiberglass tank systems fabricated prior to January 1, 1984.

There are questions concerning the compatibility of the following tank/dispensing system components and materials with E-blends: lining materials, secondary containment materials, adhesives, glues, sealants, gaskets, and any polymer or elastomer compounds found on dispensing or monitoring devices such as ATG probes.

Some component materials associated with dispensers, submersible pumps, and other distribution equipment that come into contact with E-blend gasoline (e.g., cork and Buna-N) may have long-term compatibility problems.

Ethanol in gasoline may impair the operation of capacitance ATG probes because of increased electrical conductivity to E-blend gasoline.

Most automotive manufacturers approve the use of E-blends in their newer vehicles. Many non-automotive engine manufacturers now address oxygenated fuels use and permit or approve the use of ethanol blended fuels. However, some older models may have components (e.g., swollen carburetor floats) that have exhibited some compatibility problems with ethanol. Many manufacturers, however, provide recommendations for handling and modifying their equipment when E-blend fuel is used.

At the present time, there are not sufficient ethanol life cycle analyses available to address issues surrounding the environmental impact of ethanol feedstock production as it pertains to the Northeast.

ETHANOL STORAGE AND HANDLING

RECOMMENDATIONS

If E-blend gasoline is introduced into the Northeast region, the following steps should be taken to ensure that tank owners and operators are informed and prepared to make the transition with regard to ensuring tank system integrity:

- To prevent releases due to the degradation of non-compatible materials in UST systems, there should be a program requiring UST owners and operators to obtain certification that their UST system(s) is compatible with E-blend fuels.
- A guidance document should be developed to standardize a process by which owner/operators or their contractors may assess and certify the compatibility/functionality of their storage tank systems with regard to any component coming into contact with E-blend fuels. The document should inform owner/operators of proper operating procedures for the continuous management of storage tank systems, particularly focusing on initial conversion of facilities to E-blends and problems associated with ethanol introduction. Such a document would include information on issues such as replacement of filters, system checks for loosened deposits (e.g., rust and scales and other loosened deposits), dewatering of the system, especially at the time of initial conversion, and the continuous monitoring of water in the system.
- Based on the inspection rate at operating facilities, state and/or the federal governments should look for ways to increase inspection resources, especially during a transition to E-blend fuels.
- More studies must be conducted on the compatibility of FRP tanks (especially with respect to structural integrity) particularly single-walled FRP tanks fabricated before January 1, 1984 and FRP and flexible piping that haven’t been specifically fabricated for E-blends.
- Educate automobile and power engine equipment owners on the need to check fuel compatibility specifications in their owners manuals. E-blends may have some minor impacts on engine operation and may adversely effect some fuel system components, particularly those that depend on lubrication.

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CHAPTER 6

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

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THE SCOPE OF THIS CHAPTER

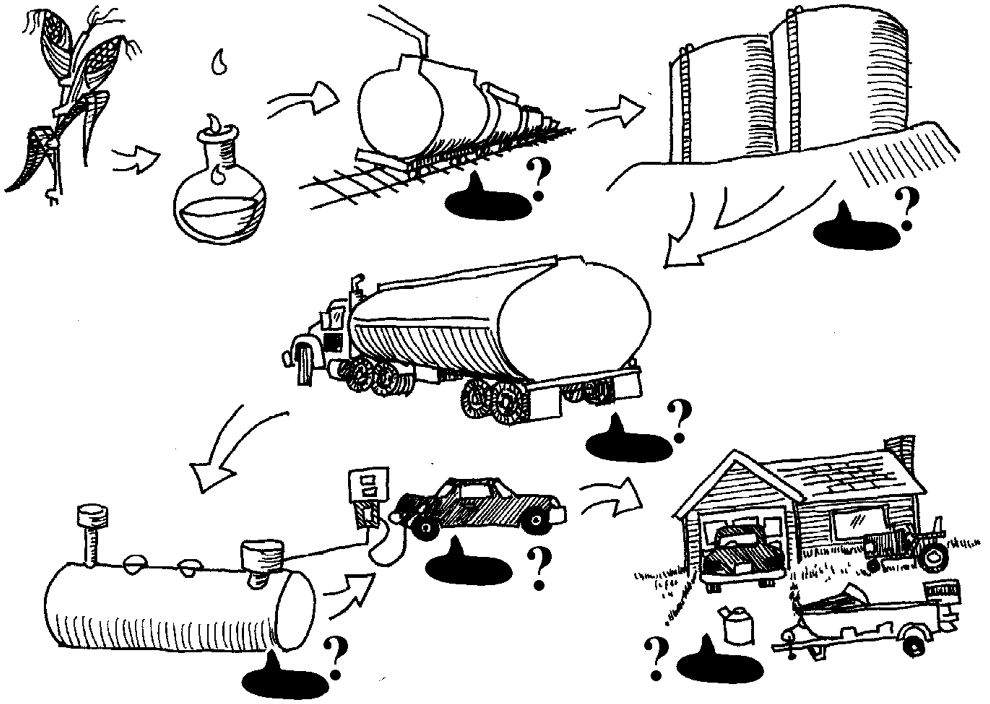
A review of the life cycle of ethanol-blended (E-blend) gasoline highlights the unique problems this fuel poses as a threat to human health and the environment as a result of a release to soils and groundwater. (See Figure 6.1.) One key difference between M*t*BE and ethanol is that M*t*BE is blended with gasoline at the refinery. Thus concerns about potential releases associated with the storage and transport of M*t*BE as a pure substance are minimized. On the other hand, neat, denatured, ethanol is not blended with gasoline until it has been transported to a bulk terminal. Thus ethanol has the potential for release into the environment both as a pure product and as a gasoline blend—and this is a concern.

In evaluating the potential impact of any substance that is released into the environment, it is essential to take into account the pathways that the substance could travel from the release point. (See Figure 6.2.) In the case of a fuel spill, these pathways include:

- ▲ **Surface runoff** - A surface spill of fuel will flow over pavement and soil to ultimate discharge into storm sewers, wetlands, lakes, and streams. During flow over porous soil, most of the fuel will infiltrate the soil. While on the land surface, volatile constituents of the fuel (e.g., benzene and ethanol) will partially volatilize from the liquid. If the fuel makes it to a wetland or water body, it will collect and float on the water (ethanol and M*t*BE will go into solution). Natural biodegradation will begin to degrade the fuel shortly after release. The various fuel constituents degrade at different rates.
- ▲ **Infiltration into soil or fractured bedrock** - When gasoline infiltrates the soil or fractured bedrock, or both, it slowly flows down through the pores of the soil or fractures of the rock until it reaches the top of the water table, where it will stop. During this process, some of the fuel is retained in the pore space of fractures or soil grains. The fuel that is not retained in the unsaturated zone ends up floating in a pool on top of the water table (again, ethanol and M*t*BE will go into solution). It floats because it is less dense than water.
- ▲ **Groundwater transport** - When gasoline reaches groundwater, the most soluble components, such as benzene, toluene, ethylbenzene and xylenes (BTEX) will partially dissolve (ethanol and M*t*BE will dissolve) into the groundwater and move with the groundwater in the direction of groundwater flow. The BTEX constituents have limited solubility (ethanol is completely soluble), and a portion will adsorb to soil particles. Some then desorb from the soil to become dissolved again in the groundwater.

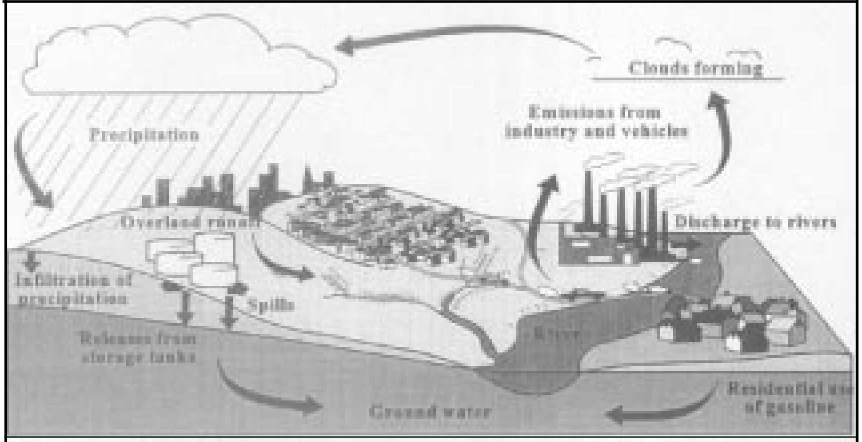
In this movement, gasoline constituents travel at a slightly slower rate than groundwater flow. The non and lesser soluble constituents of fuel are left stranded on the water table and hardly move at all, unless the water table is steep, in which case the pool might move a little. In the end, the gasoline contamination is separated into a hydrocarbon phase termed LNAPL (light non-aqueous phase liquid), a dissolved phase in groundwater, and a vapor phase in soil vapors. Not all the fuel makes it to the water table. The oily portion left behind that is adsorbed onto the soil particles, is referred to as the residual.

Figure 6.1 Ethanol and E-blend gasoline life cycle showing where potential releases can occur.



In terms of potential release scenarios, neat ethanol could be released during transport as the result of an accident involving a tanker truck, marine tanker, or a rail car. It could also be released from a tank at the bulk terminal or during the ethanol/gasoline blending process. (See Chapter 5, page 59 for further discussion on the blending process.) One blending technique, called splash blending, is done by mixing the ethanol with the gasoline during loading of the tanker trucks. Two hoses, one with ethanol, the other with gasoline simultaneously disgorge their contents into the truck. This process is another potential release situation. (See Figure 6.1.) There may also be potential for releases from pipelines if they are chosen to be used for ethanol transport.

Figure 6.2 Hydrologic cycle showing potential environmental pathways of a gasoline/E-blend spill.



Source: Reprinted from National Science and Technical Council Committee on Environment and Natural Resources, June 1997. *Interagency Assessment of Oxygenated Fuels.* Page 2-20.

E-blend can be released into the environment by way of tanker truck accidents, leaks and spills at retail and non-retail gasoline stations, inefficient marine motors, or small spills at homes or other places where gasoline is used. (For a more in-depth discussion of the E-blend life cycle, see Chapter 5 of this report.)

The fate and transport issues associated with a release of neat ethanol into the environment are different from those of an E-blend release. This chapter examines those issues from the standpoint of potential impacts to human health and the environment. It discusses :

- ▲ Neat ethanol versus E-blend releases.
- ▲ The behavior (fate and transport) of neat ethanol and E-blend releases in the soil, groundwater, and surface water environments.
- ▲ The behavior of ethanol in contrast with that of M*t*BE.
- ▲ Drinking water impacts.
- ▲ The remediation of neat ethanol and E-blend releases into the environment.
- ▲ Remediation costs in comparison with M*t*BE.

In December 1999, the Lawrence Livermore National Lab (LLNL) completed an extensive literature review of ethanol and E-blend gasoline (Rice et al. 1999) to address the Governor of California's concerns about using this fuel. Much of the information being presented in this chapter comes from the Lawrence Livermore report.

POTENTIAL EFFECTS OF NEAT ETHANOL VERSUS E-BLEND RELEASES

Effects of a Neat Ethanol Release

Neat ethanol releases would most likely occur as the result of either a structural failure at an ethanol bulk storage terminal or a transport accident involving a tanker truck, marine tanker, or rail car. An ethanol release from such sources would start out as a surface spill and then either migrate over land until it reaches a surface water discharge point or infiltrate the soil, eventually reaching the groundwater.

Surface runoff of ethanol will only occur when very large quantities are spilled—small quantities will likely infiltrate the soil or fractured rock. If the spill is large enough, ethanol will end up in wetlands, lakes, streams or rivers. Flow into a confined space (e.g., storm sewer) may create an explosive situation when vapors of the ethanol collect in air pockets in the sewer. Ethanol is highly flammable and easily ignited. This scenario would be much the same as that of surface runoff of conventional gasoline.

Neat ethanol in soil or groundwater may have a severe localized impact. However, there have been few field studies on neat ethanol releases, therefore the behavior of ethanol in the environment is not understood. A study was completed on a Savasol (a solvent composed almost entirely of ethanol) release that took place in Massachusetts in the early 1990s. In this instance, ethanol concentrations were initially high but degraded to non-detectable within six to eight months after the spill occurred (Rice et al. 1999). The detection limit was not stated in this study, so it is not clear what concentration of ethanol was present when the tests measured nondetect.

Biodegradation of ethanol in soil or groundwater can be rapid in comparison with gasoline, given that there are sufficient levels of electron acceptors and nutrients where the ethanol is spilled. In a laboratory setting ethanol is more degradable than M*t*BE; this is expected to be also true of an environmental spill. However, because there are many environmental variables and little field experience with surface spills of ethanol, there is some uncertainty associated with predicting how easily ethanol will degrade and how far it will travel in the environment.

The ethanol biodegradation process results in the depletion of oxygen in soil and groundwater, causing anaerobic conditions that can mobilize inorganic elements such as iron (Fe) and manganese (Mn). In addition, noxious odors may be produced by the generation of butyrate, a metabolite of ethanol biodegradation.

If pure ethanol is released into a soil where gasoline contamination has already occurred or where gasoline is present in the subsurface, the mobility of that gasoline can be increased. This is most likely to happen when ethanol is spilled at a terminal, where previous spills of gasoline are likely to have occurred (Rice et al. 1999, Buscheck et al. 2001). A 1994 survey by the American Petroleum Institute (API) found that 85 percent of tank farms, nationwide, have been the site of previous spills. In these situations, the ethanol mixes with the gasoline and causes any lens of pure gasoline free product that may lie on the capillary zone above the water table to thin and broaden (Powers et al. 2000). When this happens, free product recovery becomes more difficult and expensive than it would be with just conventional gasoline.

When there is gasoline-contaminated soil and no free product is present, ethanol, an effective solvent, can remobilize gasoline that was previously trapped in the soil. When this happens, plumes of dissolved gasoline in groundwater will enlarge. Rice et al. 1999 describe an example where groundwater concentrations of toxic constituents of gasoline benzene, toluene, ethylbenzene, and xylenes (BTEX) increased approximately 10-fold during the two to five years after a spill of neat ethanol.

Preliminary Findings at a Neat Ethanol Release Site

A recent study of a 19,000-gallon neat ethanol release from an aboveground storage tank (AST) at an oil terminal in the Pacific Northwest (U.S.) sheds some light on what happens to ethanol in the environment (Buscheck, et. al., 2001). The closest point of ethanol detection in a groundwater sample came from a well located within 40 feet of the AST. Ethanol was measured at 16,100,000 µg/L in the most contaminated sample taken from this well less than 3 months after the release (this concentration is equivalent to 1.6% ethanol in the aqueous phase). Within 6 months of the release, ethanol had migrated in the groundwater more than 250 feet downgradient of the tank. The highest concentration measured at this point was 4,170 µg/L. Shortly after, the ethanol concentrations started to decrease; it was never detected above the practical quantitation limit at this well again. Other evidence collected at the site showed that biodegradation of ethanol in groundwater was significant and rapid.

As this was an oil terminal, there was residual contamination of refined petroleum products (including gasoline, diesel fuel, and other oils) in the soil where the ethanol was spilled. There was also a documented hydrocarbon plume in the groundwater that was created by previous spills. Six months after the neat ethanol spill, liquid petroleum (NAPL or non-aqueous phase liquid) appeared in a well located 20 feet upgradient of the release. At this time, petroleum NAPL was found to be 2.5-feet thick; it has since increased to 2.79-feet thick. The liquid petroleum was apparently remobilized when it came into contact with the ethanol that permeated the soil.

Measurements of benzene concentrations in groundwater showed that benzene increased by a factor of 15 within 5 months of the spill at a location 200 feet downgradient from the neat ethanol release. This increase could have been caused by two factors: (a) oxygen depletion in upgradient groundwater that inhibited natural attenuation of the benzene or (b) a cosolvency effect that increased solubility of benzene in groundwater (Buscheck, et. al., 2001). This research has not yet resolved which of these factors may have caused the high benzene concentrations in the monitoring wells. Indeed, both factors could be working to contribute to this effect.

Effects of E-blend Releases

E-blend releases are most likely to occur as a result of surface spills during splash blending of ethanol with gasoline, tanker truck accidents, underground or aboveground gasoline storage system failures, or end user (e.g., cars, gasoline powered equipment) spills. Currently, not much has been learned from field observations of E-blend releases into the environment. Most regulators have not been testing for ethanol at sites where groundwater contamination has occurred, even in the Midwest where E-blend has been used for 20 years or more (Rice et al. 1999).

According to recent research, ethanol dissolves rapidly from gasoline when rain washes it into the soil matrix and into groundwater or when a large E-blend release sinks deep into the soil and mixes with groundwater. When ethanol reaches groundwater, it is expected to be rapidly biodegraded by microorganisms. This rapid biodegradation process can deplete the groundwater or soil of oxygen.

The major potential human health effect from adding ethanol to gasoline is an increased risk of exposure to benzene, a known human carcinogen. An E-blend release into the environment may extend the length of a benzene plume in groundwater in comparison with a plume associated with conventional gasoline and M*t*BE-blended gasoline due to reduced natural attenuation of benzene. This has been shown by laboratory studies and mathematical groundwater flow models but has not been substantiated by field studies (Rice et al. 1999).

Because the primary effects of E-blend gasoline releases in the environment are most likely to be associated with groundwater fate and transport issues, a detailed discussion is put forth in the Fate and Transport Mechanisms section below.

Spill Size

The difference between the effects of large spills and small spills can be expected to be significant. Large spills (e.g., greater than 10 gallons) are typically associated with underground and aboveground storage systems at gasoline dispensing facilities and tanker truck accidents. It is at large spills where the full effects of oxygen depletion and benzene mobilization can be expected.

Small spills are more typically associated with household sources such as leaking automobile gas tanks and yard maintenance equipment, such as lawnmowers, tractors, weedwackers, and rototillers. In these situations it is expected that the less soluble constituents of spilled gasoline, including BTEX, will be retained in the unsaturated zone, and only ethanol will reach the groundwater where it will be biodegraded rapidly. It is likely that any ethanol or gasoline in groundwater from such small spills would be difficult to detect.

Denaturants

Denaturants, which are mixed in ethanol when it is not produced for use in liquor, are not likely to be an added environmental concern. In the past, methanol was typically used as a denaturant; however, gasoline is now used as the denaturant for ethanol used for blending in fuels. (See Chapters 1 and 5 for more information on the composition of fuel-grade ethanol.)

FATE AND TRANSPORT MECHANISMS IN GROUNDWATER

As discussed earlier, ethanol, by itself, does not appear to pose as serious a problem with respect to the contamination of groundwater as it does when it is blended with gasoline. If released into the subsurface as a neat substance, ethanol can be degraded rapidly by microorganisms until the necessary electron acceptors are depleted. E-blend gasoline, however, will enhance the groundwater transport of toxic components (BTEX) in gasoline (Powers et al. 2000).

Three environmental transport properties associated with ethanol are of particular concern:

- ▲ Depletion of oxygen and other nutrients in groundwater due to rapid biodegradation of ethanol that may inhibit the degradation of more toxic components in gasoline (e.g., BTEX) and make the dissolved plume of these components longer.
- ▲ A surface tension effect that takes place when ethanol is in contact with a layer of gasoline at the top of the water table. This effect can cause the gasoline to spread laterally.
- ▲ A potential cosolvency effect from a release of neat ethanol or E-blend with high concentrations of ethanol (e.g., 80% ethanol) that may make other gasoline constituents (e.g., BTEX) in soil or groundwater more soluble.

Oxygen Depletion

Depletion of oxygen, nutrients, and electron acceptors by rapid degradation of ethanol in a groundwater plume following a gasoline spill can be expected to have a significant impact on the length of benzene plumes. Microbes consume hydrocarbons to provide energy for themselves in much the same way that humans use food. The energy is derived from breaking the bonds in the hydrocarbon structure as the molecule is dismembered. To break the bond, an electron must be transferred to another chemical ion in groundwater to make this reaction proceed. The chemicals involved in this reaction are called electron acceptors. Oxygen, nitrate, ferric iron, sulfate, and carbon dioxide are the most common electron acceptors in this process (Corseuil et al. 1998).

Lab studies have shown that, due to biodegradation, ethanol has a half-life of two to three days in the presence of oxygen and nitrate. The half-life can be up to six or seven days when ethanol is in the presence of other electron acceptors. A half-life of three days means that ethanol will be reduced to less than 1 percent of its original concentration in as few as 21 days.

Benzene biodegrades most rapidly in the presence of oxygen. Its rate of degradation is on the order of 100 times slower in anaerobic (oxygen-depleted) groundwater. The early separation of ethanol from a gasoline spill can deplete the groundwater of dissolved oxygen (DO) very quickly so that the remaining benzene plume becomes subject to anaerobic conditions. The degradation of ethanol also consumes nutrients in groundwater that microbes need to degrade benzene anaerobically.

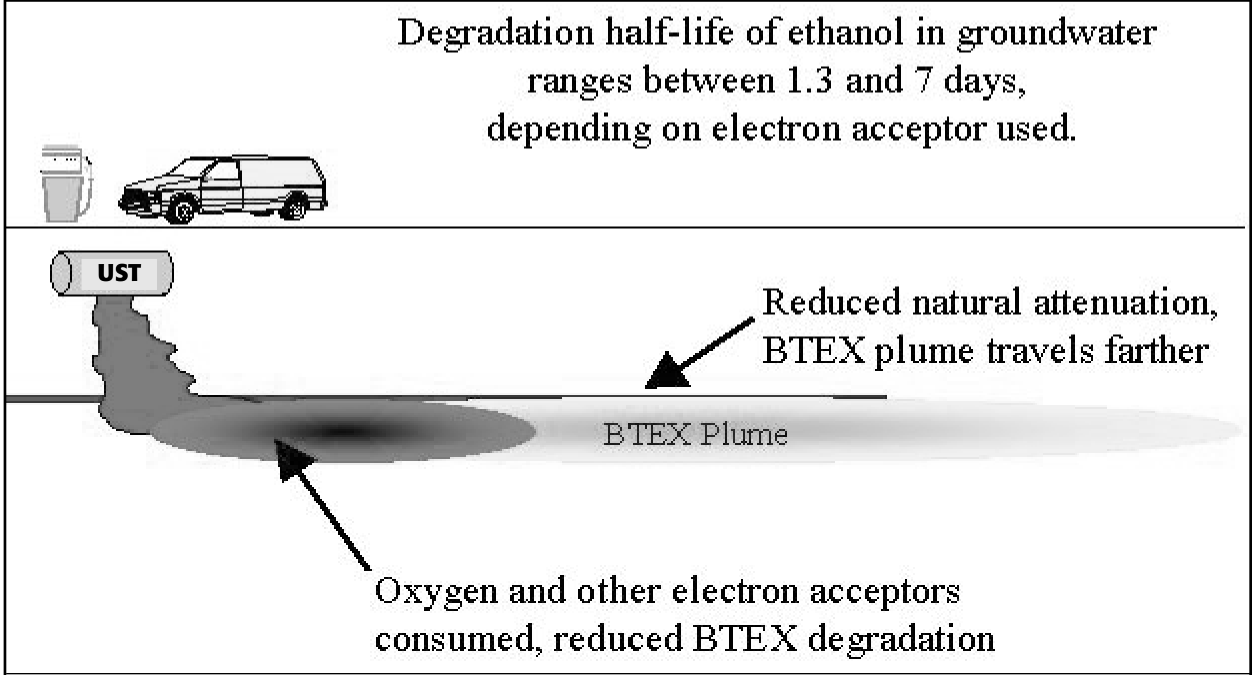
If both the benzene and the oxygen-depleted zones move at the same rate of speed, so that the benzene can't emerge from the oxygen-depleted zone, the benzene will degrade very slowly and travel significantly farther in a spill scenario. (See Figure 6.3.) As a result, the benzene plume may extend 10 to 150 percent longer than it would with an M*t*BE or conventional gasoline plume. Mathematical models have shown that benzene plumes may travel 1.1 to 2.5 times farther in this scenario than in a typical spill of M*t*BE-blended or conventional gasoline. (See Table 6.1.)

There is a degree of uncertainty in these predictions, because this process has never been observed closely in field studies. Benzene may, indeed, travel slightly slower than the oxygen shadow in groundwater. Proper field experiments are needed to determine the degree of truth in the modeling predictions.

Table 6.1 Predicted increase in the length of benzene plumes in E-blend compared with conventional gasoline.

MODEL REFERENCE	INCREASED BENZENE PLUME LENGTH
Malcolm Pirnie (1998)	+17-34%
McNabb et al. (1999) LLNL	Approx. + 100%
Molson, et al. (1999) Waterloo	+10-150%

Figure 6.3 Biodegradation impacts of ethanol on a BTEX plume.



Source: Powers, S. E. (2000) Subsurface Fate of Ethanol as a Gasoline Oxygenate, oral presentation at the Forum on Ethanol Blending in Gasoline in the Northeast and Mid-Atlantic, in Manchester, New Hampshire, June 27, 2000.

Surface Tension

If neat ethanol is spilled in sufficient quantities it can decrease the surface tension of the gasoline, and when it comes into contact with a layer of gasoline at the top of the water table it can cause lateral spreading of the gasoline layer (Powers et al. 2000). This type of effect can be expected to occur at sources such as gasoline distribution terminals, where soils have been contaminated by previous spills.

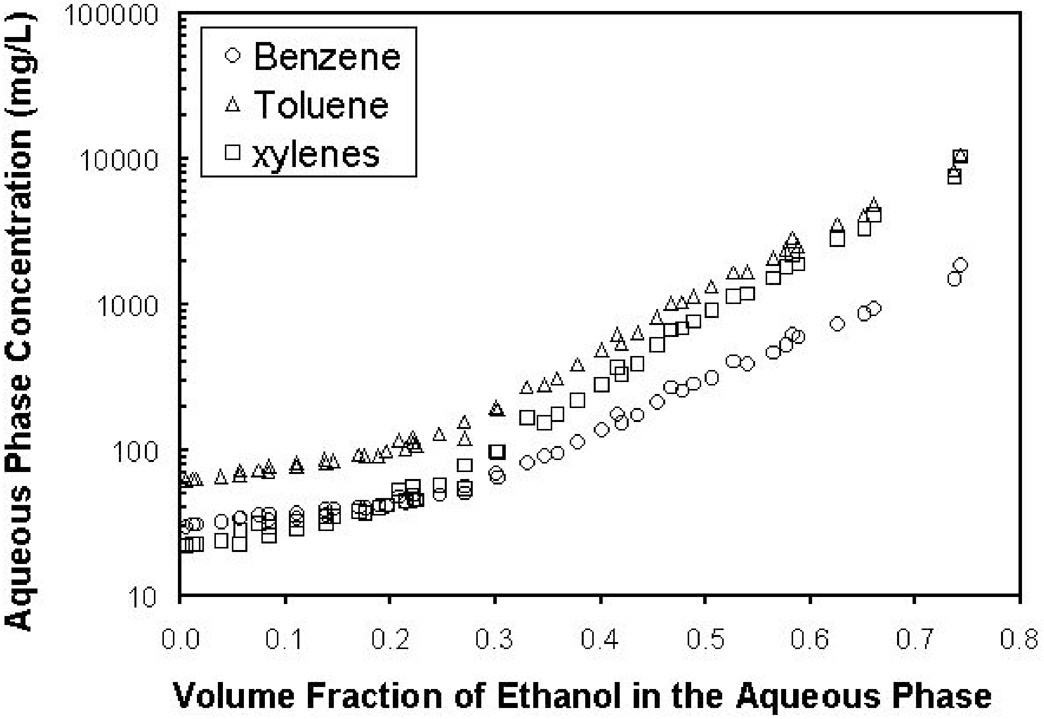
Cosolvency

Cosolvency occurs when one compound that is dissolved in water increases the solubility of another. When ethanol is present in water at concentrations greater than 20 percent, cosolvency becomes a factor. When an E-blend gasoline is released to soil, the hydrophilic ethanol rapidly and completely transfers from the gasoline blend into the aqueous phase. This quickly creates a halo of dissolved ethanol in the groundwater in the vicinity of the spill which, in turn, affects the other soluble constituents of gasoline.

The most soluble and toxic compounds in gasoline are the aromatics (i.e., BTEX). Most other components of gasoline are *not* readily soluble in water. The BTEX compounds begin dissolving quickly after reaching groundwater. Benzene travels the fastest and farthest of all nonoxygenate gasoline constituents and has the greatest impact on the toxicity of drinking water wells from a gasoline spill. Benzene plume lengths have been known to extend up to 1,000 feet. Although benzene and the other BTEX compounds dissolve, they do not do so as rapidly and completely as ethanol.

Laboratory studies show that there is a cosolvency effect in E-blends with high concentrations of ethanol. However, in mixtures of 15 percent or less ethanol in the aqueous phase, as expected from a typical spill of E-blend, the cosolvency effect would likely be insignificant. (Powers et al. 2000; Rice et al. 1999) (See Figure 6.4.) Thus in the scenario expected in the Northeast, cosolvency should only be a problem at bulk terminals where pure ethanol is released in gasoline-contaminated soil environments.

Figure 6.4 Effects of cosolvency on the solubility of benzene, toluene, and xylenes.



Source: Reprinted from the Journal of Contaminant Hydrology, Vol. 34, S.E. Heermann, p 377, 1998.

Ethanol versus M*t*BE in Groundwater

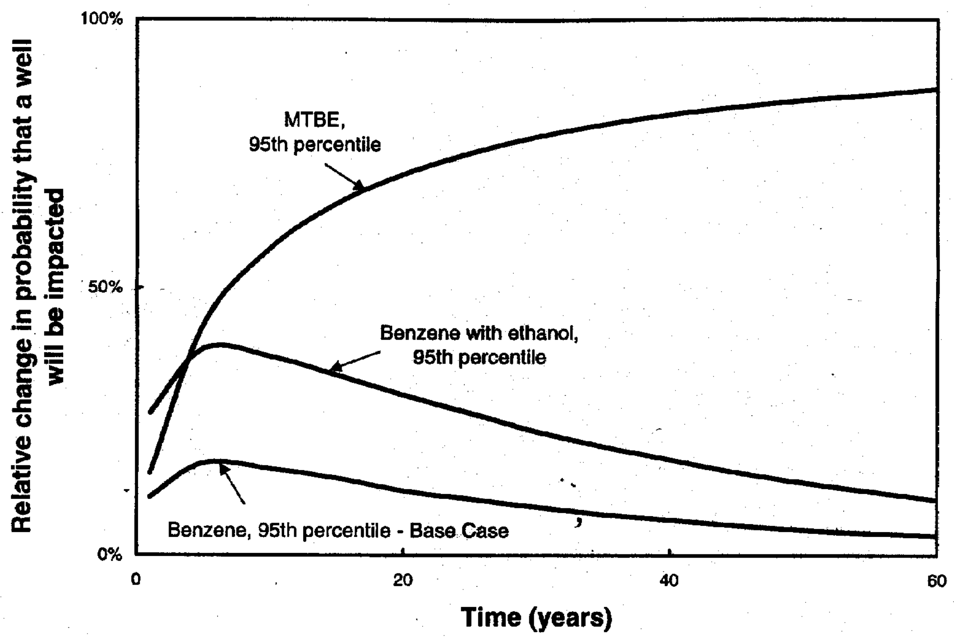
It is difficult to say with any certainty how ethanol or E-blend gasoline will behave in contrast with M*t*BE-oxygenated gasoline in similar spill scenarios because there is so little field experience with the effects of ethanol in groundwater. Based on the known principles, however, some differences can be predicted.

Because M*t*BE is both highly soluble and recalcitrant to biodegradation, it has the capability of traveling great distances in groundwater (3,000 to 5,000 feet or more). Thus reformulated gasoline with M*t*BE has the potential to affect higher numbers of drinking water wells than all other components of gasoline.

E-blend gasoline may not be as likely to contaminate wells with ethanol as are M*t*BE gasolines, however, they are believed to have the capacity to lengthen benzene plumes to distances of 1.1 to 2.5 times their typical length. The health effects of benzene are well known. Benzene is a known human carcinogen and is the most toxic component of gasoline.

In the interest of comparing M*t*BE and ethanol fuels with respect to their impact on groundwater, Dooher (Rice et al. 1999; Powers et al. 2000) built a complicated computer model to determine this effect. Such a large number of assumptions were needed that Dooher chose to present the trends graphically rather than numerically. The resulting graph in Figure 6.5 shows that, in the first five years, the number of wells that were affected by benzene after a spill of E-blend gasoline exceed the number of wells that were contaminated by M*t*BE. At five years the lines cross, and the number of wells contaminated by benzene start to decrease, while the number of wells contaminated by M*t*BE continue to increase.

Figure 6.5 A comparison of the impacts of M*t*BE gasoline and E-blend on drinking water wells.



Source: Powers et al. (2001) Will Ethanol-Blended Gasoline Affect Groundwater Quality? Environmental Science and Technology. Vol. 35 No. 1, pages 24a-30a.

Hence, Dooher predicts that the risk of wells being contaminated by benzene in E-blend (< 15 percent ethanol) is greater than the risk that they will be contaminated by M*t*BE during the first five years after an accidental release. However, over the long term (greater than five years), the risk of well contamination by M*t*BE greatly increases, while the risk of well contamination by benzene decreases gradually. With the significant uncertainties in this analysis, especially biodegradation rates, it can be concluded that the general trends presented in Figure 6.5 are realistic, although the numerical values (i.e., five years) could have significant error.

SURFACE WATER IMPACTS

The water quality benchmarks discussed in Chapters 3 and 4 of this report can be used to screen potential environmental ethanol concentrations to determine if any adverse impacts on surface water can be anticipated as the result of a release. The key surface water quality benchmarks for ethanol are as follows:

DRAFT DRINKING WATER COMPARATIVE VALUE	**0.4 mg/L**

Instream Ethanol Concentrations Capable of Depleting Instream Dissolved Oxygen

Small Stream	56 mg/L ethanol
Average River	32 mg/L ethanol
Large River	13 mg/L ethanol

Aquatic Life Water Quality Benchmarks for Ethanol

Acute	564 mg/L
Chronic	63 mg/L

Considering the Sources

Ethanol can enter surface water from three main sources: rainwater (through atmospheric volatilization and deposition), direct discharges (from spills or motor boats), and contaminated groundwater plume migration.

- ▲ **Rainwater** - The contribution of ethanol from rainwater is likely to be minimal. For example, air concentrations of ethanol ranging from 5.1 to 8.8 ppb (by volume) (Layton and Daniels 1999) are predicted to yield rainwater concentrations of 37 to 64 ppb. Ambient concentrations of ethanol at these levels are below any of the water quality benchmarks listed above. Furthermore, because ethanol is not persistent in the environment due to its high rate of biodegradation, it will not accumulate in the aquatic environment. Thus these ambient levels should not be harmful to the public or aquatic life, and it is likely that rainwater containing ethanol will not have a significant affect on surface water quality.

- ▲ **Direct discharges** - Releases of neat ethanol from bulk plants or terminals or from accidents during transport can pose a serious threat to the surface water environment. Direct spills to surface waters could yield very high concentrations of ethanol. This, of course, depends on such factors as the depth and width of water and the flow rate of the receiving water. Given that E-blend gasoline is likely to be comprised of 10 percent ethanol, high concentrations in direct proximity to the product spill could be expected. Poorly aerated water bodies (e.g., lake, pond, large river) can experience severe depletion of dissolved oxygen because of the biodegradation of ethanol. Oxygen depletion can result in massive kills of aquatic life. Large fish kills have resulted from such spills. For example, in May 2000, an estimated 500,000-gallon release of Wild Turkey bourbon (250,000-gallons ethanol) into the environment, including the Kentucky River, caused the worst fish kill in 50 to 60 years (Mead and Lander, 2000). A discharge of 2,500 barrels of beer into Clear Creek, near Golden, Colorado, killed more than 50,000 fish in August, 2000 (Gerhardt, 2000). A similar spill (which killed 17,000 fish) occurred in the same location in 1991.

- ▲ **Groundwater discharges** - High concentrations of ethanol may also be expected from groundwater discharges to surface water, particularly where the source of groundwater contamination is close to a surface water body. It is not possible to generalize what impacts contaminated groundwater plumes containing ethanol will have on surface waters. The contaminant concentration and mass transport will vary with the releases, and these factors make predictions of stream impact impossible. Any impact on surface water from a migrating contaminated-groundwater plume is affected by the distance of the contaminant source from the surface water body, the degree of attenuation and biodegradation that may take place, the hydrogeology of the groundwater environment, the hydrology of the surface water body, and the amount of contamination.

Primary Impact on Aquatic Life

There may be effects on aquatic life from the toxic properties of ethanol and because of the depletion of oxygen by ethanol biodegradation. High concentrations of ethanol could rapidly deplete or substantially lower dissolved oxygen (DO) concentrations in a receiving water. It would, therefore, be likely that a fish kill would be observed very shortly after the introduction of high ethanol concentrations. Although the human health-based benchmark is lower, the duration of exposure needed to have an impact on people is longer than the exposure needed to affect aquatic organisms. (See Impacts to Aquatic Life, Chapter 4.)

DRINKING WATER IMPACTS

In the Northeast, concern about the impact of E-blend on drinking water resources focuses on groundwater—the source of both public and private drinking water wells. Significant portions of the region derive drinking water from groundwater resources. In Connecticut, for example, more than 250,000 public and private groundwater wells serve more than one-third of the state's population. In Massachusetts, 29 percent of the population served by public water systems uses groundwater exclusively and 44 percent use a mix of groundwater and surface water.

Public water systems served by surface water reservoirs have historically been less susceptible to gasoline contamination. This fact was borne out in Connecticut, where no public supplies derived from surface water have violated any of the drinking water standards (maximum contaminant levels, MCLs) established for gasoline components, and in Massachusetts, where the state database, going back to 1993, shows that no public systems (using either surface water or groundwater) have violated any of these MCLs.

The tendency for gasoline to volatilize and biodegrade in surface water is such that the water quality in reservoirs has not generally been at risk. In addition, compliance with the MCL for this class of compounds is based on a state-specific process, such as a running annual average of quarterly sample results. Typical spills would not result in contamination sufficient to persist in surface water over the course of a year. Although one sampling event may trigger an MCL violation, the levels of contamination would have to exceed the MCL by a factor of four.

Drinking Water Issues Associated with M*t*BE

Throughout the Northeast, drinking water wells have been contaminated by gasoline that has found its way to groundwater as the result of a leak or spill. In Connecticut, since the start of recordkeeping in 1980, nearly 400 drinking water wells, primarily private wells serving residential or commercial properties, have been contaminated with components of gasoline at concentrations exceeding health standards. Leaking underground storage tank (LUST) systems have been the primary cause of these occurrences, although overfills, incidental spills of small volumes, and transportation accidents have also played a part.

M*t*BE was introduced as a gasoline additive in 1979 to enhance octane when lead was removed from gasoline. It was usually present in concentrations of 2 to 8 percent by volume. It was found to be a common contaminant of groundwater when investigators sampled specifically for it. Prior to the early-1980s, the primary gasoline components found in wells were the BTEX compounds. These remain the only gasoline components regulated in the federal Safe Drinking Water Act. However, in the mid 1990s, when M*t*BE was added to gasoline at 11 percent by volume for RFG, it became the most common gasoline component found in drinking water.

In Massachusetts, since 1993, BTEX compounds have been detected in 157 sampling locations at public water systems. Since mid 1999, when M*t*BE sampling was mandated by the state, the ratio of detections of M*t*BE to BTEX has been about 4:1. In Connecticut, since 1980, BTEX compounds have polluted 159 public and private wells. Since 1987, another 243 wells have been contaminated by M*t*BE at concentrations above state health standards. Of the Connecticut wells polluted by M*t*BE from LUSTs, about 80 percent have also been affected by other components of gasoline. In contrast, the wells polluted by M*t*BE from small incidental spills of gasoline are affected primarily by M*t*BE alone.

Since 1995, RFG containing M*t*BE has been widely used in the southern New England states and New York. Trace levels of M*t*BE (less than 10 ppb) have been found in drinking water wells, even in areas where USTs or direct spills of gasoline have not been identified as the source of contamination.

In a 1998 survey by the Maine DEP of more than 1,000 public and private drinking water wells, 15.8 percent were found to have detectable concentrations (greater than 0.1 ppb) of M*t*BE. The Connecticut DEP samples about 1,000 private and non-community drinking water wells for volatile organic compounds (VOCs) annually. These samples have revealed that 25 to 30 percent of the wells located in areas where there have been no identified spills of gasoline contained trace but quantifiable concentrations of M*t*BE.

In Massachusetts, during the period of July 1999 through June 2000, 640 public water systems conducted routine VOC monitoring, required by the state to include M*t*BE. One hundred (16 percent) of these systems reported M*t*BE detects (greater than 0.5 to 1.0 ppb). Looking at these data by sampling locations (since many public water systems rely on more than one source of water), Massachusetts found that 11 percent (147 of 1,366 locations) detected M*t*BE. The average detected concentration was 3.1 ppb. Four samples exceeded 20 ppb, but none were over the state guideline of 70 ppb. By comparison, only 40 locations (3 percent) detected any of the BTEX compounds (greater than 0.5 ppb).

The regional use of M*t*BE-RFG has also amplified the impact that incidental spills of small volumes of gasoline have had on drinking water wells. In Connecticut, for example, from 1994 through 1995, 33 drinking water wells polluted with M*t*BE were found. LUSTs were identified as the source of the contamination in all but two of these cases. Small incidental spills of gasoline at properties other than gas stations accounted for the rest.

More recently (1999 through 2000) in Connecticut, 29 drinking water wells were identified that were contaminated with M*t*BE above the state drinking water standard. Of those, only six cases were linked to releases from LUSTs or other gas station-related releases. The other 23 wells (80 percent) found to be polluted by M*t*BE were associated with small spills at homes and businesses. Many of the wells were affected by spills of no more than a few gallons.

In general, spills of gasoline, whether from LUSTs or accidental surface spills, have contaminated hundreds of water supplies in the Northeast.

Drinking Water Issues Associated with E-Blend

Although it is not possible to quantify the effects of replacing M*t*BE with ethanol in gasoline on drinking water resources, some changes can be anticipated. Because of ethanol's significantly higher rate of biodegradation compared with M*t*BE, it is anticipated that ethanol itself would contaminate significantly fewer drinking water wells in the region than has M*t*BE.

It is estimated that ethanol will be present as a groundwater pollutant only in the immediate vicinity of a significant spill and for a relatively short duration compared with M*t*BE. This situation, however, can vary depending on the site-specific conditions and the possibility of an undetected continuous source of E-blend (e.g., from a LUST). It is also anticipated that the effect on drinking water quality from incidental small spills of E-blend would be no different than spills of conventional gasoline.

If this oxygenate replacement takes place, future M*t*BE contamination in groundwater and drinking water wells should be reduced or even eliminated. This trade off, however, between M*t*BE and ethanol must be weighed against the relative risk of a small but potentially significant increase in BTEX contamination in drinking water resources when using E-blend. This concern is due to interactions yet to be fully explored, such as the increase in solubility of aromatic hydrocarbons (cosolvency) and ethanol's potential to delay the biodegradation of BTEX compounds. These effects could lead to more extensive benzene plume lengths than would be expected from an M*t*BE-RFG spill. The debate on balancing this trade off must incorporate the current diversity of opinion on the appropriate M*t*BE health standard against the known carcinogenicity of benzene.

The potential effects of E-blend on drinking water supplies should also be evaluated in light of how easily such impacts can be remediated. Currently, M*t*BE-contaminated wells are treated primarily with conventional absorptive filtration systems. M*t*BE, however, is more difficult to remove with activated carbon than BTEX, thus larger treatment systems and more frequent replacement of the activated carbon has been necessary. Removing M*t*BE from this remediation scenario, even if this results in an increase in easily treatable BTEX contamination, may result in less costly and extensive treatment solutions.

Releases of Neat Ethanol

As in the case with E-blend gasoline, it is not possible to quantify the impact of releases of neat ethanol to drinking water resources in the region. It is anticipated that spills of ethanol are not likely to migrate in significant amounts to drinking water resources. In the event that a large quantity does reach a surface water body or groundwater resource, the rate at which ethanol degrades suggests that drinking water impacts would be short in duration and restricted to a large-volume spill scenario.

Outside of ethanol-BTEX interactions discussed above, neat ethanol spills raise a few new concerns. Large-volume spills have the potential to mobilize both naturally occurring and anthropogenic contaminants present in soils. These would include natural deposits of certain metals, such as iron and manganese, which could be made soluble, due to a change in the oxidation state of components of the soils, and dissolve into groundwater at concentrations that exceed either aesthetic or health-based standards.

In addition, previously contained organic contaminants from past spills (e.g., gasoline components adsorbed to soils) may spread and enter water resources. It is expected that such impacts could be reversible and of short duration, because after the ethanol biodegrades, rainwater infiltration returns soil conditions to their pervious state. However, more evidence is needed to support this prediction. Small spills of a few gallons of ethanol on the ground surface would be expected to have no impact on groundwater or drinking water quality.

REMEDIATING ETHANOL-CONTAMINATED SOIL, GROUNDWATER, AND SURFACE WATER

The remediation of gasoline spills is driven by remedial goals (set by a regulatory authority), the physical properties of the material to be removed (see Table 6.2), and, in some cases, the ease with which microorganisms can utilize the contaminants in question as a source of food.

In considering the potential for a change from the use of M*t*BE to ethanol as the primary oxygenate in gasoline, it is important to recognize that the physical properties of gasolines that contain ethers differ from those that contain alcohols. These differences will affect the behavior and distribution of the gasoline constituents in the subsurface and the applicability of remedial technologies used to clean up these materials in the environment.

Site Characterization

The characteristics of a contaminated site must be thoroughly understood so that an effective remediation plan can be designed. In many ways the site characterization of an E-blend release will be similar to that of a conventional gasoline release. The rapid rate at which ethanol may degrade in the environment or flow down gradient of the site as an aqueous plume, however, makes the behavior of E-blend slightly different from conventional gasoline. This factor must be considered in the site investigation. A site characterization will be done the same way for E-blend releases as for M*t*BE-blended gasoline sites with the exception that it is important to measure for ethanol, dissolved oxygen, and the anaerobic electron receptors iron (Fe), nitrate (NO_3), and sulfate (SO_4) at E-Blend sites to estimate the capacity of the aquifer to attenuate the plume naturally.

Table 6.2 Properties of benzene, M*t*BE, and ethanol.

PROPERTY	UNITS	BENZENE	M*t*BE	ETHANOL
Molecular weight	g/mol	78.11 (10)	88.15 (10)	46.07 (10)
Density @ 20°C	specific gravity	0.8765 (10)	0.7405 (10)	0.7893 (10)
K_{ow}	dimensionless	36.3 – 141.0 (2)	8.7 (1)	0.5 (1)
K_{oc}	ml/g	38 (8)	11.5 (8)	1.5 to 16.2 (2)
Vapor pressure	mm Hg	76 – 95 (2)	245 - 256 (2)	59.26 (4)
Boiling point	°C	80.1 (10)	55.2 (10)	78.5 (10)
Auto-ignition	°F	1044 (5)	371 (6)	793 (5)
Solubility in H_2O	mg/L	1,780 (2)	43,000 (9)	miscible (2)
Henry's law constant	atm	230	27	0.35 (7)
Henry's law constant	dimensionless	0.22 (8)	0.0216 (1) – 0.0416 (8)	0.00026 (1)
Adsorption Capacity at 1ppm	mg contaminant/g carbon	32 (3)	13 (3)	0.02 or not adsorbed (3)
Concentration in "plume"	mg/L	8 *	473 **	4000 *

* see Rice et. al., 1999, Ch.2, pg 2-23.

** effective solubility of 11% M*t*BE in Reformulated Gasoline with a 10 fold dilution.

Table 6.2 References

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Available Cleanup Technologies

Over the course of time, regulatory agencies have developed a "tool box" of technologies that they rely on for the majority of their LUST site cleanups. Table 6.3 lists the technologies most commonly used in the Northeast.

These technologies can be grouped into three major treatment categories that are based on gross physical descriptions of the distribution, phase, and mobility of the contaminants. These categories are mobile light non-aqueous-phase liquid (LNAPL), residual LNAPL/gross soil contamination, and groundwater. We'll discuss the available treatment technologies within the context of their respective treatment categories.

Table 6.3 Remedial technologies for gasoline-contaminated soil and groundwater.

Soil Remediation	Groundwater Remediation
Soil vapor extraction (SVE)	Pump and treat w/granular-activated carbon
Excavation and disposal	Pump and treat with air strippers
Dual-phase extraction	Pump and treat with biological treatment
Excavation and land farming	Air sparging/SVE
Excavation and biopiles	Biosparging with air
Excavation and low temperature thermal desorption	Biosparging with oxygen
Bioventing	In-Situ bioremediation with oxygen release compound
Monitored natural attenuation	In-Situ bioremediation (other)
	Monitored natural attenuation

SOIL AND GROUNDWATER REMEDIATION TERMS

Mobile LNAPL - Light non-aqueous-phase liquid that fills a sufficient percentage of the pore spaces in a soil formation to induce flow under the influence of gravity or a pressure gradient.

Residual LNAPL - Soil in which light non-aqueous-phase liquid is present. The LNAPL fills few enough pore spaces that it is held in place by capillary forces.

Gross Soil Contamination - Soil that has absorbed as much contaminant as it can and may function as a source of groundwater contamination into the future.

Groundwater - Water in the saturated zone of a formation where the hydraulic pressure equals or exceeds the atmospheric pressure.

Options for Treating Mobile LNAPL (free product)

Soil Vapor Extraction (SVE)

Soil vapor extraction is used to remediate unsaturated (vadose) zone soil by applying a vacuum to extraction wells placed in the soil and inducing a controlled movement of soil vapors toward the wells. Extracted vapors are treated and discharged above ground. This technology is expected to be less effective with ethanol than with M*t*BE gasoline spills, but it is still applicable to E-blend gasoline sites.

E-blend LNAPL in which ethanol is still present will have lower interfacial and surface tensions (Rice et al., 1999) than M*t*BE gasoline. This characteristic may reduce both the amount of product retained in the vadose zone and the height of the capillary fringe, making the LNAPL less amenable to remediation via soil vapor extraction. The E-blend LNAPL pool may also be vertically thinner and horizontally wider than that of an M*t*BE gasoline spill of similar volume.

The vapor pressure of ethanol is considerably less than M*t*BE but similar to benzene (see Table 6.2), therefore the response of E-blend to soil vapor extraction should be no worse than that of a weathered M*t*BE gasoline. This technology will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Excavation and Treatment or Disposal

These technologies are expected to be applicable to E-blend gasoline spill sites and will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

E-blend LNAPL in which ethanol is still present will have lower interfacial and surface tensions (Rice et al., 1999) than M*t*BE gasoline. Although the LNAPL pool may be vertically thinner and horizontally wider than a pool with an M*t*BE gasoline source, excavation costs are not expected to rise tremendously in relation to the increased aereal extent of the LNAPL pool. The extent of the LNAPL pool usually does not determine the extent of the excavation, and if LNAPL were left in place, it would have to be addressed with a different technology.

E-blend-contaminated soil should respond at least as well as or better than M*t*BE gasoline-contaminated soil to remediation through biopiles or thermal desorption.

Disposal of groundwater from dewatering operations may be problematic if large volumes of water with high ethanol concentrations are produced.

Dual-Phase Extraction

Dual-phase extraction is an in-situ technology that uses a vacuum system to remove groundwater, free product, and vapors from the subsurface. This technology is expected to be applicable to E-blend gasoline spill sites.

E-blend LNAPL in which ethanol is still present will have lower interfacial and surface tensions (Rice et al., 1999) than M*t*BE gasoline. This characteristic may enhance the recovery of product through dual-phase extraction because of better drainage from the vadose zone and freer flow in the capillary fringe. Ethanol-depleted E-blend should respond in a manner similar to M*t*BE gasoline, however, the LNAPL pool may be thinner and wider than a pool with an M*t*BE gasoline source.

This technology will most likely be employed in combination with remedial technologies that treat residual LNAPL/gross soil contamination and/or those that control the migration of, or treat the aqueous-phase plume.

Options for Gross Soil Contamination and Residual LNAPL

Excavation and Disposal

Generally 10 to 20 percent of the pore spaces in the portion of the vadose zone through which a mobile LNAPL passes will remain filled with immobile drops of LNAPL (USEPA, 1995) (the residual LNAPL saturation). If soil with residual LNAPL is excavated, it must be recycled, treated, or disposed of in a permitted landfill.

E-blend LNAPL in which ethanol is still present will have lower interfacial and surface tensions (Rice et al., 1999) than M*t*BE gasoline. This characteristic may reduce the amount of product retained in the vadose zone. In theory, a lower percentage of the released product would be recovered with the excavated material.

Compared with benzene and M*t*BE, ethanol has a fairly low organic carbon partitioning coefficient (K_{oc}). Ethanol will not adhere well to the fractional organic content in soils (Davidson and Creek, 2000). Once the product is no longer present, very little ethanol should remain in the contaminated soil, and excavation and disposal should be similar to an M*t*BE gasoline source.

These technologies will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Excavation and Biopiles

Biopile technology involves placing excavated contaminated soils into piles on a lined surface and stimulating microbial biodegradation of the contaminants by the injection or extraction of air through perforated piping placed throughout the pile or through periodic tilling. If necessary, it may involve the addition of minerals, nutrients, and moisture. Ex-situ bioremediation through biopiles should be an applicable technology for E-blend-contaminated soils as long as the TPH is below 50,000 ppm. Higher concentrations are found to inhibit microbial growth (USEPA, 1995).

Compared with benzene and M*t*BE, ethanol has a fairly low K_{oc}. Ethanol will not adsorb well to the fractional organic content in soils (Davidson and Creek, 2000). Once the product is no longer present, very little ethanol should remain in the contaminated soil.

These technologies will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Excavation and Landfarming

Landfarming involves spreading excavated contaminated soils in a thin layer directly on the ground surface and stimulating microbial biodegradation of the contaminants by aeration (tilling or plowing) and/or the addition of minerals, nutrients, and moisture.

Because ethanol is moderately volatile in the non-aqueous phase (Davidson and Creek, 2000), and the compound is highly biodegradable, E-blend-contaminated soils should respond to landfarming at least as well as those contaminated with M*t*BE gasoline. If residual saturation with LNAPL is present, however, there is an increased risk of groundwater contamination due to the exceptionally low Henry's law constant of ethanol (see Table 6.2) because there is no liner present as is the case with a biopile. There will also be an increase in air emissions.

These technologies will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Excavation and Low Temperature Thermal Desorption

Low temperature thermal desorption (LTTD) is an ex-situ technology that uses heat (90°C to 320°C) to volatilize and strip out water and organic contaminants from contaminated soils. The applicability and effectiveness of LTTD as a remedial technology for petroleum-contaminated soils is dependent upon both the characteristics of the soil to be treated and the composition of the petroleum product present. Assuming soil conditions are within the desirable range, LTTD will be as applicable for E-blend-contaminated soils as it is for those contaminated with M*t*BE gasoline-contaminated site.

Boiling point is one of the physical characteristics of a compound that can be used to assess the appropriateness of LTTD (USEPA, 1995). The boiling point of ethanol (78.3°C) is between those of benzene (80.09°C) and M*t*BE (55.2°C) and therefore should not have an adverse effect on the applicability of this method.

Compounds with high octanol/water partitioning coefficient (K_{ow}) values tend to stay sorbed to the soil longer and are more difficult to desorb than those with low K_{ow}s (USEPA 1995). The K_{ow} of ethanol is an order of magnitude lower than that of M*t*BE and two to three orders of magnitude lower than that of benzene. This low K_{ow} should promote relatively rapid desorption.

Vapor pressure also influences the rate of desorption (USEPA, 1995). The vapor pressure of ethanol (59.26 mm Hg) is lower than that of M*t*BE (245 mm Hg) but similar to that of benzene (76 mm Hg). In addition, the vapor pressure of a compound increases exponentially with temperature. Neither K_{ow} nor vapor pressure of ethanol would preclude the use of LTTD on E-blend-contaminated soils when compared with M*t*BE gasoline.

Petroleum hydrocarbons are not expected to decompose or combust within LTTD units (USEPA. 1995). To discourage decomposition and combustion, the off-gas temperature should be below the temperature at which the compounds being treated spontaneously combust (the auto-ignition temperature). While the auto-ignition temperature of ethanol is lower than that of benzene, it is considerably higher than that of M*t*BE and therefore should not be a controlling factor when comparing the applicability of this technology in treating E-blend-contaminated soils to that of M*t*BE gasoline-contaminated soils.

These technologies will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Soil Vapor Extraction

At sites where there is residual saturation of E-blend LNAPL, this technology is expected to be effective, but less so than at M*t*BE gasoline-contaminated sites. The high solubility, low K_{ow}, and low Henry's law constant associated with ethanol all promote the dissolution of the compound into water rather than volatilization and transport as soil vapor or sorption onto the soil. Once the ethanol has been dissolved out of the E-blend gasoline, the remaining product should respond like a weathered M*t*BE gasoline.

One other factor affecting the efficiency of this remedial technology is the reduced interfacial and surface tensions of the E-blend LNAPL when compared with M*t*BE gasoline (Underground Tank Technology Update, 2000). These reduced tensions would result in lower residual saturations in the vadose zone and reduced thicknesses of capillary fringes. Both of these phenomena would result in less surface area available for the evaporation of the immobile portion of the LNAPL.

This technology will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Bioventing

Bioventing is an in-situ technology that relies on naturally occurring soil bacteria to break down contaminants in the vadose zone using aerobic respiration. Assuming a soil-volumetric air content of 28 percent (Kou, 1999) and an oxygen content in the soil gas of 20 percent, a pore volume of soil gas can supply enough oxygen to mineralize about 14 ppm of hydrocarbon. In theory, when the contaminant concentrations in soil exceed this value, remediation could be stimulated by promoting the exchange of soil gas by injection under pressure, or removal under vacuum.

Bioventing should be effective in the treatment of midweight hydrocarbons (USEPA, 1995) that remain after the lighter weight components of E-blend gasoline have dissolved into groundwater or evaporated into the soil gas. Bioventing may be more effective at E-blend sites than at M*t*BE gasoline sites, because ethanol would preferentially dissolve into groundwater (Rice et al., 1999), resulting in lower initial contaminant concentrations in soil. In addition, any remaining ethanol would be amenable to biotransformation, as opposed to M*t*BE, which is often considered to be recalcitrant.

This technology will most likely be employed in combination with a remedial technology that treats or controls the migration of the aqueous-phase plume.

Monitored Natural Attenuation

Monitored natural attenuation (MNA) refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored cleanup approach) to achieve remedial objectives within a time frame that is reasonable compared to that offered by more active methods (USEPA OSWER, 1999).

Due to the physical effects that the addition of large amounts of ethanol to gasoline will have on the ability of LNAPL to flow and its distribution in the subsurface (less retention in the vadose zone and a thinner capillary fringe (Rice et al., 1999)), the recoverability of E-blend LNAPL may initially be improved over that of M*t*BE gasoline. Conversely, aged E-blend LNAPL may form thin but extensive lenses on the water table that could be difficult to remove.

If recoverability is in fact enhanced, this would lead to a lower residual-phase mass, which would be favorable to MNA subsequent to source removal.

On the other hand, the ethanol fraction of E-blend gasoline is highly mobile and will readily biotransform. These characteristics will affect the concentration and distribution of terminal electron acceptors (TEAs), which may in turn lead to erroneous predictions of the assimilative capacity of the affected formation/aquifer system and an inaccurate prediction of the time frame used in the evaluation of this remedial option.

More information (and experience) about the behavior of E-blend in the subsurface needs to be acquired before this option can be addressed.

Options for Groundwater Contamination

Pump and Treat

Regardless of the treatment alternative, all groundwater plumes resulting from E-blend gasoline spills will have some characteristics in common. These characteristics are a function of the physical properties of ethanol—high solubility, hygroscopic nature, low retardation due to low K_{oc}, high oxygen demand due to rapid biodegradation.

In theory, E-blend gasoline should form long plumes that have been depleted of TEAs and should have elevated concentrations of soluble iron and manganese due to anaerobic processes. A “shadow” of low dissolved oxygen (DO) groundwater may precede the contaminant down gradient. Because of the inhibitory effect the presence of ethanol may have on biotransformation (Rice et al., 1999), the BTEX may also extend further down gradient than it would with M*t*BE gasoline. These characteristics may increase both the cost of delineating a contaminant plume and the time and resources required for remediation. Confirmation or contradiction of this pattern has not yet been obtained from areas of the country where E-blend is currently in use.

Pump and Treat with Granular Activated Carbon

Adsorption of ethanol from water that is passed through beds of granular activated carbon (GAC) is not expected to be an efficient treatment technology for E-blend because of a low K_{oc} value. As shown in Table 6.2, the adsorption capacity of ethanol is three orders of magnitude lower than that of either benzene or M*t*BE. This indicates that, for practical purposes, ethanol will not adsorb onto GAC (Sutcliffe 2000). If GAC treatment were to be used on groundwater contaminated with E-blend, it would remove the petroleum hydrocarbons (which are the most toxic constituents) and allow the ethanol to pass through.

Pump and Treat with Air Strippers

Air stripping is an ex-situ technology that enhances the volatilization of organic compounds from water by passing clean air through the water. Air strippers are not expected to be an efficient technology for the removal of ethanol from water.

The minimum air to water ratio can be used to obtain a general estimate of the efficiency with which a given compound will strip out of contaminated water. Benzene, which responds relatively well to this technology, has a minimum air to water ratio of 4.5 to 1. M*t*BE, which is a compound that is difficult to treat with an air stripper, has a minimum air to water ratio of 46 to 1. The minimum air to water ratio for ethanol is estimated to be around 3,800 to 1 (Kou 1999), almost three orders of magnitude greater than that for benzene. This high air to water ratio makes this option impractical.

If the remedial goal is to remove petroleum hydrocarbons from the groundwater with the treatment system but let the ethanol pass through, air strippers still may not be an applicable technology. If elevated concentrations of iron and manganese are encountered due to anaerobic degradation of aqueous-phase ethanol, these dissolved constituents may cause fouling of the equipment when the water is reoxygenated. The insoluble oxides would precipitate. In theory, this effect may drive up the equipment maintenance costs.

Pump and Treat with Biological Treatment

As discussed previously, ethanol is highly amenable to treatment through biological degradation. Bacteria will metabolize the ethanol and covert it to carbon dioxide, water, and new bacterial cells. Aboveground treatment in bioreactors can be a viable alternative if the concentration of ethanol and other organic contaminants in the groundwater is sufficiently high to maintain a bacterial population. Treatment in bioreactors allows for the control of oxygen, nutrients, and bacterial population to insure the treatment process operates at maximum efficiency over the shortest period of time (hours rather than days). The types of bioreactors used in a pump-and-treat system include fixed-film bioreactors, fluidized-bed reactors, and sequencing batch reactors.

The biological treatment process would generate waste sludge that would have to be handled properly. Similarly, the effluent from the process would likely have to be disinfected prior to recharge back to the groundwater.

Biological treatment may not be effective for low concentrations of ethanol (i.e., less than 10 ppm). The concentration may be too low to support an active biological population. A supplemental food source would be required to maintain the treatment process, adding to the cost. As an alternative, the contaminated groundwater could be discharged to a sewer system for treatment at a nearby treatment facility. Local municipal approval would be required and would have to consider other VOCs that might be present in the groundwater.

Air Sparging

Air sparging is an in-situ remedial technology that reduces the concentration of volatile contaminants in groundwater. This technology involves the injection of air into the saturated zone to allow a phase transfer of contaminants from the dissolved phase into the vapor phase. Soil vapor extraction systems are often used in conjunction with air sparging to control off-gas at sites where there is highly contaminated groundwater and /or residual LNAPL beneath the water table or within the capillary fringe.

Air sparging works best for compounds with Henry's law constants that are above 100 atm (USEPA, 1995). The Henry's law constant for ethanol is 0.35 atm, indicating that ethanol is a poor candidate for removal from groundwater by means of air sparging.

Biosparging and In-Situ Bioremediation

Biosparging and in-situ bioremediation are technologies that use indigenous micro-organisms to biodegrade organic constituents in the saturated zone (USEPA, 1995). The biosparging process is similar to air sparging but uses lower airflow rates. However, while air sparging removes constituents primarily through volatilization, biosparging primarily promotes biodegradation of the constituents of concern (USEPA, 1995).

Ethanol is readily biodegradable (Davidson and Creek, 2000) and should respond to both biosparging and in-situ bioremediation as well as or better than the petroleum hydrocarbon components of gasoline. The completeness of the remediation of E-blend gasoline plumes may be strongly dependent on the concentration of ethanol at the point of treatment and the technology/design chosen.

Biosparging with Air

Although the oxygen transfer efficiency associated with sparging using air may be low (Kou, 1999), air is available at no cost. Provided enough air is injected into the saturated zone, it may be possible to achieve DO levels approaching those of water at equilibrium with the atmosphere (9 ppm @ 20°C). From a stoichiometric perspective, this would be enough oxygen to mineralize about 3 ppm of ethanol.

If a dissolved E-blend plume had a 4,000 ppm concentration of ethanol near the source, it is unlikely that a single line of sparge points perpendicular to groundwater flow would be sufficient to remediate it effectively. The number and spacing of the additional sparge points would depend on the permeability of the formation, the groundwater seepage velocity, and the radius of influence for each point.

Biosparging with Oxygen

Air is only about 20 percent oxygen. Water saturated with air has a DO content of about 9 ppm (Kou 1999). By sparging with pure oxygen the DO content can be raised to about 45 ppm. From a stoichiometric perspective, this would be enough oxygen to mineralize about 15 ppm of ethanol.

If a dissolved E-blend plume had a 4,000 ppm concentration of ethanol near the source, it is unlikely that a single line of sparge points perpendicular to groundwater flow would be sufficient to remediate it effectively. The number and spacing of the additional sparge points would depend on the permeability of the formation, the groundwater seepage velocity, and the radius of influence for each point.

In-Situ Bioremediation (ORC)

The most commonly used oxygen release compound (ORC) is produced by Regenesis and contains 10 percent oxygen by weight. It is commonly applied as a powder to excavation backfills or as a dilute (< 30 percent) slurry through pressure injection into the saturated zone. Over time, the ORC reacts with groundwater to release oxygen:

$$MgO_2 + H_2O \rightarrow 1/2O_2 + Mg(OH)_2$$

The maximum DO concentration can reach 40 to 50 ppm. The oxygen release duration may be 6 months, but it will vary depending on the mass of ORC injected, the groundwater flux, and the temperature (Regenesis, 1996-97). The major advantage to this technology is that it requires no permanent infrastructure other than access for monitoring. High cost of the ORC is one of the drawbacks.

If a dissolved E-blend plume had a 4,000 ppm concentration of ethanol near the source, it is unlikely that a single line of injection points perpendicular to groundwater flow would be sufficient to remediate it effectively. The number and spacing of the additional injection points would depend on the permeability of the formation, the groundwater seepage velocity, and the radius of influence for each point. It may be necessary to perform multiple rounds of ORC injection. With such a high concentration, ORC may be costly.

In-Situ Bioremediation (other)

When injected into the saturated zone, hydrogen peroxide disassociates into oxygen and water. Dissolved oxygen concentrations of up to 500 ppm can be achieved to promote aerobic biodegradation. It is possible to generate even higher DO concentrations through this technique, however, the point at which H_2O_2 is toxic to microorganisms would be approached or exceeded (Kou, 1999).

From a stoichiometric perspective a DO concentration of 500 ppm would be sufficient to mineralize about 160 ppm of hydrocarbon. It should be remembered, however, that the H_2O_2 is injected as a solution and will displace contaminated groundwater through radial flow away from the well screen. Complete mixing of the H_2O_2 and groundwater may be limited to diffusion and dispersion after the regional advective flow is reestablished.

Another product that can be used for in-situ bioremediaton is calcium peroxide. It will release the oxygen more quickly than ORC. However, it will have a shorter period of effectiveness.

Monitored Natural Attenuation

Monitored natural attenuation (MNA) refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored cleanup approach) to achieve remedial objectives within a time frame that is reasonable compared to that offered by more active methods (USEPA OSWER, 1999). It is to be expected that MNA would not be an acceptable alternative for sites situated in proximity to sensitive receptors.

MNA can utilize mechanisms that may be classified as destructive and nondestructive. Biodegradation is generally the most important destructive mechanism (Wiedemeier et al., 1999).

When dissolved in groundwater, the ethanol fraction of E-blend is highly mobile and will readily biotransform under both aerobic and anaerobic conditions (Underground Tank Technology Update, 2000). Because microorganisms can utilize DO and nitrate in areas of dissolved-phase hydrocarbon contamination at rates that are instantaneous relative to the average advective transport velocity, the use of these electron acceptors is a mass transport-limited process (Wiedemeier et al., 1999).

The rate of TEA utilization within a contaminant plume versus the rate of replenishment through advection, diffusion, and dispersion will affect the ability of an aquifer to attenuate the contaminant (the assimilative capacity) and, consequently, the distance over which the plume will migrate and the time frame anticipated for its return to a useful state.

As stated previously, water at equilibrium with air contains about 9 ppm of dissolved oxygen. This is sufficient to degrade about 3 ppm of hydrocarbon, but it would be insufficient to mineralize the high ethanol concentrations expected to be associated with leaking USTs storing E-blend. Given that aqueous-phase ethanol is not expected to be retarded in its flow through an aquifer (it will travel essentially at the seepage velocity), advective replenishment of DO should assume diminished importance. Diffusion and dispersion may become the factors controlling the DO supply.

In addition to the aerobic degradation pathway that utilizes oxygen, ethanol can also degrade anaerobically. Electron acceptors for this pathway include nitrate, manganese IV, iron III, sulfate, and water (methanogenesis). Table 6.4 lists the mass ratios of the amount of these compounds required (or produced) when degrading one gram of hydrocarbon. In the case of Table 6.4, the hydrocarbon is benzene, but the relative amounts should provide a rough idea of the requirements for ethanol.

Unlike DO, no easy “best case” assumptions can be made about the initial concentrations of the anaerobic TEAs, the rates at which they are being used (except nitrate - see above), or whether their use is significant at all. Site-specific conditions will determine these factors, and a site-specific assimilative capacity would have to be calculated. It is also important to note that these values do not portray differences in the rate of biodegradation, which can vary greatly among these electron acceptors.

More information (experience) about the behavior of E-blend gasoline in the subsurface needs to be acquired before the MNA option can be addressed.

Table 6.4 Electron acceptor requirements for benzene degradation. (Wiedemeier et al., date unknown)

COMPOUND	MASS REQUIRED	MASS BENZENE DEGRADED
Oxygen	3.08 gm	1 gm
Nitrate	4.77 gm	1 gm
Manganese IV	16.7 gm	1 gm
Manganese II	10.56 gm*	1 gm
Fe(OH)3 / Iron III	41 gm	1 gm
Iron II	21.5 gm**	1 gm
Sulfate	4.6 gm	1 gm
Methane	0.77 gm**	1 gm

* 10.56 grams of Manganese II are produced for every gram of benzene degraded.
** 21.5 grams of Iron II are produced for every gram of benzene degraded.
*** 0.77 grams of methane are produced for every gram of benzene degraded.

SURPRISING NEWS FROM BRAZIL

Brazil has been using E-blend for over 20 years. Approximately 75 percent of all vehicles in the country run on E24-blend (24 percent ethanol, by volume, more than 2 times the ethanol proposed for E-Blend). Petrobras, the Brazilian Oil Company, has been studying the effects of ethanol gasoline mixtures on soil and groundwater since 1995.

At a recent conference in November, 2000, Henry Corseuil et al. reported on the results of a controlled release of E24 that showed that ethanol has a much longer life in groundwater than has been projected from laboratory studies. His study showed a first order decay rate for ethanol of 0.42 yr-1, roughly equivalent to toluene. This is a half-life in groundwater of approximately 600 days, which differs greatly from the 3- to 7-day half-life estimated from lab studies by Corseuil et al. 1998.

If this behavior were true it would have a significant impact on the lengthening of benzene plumes from E-blend spills. It would mean that predictions may indeed be true that ethanol can extend benzene plumes 1.1 to 2.5 times current lengths observed with spills of conventional gasoline.

The research team led by Corseuil (2000) released 100 liters (26 gallons) of E24-blend to a sandy aquifer at a depth of 0.5 meter (1.6 feet) over an area of 12 X 30 meters (40 X 98 feet). Depth to groundwater is 0.7 to 1.1 m (2.3 - 3.6 feet) at the site. After 480 days the front end of the plume reached 10 meters (33 feet) and was expanding. It was determined that iron reduction is the dominant biological process responsible for the E-blend biodegradation. (See below for gasoline constituent decay rates.)

Decay rates for the major gasoline constituents dissolved in groundwater, according to the Brazilian field experiment. (Corseuil, 2000)

Gasoline Constituent	Decay Rate
Toluene	0.41 yr^{-1}
Benzene	0.17 yr^{-1}
Xylenes	0.07 - 0.15 yr^{-1}
Ethanol	0.42 yr^{-1}

REMEDIAL COST OF ETHANOL VERSUS M*t*BE AS AN OXYGENATE IN GASOLINE

When the Clean Air Act of 1990 mandated the use of oxygenates in gasoline, M*t*BE became the most common oxygenate used in the Northeastern United States to satisfy this mandate. The presence of M*t*BE in aquifer-derived drinking water supplies has raised concerns about the use of this compound in gasoline. Light non-aqueous phase liquids (LNAPLs) and grossly contaminated soil resulting from spills of M*t*BE gasoline respond to treatment technologies in a fashion similar to non-M*t*BE gasolines. Once M*t*BE forms an aqueous-phase plume, however, it causes a series of unanticipated problems.

The introduction of M*t*BE into the fuel supply has increased the cost of gasoline spill cleanups in the Northeast states in two ways: (a) M*t*BE plumes travel farther than BTEX plumes, resulting in the need to characterize larger plumes over longer periods of time, and (b) M*t*BE is more difficult to separate from water than the BTEX compounds, which results in increased operational expenses.

M*t*BE travels farther than BTEX in groundwater for several reasons. It starts at a higher aqueous-phase plume concentration at the source area because of its high mass ratio in the LNAPL and higher solubility than the BTEX compounds. M*t*BE is also less likely to adsorb onto organic carbon in the aquifer than the BTEX compounds, making it less likely to be affected by a phenomena known as retardation. In addition, M*t*BE resists biodegradation.

Although perceived to be less toxic than M*t*BE, ethanol has the potential to pose a unique set of problems for both the treatment of groundwater for potable water supplies and the restoration of aquifers affected by spills or leaks of E-blend.

Although E-blend gasoline has been in use in the central United States for several decades, no reports of increased cleanup costs have been attributed to ethanol. This may be because the cost differential is insignificant or because, as yet, cost factors and impacts have gone unrecognized.

Remediation and Cost

The physical properties of ethanol differ significantly from those of petroleum hydrocarbons and M*t*BE. These properties cause ethanol to behave quite differently when it is dissolved in an LNAPL than when it is dissolved in groundwater. Thus the remediation of soils (which may contain LNAPLs) must be addressed differently from that of groundwater.

Soil

E-blend gasoline has three characteristics that differ from M*t*BE gasoline and that may have an affect on the remediation of E-blend-contaminated soils:

- E-blend may flow more easily in the vadose zone,
- The potential for phase separation may increase the rate of interphase mass transfer of the ethanol from LNAPL to groundwater, and
- Ethanol can readily biotransform once it dissolves in water (Rice et. al., 1999).

Regardless of the oxygenate used, gasoline in soil will consist of approximately 90 percent petroleum hydrocarbon. This major fraction of the fuel is anticipated to control the technologies employed in soil remediation.

As with M*t*BE-gasoline spills, the standard course of action for E-blend spills will be to perform an investigation after the initial response to characterize the nature and extent of contamination and then to design a remediation system using the technology most suited to the site conditions.

Because the additional extent (if measurable) of an E-blend LNAPL pool has not yet been quantified, it is premature to speculate on how E-blend will affect either capital or operation and maintenance costs. The enhanced interphase mass transfer and ready biotransformation of ethanol may serve to reduce the time required for soil remediation compared with M*t*BE-gasoline spills, but once again, the significance of these phenomena as applied to cost and effort is speculation.

Water

The experience of regulatory agencies regarding the addition of M*t*BE to gasoline may provide some general insight into the potential switch over to ethanol as a fuel additive. Groundwater that is contaminated with M*t*BE can be treated, but with more difficulty and at greater expense than contamination with BTEX compounds.

M*t*BE-contaminated groundwater can be treated by air stripping and the use of granular activated carbon. MtBE is difficult to separate from water because of its physical properties. It does not volatilize from water into air as easily as BTEX compounds and does not adsorb strongly onto granular activated carbon (GAC). It has been estimated that the introduction of M*t*BE into the fuel supply has increased the cost of spill cleanups by approximately 30 percent (NESCAUM, 1999).

The problems associated with the treatment of ethanol in a drinking water supply could be the same type as those posed by M*t*BE, only at a level that is orders of magnitude more difficult. The commonly employed wellhead treatment technologies rely on physical processes to separate a contaminant from the water within which it has dissolved. These technologies take advantage of the compound's ability to effect a phase transfer of the dissolved contaminant between water and either a gas or a solid, without reducing the mass or toxicity of the contaminant itself.

The best examples of such technologies are air strippers and GAC. Based on minimum air to water ratios, M*t*BE is 10 times more difficult to treat with an air stripper than benzene. In theory, ethanol will be 82 times more of a problem than M*t*BE. The adsorption capacity of GAC for M*t*BE is about a third of that for benzene. In the field, this causes rapid M*t*BE breakthrough and requires oversized carbon vessels that are closely monitored and changed often to ensure reliable treatment. The adsorptive capacity of GAC for ethanol is 1/1600th of that for M*t*BE.

The difficulty with trying to forecast the effects of ethanol on the costs of groundwater remediation is rooted in several significant factors regarding the fate and transport of ethanol in the environment that are unknown at this time:

- The rate at which ethanol is dissolved into groundwater from LNAPL at the source area is unknown. In the case of catastrophic tank failures, will this rate be "instantaneous," rapid, or slow? What will be the duration of this loading? Will an aqueous-phase ethanol plume form and for all practical purposes leave the source area while the LNAPL pool remains and continues as a BTEX source?

- Will the ethanol within the plume rapidly biodegrade? Will it "instantaneously" (Wiedemeier et al., date unknown) utilize dissolved oxygen and nitrate and create a zone depleted of dissolved oxygen that moves with the ethanol plume at the speed of groundwater seepage and that inhibits aerobic biodegradation within it's borders? At what rate will the anaerobic processes take place within the plume, and will ethanol be the hydrocarbon of choice for the active bacteria?

- There is concern that E-blend gasoline will increase iron problems in remedial extraction wells and drinking water wells. It is well known that the biodegradation of fuels causes oxygen depletion in an aquifer. The geochemical environment created by oxygen depletion causes iron and manganese to become considerably more soluble in groundwater. When the deoxygenated water reaches an oxidized environment around a pumping well, the iron and manganese will precipitate out of solution, encrusting well screens to the point that they must be cleaned often or replaced. This reaction also causes a foul smell in the water and leaves stains on sinks, toilets, and clothing. Will such problems become more prevalent with ethanol, and increase remediation cleanup costs?

- Will dissolved oxygen diffuse and disperse into the tail end of a retarded BTEX plume at a rate sufficient to significantly limit the eventual extent of the BTEX plume as compared to the ethanol plume or its potential terminal electron acceptor (TEA) depleted shadow?

An in situ groundwater study investigating the impact of ethanol in gasoline on BTEX plumes in groundwater may help generate field data that will provide additional information regarding these issues.

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

CONCLUSIONS

The differences between ethanol and M*t*BE with regard to their expected impacts on the subsurface environment are largely based on their initial concentration in the aqueous plume, the very different rates at which they biodegrade, and possibly their residence time in the non-aqueous phase. M*t*BE is relatively recalcitrant to biodegradation and therefore able to migrate a significant distance from the release. Thus it can have a negative impact on groundwater quality for extended periods. Ethanol is rapidly biodegraded, preferentially to the other components of gasoline, however, its behavior in the environment is not well documented. It is expected that a release of neat ethanol will potentially be degraded in periods from several days to one or two years.

Both ethanol and M*t*BE have a relatively high solubility in water and high mobility in the subsurface. Ethanol, the more soluble, is completely miscible in water (100 percent soluble, compared with 4 to 5 percent for M*t*BE). Once released to the environment, alone or in a gasoline mixture, both ethanol and M*t*BE readily dissolve in rainwater, surface water, and groundwater.

Three environmental transport properties associated with ethanol are of particular concern:

- ▲ Depletion of oxygen and other nutrients in groundwater due to rapid biodegradation of ethanol that may inhibit the degradation of toxic components in gasoline.
- ▲ A surface tension effect that takes place when ethanol is in contact with a layer of liquid petroleum (i.e., gasoline, diesel, or other oil) on top of the water table and could cause greater lateral spreading of the gasoline.
- ▲ A potential cosolvency effect that may make other gasoline constituents more soluble in groundwater.

This analysis has led to the following specific conclusions on the effects of ethanol and E-blend gasoline releases to the environment:

- ▲ The biodegradation of ethanol in the soil and water environment would first deplete the oxygen and then the anaerobic electron acceptors, potentially preventing or reducing the rate of biodegradation of the benzene, toluene, ethylbenzene, and xylene (BTEX) constituents in gasoline. This may result in longer BTEX plumes. M*t*BE does not interfere with the natural biodegradation of the other gasoline components, most importantly BTEX.
- ▲ Lab studies and mathematical models have estimated the potential for E-blend to cause the toxic BTEX compounds of gasoline to travel from 1.1 up to 2.5 times farther than a standard gasoline blend without ethanol. This may be a serious problem, however, the predicted lengths of the E-blend BTEX plumes will still be shorter than M*t*BE plumes resulting from reformulated gasoline.
- ▲ Although ethanol degrades rapidly when released to the environment under favorable conditions, if spilled as a neat product where a stabilized zone of petroleum-contaminated soil and groundwater plumes already exist (e.g., oil terminals), it can remobilize the gasoline components and cause lateral spreading of liquid petroleum and 10-fold increases in the concentration of benzene and other aromatic constituents of gasoline (i.e., BTEX). This may cause contamination of groundwater and nearby wells.

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

CONCLUSIONS continued

- Due to the oxygen depletion and cosolvency factors associated with ethanol in groundwater, there is a concern that significant or continuing releases of E-blend (e.g., from a significant undetected UST leak) could result in an extended plume of benzene (and other gasoline components).

- Environmental concentrations of ethanol expected as a result of atmospheric deposition through precipitation or from recreational boating activities are unlikely to pose a problem to either human or environmental receptors since these predicted concentrations are below benchmark values derived.

- Although environmental benchmarks for the protection of human health are lower than those derived for aquatic life protection, it is likely that impacts to the aquatic community would be observed before human health impacts were detected if high concentrations of ethanol were to reach a surface water body. High concentrations of ethanol could deplete or substantially lower dissolved oxygen content in the surface water within a short period of time, potentially leading to a fish kill from oxygen stress.

- Significant spills of ethanol into surface water bodies that have low aeration rates (e.g., ponds, lakes and large, nonturbulent, rivers) can cause massive killings of fish and other aquatic organisms by asphyxiation, the result of oxygen depletion of the water caused by ethanol degradation. For example, in May 2000, a 500,000-gallon release of Wild Turkey bourbon (250,000-gallons ethanol) into the Kentucky River caused the worst fish kill in 50 to 60 years.

- Smaller spills of E-blend, such as incidental spillage at gas stations and homeowner spills, are not expected to enhance the migration of benzene. In fact, because of the high biodegradability of ethanol, it is not expected that such small spills will have any significantly different impact on groundwater quality compared with nonoxygenated gasoline. This is in stark contrast to the widespread instances of drinking water contamination with M*t*BE from such minor spills of M*t*BE gasoline.

- For one-time releases of larger quantities of E-blend (e.g., a tanker truck accident), the effects of cosolvency are not expected to significantly affect the extent of the resulting plume. In this case, the incident would be known, and as in the case of conventional gasoline formulation, appropriate and prompt responses, evaluation, and follow-up would be taken.

- Much of the technology developed to remediate gasoline and M*t*BE in soil can be expected to work on the remediation of neat ethanol and E-blend. However these tools have not been tested on environmental releases, so until they are we will not know precisely which methods will work the best and how effective they will be.

- Ethanol plumes should be no more difficult to control hydraulically than M*t*BE plumes.

- Treatment technologies that rely on the physical separation of ethanol from groundwater are not effective. While biodegradation of ethanol in the environment is rapid, removal of ethanol from drinking water once pumped out of a well or reservoir is problematic. Its high solubility makes it very difficult to treat using carbon filters that are effective on private wells for other gasoline contaminants. However, the rapid biodegradation of

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

CONCLUSIONS continued

ethanol makes it unlikely that this oxygenate will affect as many wells as have been affected by M*t*BE unless the concentration of ethanol exceeds the attenuative capacity of the aquifer segment between the source area and the receptor.

- Biological treatment technologies are effective for ethanol contamination, as ethanol is highly biodegradable.
- The expected high concentrations of ethanol in plumes and the resulting high levels of BOD will probably require that treatment systems utilizing in-situ bioremediation technologies have larger capacities over those currently in use.
- The effectiveness of natural attenuation cannot be predicted because there is not enough information regarding the effect of ethanol plumes on the concentrations of terminal electron acceptors or the ability of those plumes to overcome the assimilative capacity of aquifers through which they are traveling prior to impacting a receptor.
- The use of ethanol as a gasoline additive will likely have minimal impact on the technology employed or the costs associated with soil remediation. The impact on groundwater remediation is not yet well understood.
- From the standpoint of soil and water contamination, the ideal gasoline additive for air pollution control should be non-toxic, less water soluble, and more biodegradable than M*t*BE.

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

UNCERTAINTIES

It is very important to understand that this evaluation is based on predictions from scientific estimations of what will happen to soil and groundwater in the event of a release of E-blend, and not from field data. The relative impacts of large-volume spills during transport, transfer, and storage are hard to generalize due to the uncertainties in quantifying the effects of ethanol on BTEX plume length, the concentration of terminal electron acceptors, and secondary effects on groundwater quality, such as increased levels of dissolved iron. The following uncertainties have been identified:

- ▲ Modeling studies have shown that benzene plume lengths increase if ethanol is in the released gasoline, but these studies have not been confirmed in the field. Although ethanol gasoline has been in use for years, little information exists on subsurface ethanol plumes, because ethanol concentrations have not been monitored significantly anywhere in the United States.

- ▲ It is likely that the overall effect of ethanol is site specific and depends on the release scenario and characteristics, such as site hydrogeology and the nature and amount of electron acceptors and nutrients in the aquifer. The relative environmental impacts expected to result from releases of neat ethanol and E-blend depend on the release scenarios.

  For example, ethanol would likely have much less impact than M*t*BE in small-volume residential spill scenarios. While gasoline hydrocarbons would be retained in the vadose zone by capillary forces and volatilize or degrade before ever reaching groundwater, both ethanol and M*t*BE would be carried to the groundwater by infiltrating rainwater. Once in the groundwater, ethanol would rapidly degrade given sufficient nutrients and electron receptors, whereas M*t*BE would persist and could contaminate drinking water wells. Soluable BTEX could still reach groundwater in this scenario.

- ▲ To understand the environmental impacts of E-blend, a thorough understanding its life cycle is necessary. Since ethanol has never been extensively distributed in large volumes in the Northeast, the logistics of the life cycle as they would take place in this region are not established.

- ▲ Finally, it is premature to attempt to compare the costs associated with the remediation of groundwater contaminated with ethanol verses M*t*BE. Additional knowledge of and experience with such issues as degradation rates and the effects of soluble iron must be understood.

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

RECOMMENDATIONS

▲ The use of E-blend gasoline instead of M*t*BE gasoline will result in a significant decrease in well contamination caused by small spills. However, for significant and continuous E-blend gasoline spills, it is premature to predict their effect on well contamination. Field experiments are needed to understand the true extent of the behavior of ethanol in the environment and confirm modeling studies.

For example, a recently published report from Brazil (November, 2000) of the first known controlled release of E-blend (24 percent ethanol by volume) in a sand aquifer showed the decay rate for ethanol to be 100 times slower than predicted from laboratory studies, meaning that ethanol can exist in the environment 100 times longer than expected. However, we do not know if ethanol would be more persistent than expected in an E-blend of the ethanol concentration associated with the U.S. RFG program—5.7 to 10 percent by volume. The depletion of oxygen and other electron acceptors would likely be much faster and complete with higher concentrations of ethanol.

Thus, before their widespread introduction to the area, controlled field experiments of neat ethanol and E-blend gasolines must be carried out to determine the precise nature of their impact on the environment and the potential for threats to human health. As these field experiments may take two to three years to produce reliable results, the experiments should be done as soon as possible so that fate and transport principles are better understood with regard to addressing the cleanup of neat ethanol and E-blend gasoline releases. These investigations must include:

- A controlled field study to measure the rate at which ethanol dissolves or separates out of E-blend and is transferred into groundwater.
- A controlled field study to assess the impact of ethanol in gasoline on BTEX plumes in groundwater.
- An analysis of remedial actions and the performance of remedial technologies employed in states that have been using E-blend for the past few decades to answer questions concerning the appropriateness and efficiency of the technologies favored for cleanups in the Northeast.
- An analysis of spill investigations from states that have been using E-blend for the past few decades to answer questions about the fate and transport of ethanol, the effects of ethanol on the biodegradation of BTEX compounds at a field scale, and cosolvency.
- Field tests of remediation technologies to determine which work and their effectiveness.
- Research on effective E-blend remediation technologies and their associated costs.
- Research to provide a feasible approach to point-of-use/point-of-entry treatment of ethanol contaminated drinking water.
- Evaluation of the potential environmental impacts of an ethanol release along the entire ethanol life cycle. Work with the ethanol industry to better determine what the life cycle will look like before distribution activities are initiated.

IMPACTS OF RELEASES OF NEAT ETHANOL AND E-BLEND TO THE WATER/SOIL ENVIRONMENT

RECOMMENDATIONS continued

▲ If ethanol is adopted as a gasoline oxygenate alternative to M*t*BE, it should be used at the maximum concentration of 5.7 percent to minimize the affects of oxygen depletion and cosolvency, at least until it is determined to have fate and transport characteristics that are manageable. Accordingly, a repeal of the federal tax incentive that results in formulations exceeding the minimum necessary for air pollution benefits should be considered.

▲ Monitoring for ethanol and terminal electron acceptors should be included as a standard part of the remedial investigations at E-blend petroleum release sites. Appropriate test methods and detection limits must be identified.

▲ A standardized analytical method for the quantification of ethanol in environmental water samples should be adopted. The difficulty in separating ethanol from water in the preparation of samples for analysis has resulted in high detection limits. Consensus on acceptable detection limits is also needed.

▲ Start testing for ethanol at gasoline releases. The detrimental effects of M*t*BE on groundwater were unknown until regulatory agencies started to test for or require testing of M*t*BE.

▲ One characteristic of M*t*BE in gasoline is that it imparts a bad taste and odor to drinking water at levels that are below many state health standards. In this way M*t*BE serves as an early indicator that a well has been contaminated. Ethanol has a much higher taste and odor threshold. However, while ethanol by itself has poor warning properties, experience has shown that due to the strong preference bacteria have for ethanol, a high concentration of ethanol in groundwater would cause groundwater to become anaerobic, increasing color, turbidity, and odors in the water due to anaerobic conditions. If this is the case, the secondary effects of an ethanol spill would likely provide some warning to consumers. Studies should be undertaken to investigate this issue.

▲ Move away from the 2 percent oxygen mandate focus and create a set of performance standards for gasoline that address both air and water quality concerns. The current requirements for RFG present a set of fuel performance standards to the oil industry for VOCs, NO_x, and toxics that address air quality issues. However, performance standards should also address water quality issues and not create more of a threat to groundwater and drinking water resources than ether-free gasoline. (See NESCAUM's discussion of gasoline formulation in Volume 2.)

▲ As ethanol will not replace 100 percent of the M*t*BE currently found in RFG, aromatics, olefins, and alkylates are seen as the likely additives that will be used to make up the volume. An assessment of the environmental characteristics of these additives is needed before the widespread introduction of ethanol reformulations.

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CHAPTER 7

OTHER ALTERNATIVES TO M*t*BE

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THE SCOPE OF THIS CHAPTER

The federal Clean Air Act RFG program requires that gasoline meet a minimum oxygen requirement of at least 2 percent oxygen by weight. This requirement was instituted to provide for a more complete burn of the fuel in an automobile engine so that carbon monoxide levels in the air are reduced. Today this oxygen requirement is usually attained by the addition of M*t*BE and less frequently by ethanol.

If states ban M*t*BE and current RFG requirements remain unchanged, an alternative oxygenate must be used to comply with the 2 percent oxygen mandate. Oxygenates fall into two chemical categories: ethers and alcohols. M*t*BE had been the leading ether-based oxygenate, others include ethyl *tertiary*-butyl ether (E*t*BE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE). The primary alcohol oxygenates are ethanol and *tertiary*-butyl alcohol. Oxygenate alternatives, such as ethanol, will not necessarily replace 100 percent of the M*t*BE currently found in RFG; aromatics, olefins, and alkylates are seen as the likely additives that will be used to make up the volume.

In the event that the current oxygenate mandate is lifted, refiners would have a greater range of options in formulating RFG. Because of ethanol's octane-enhancing, low-toxicity characteristics, demand for ethanol would likely grow even in the absence of a mandate. However, depending on the relative cost of different octane enhancers, refiners could also make greater use of alkylates and—to the extent feasible within the RFG program's toxic limits—aromatics, such as benzene, toluene, and xylenes. The use of benzene, a known human carcinogen, is of concern from a public health perspective; hence its presence in RFG is capped at 1 percent. Instead, toluene is thought to be the more viable aromatic. (See NESCAUM, Volume 2 for a thorough discussion fuel formulation issues.)

In light of the negative impacts that M*t*BE has been found to have on the water environment, it is essential that alternatives be identified. While this report focuses on the use of ethanol as an oxygenate alternative to M*t*BE, we should continue to seek alternatives to M*t*BE that will ultimately do the best job of protecting both air and water quality without allowing any backsliding on current performance requirements that have reduced air toxics and improved air quality. As we continue to discuss adding yet another additive to gasoline, we must continue to be concerned about the toxicity and risks associated with any reformulation.

This chapter presents a brief overview of available information on oxygenate alternatives to M*t*BE other than ethanol. It also discusses alternatives to oxygenates in the event that the 2 percent oxygen mandate is lifted, either as a result of Congressional action to modify the RFG program or through waivers granted to individual states. All of these alternatives are viewed with regard to their potential impact on water resources.

OTHER OXYGENATES

Ethers similar to M*t*BE that could be used as oxygenates include: ethyl *tertiary*-butyl ether (E*t*BE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE). It is expected that these ethers will have the same impacts as M*t*BE because of their similar chemical compositions. However scientific data are lacking on their expected behavior and health effects. (See Table 7.1.)

Animal studies have indicated that ethers have toxic effects such as "increased adrenal gland, liver, and kidney weights and neurological effects" (NESCAUM, 1999). E*t*BE, TAME, and DIPE are all considered to be "highly soluble in water and resistant to biodegradation" (NESCAUM, 1999) and, therefore, are not viable alternatives to M*t*BE until more study is conducted on their behavior.

Tertiary-butyl alcohol (TBA), an alcohol, is not considered to be a viable alternative to M*t*BE given that animal studies have produced evidence that it may be a carcinogen (NESCAUM, 1999).

ALTERNATIVES TO OXYGENATES

Increasing alkylates in gasoline is a likely solution for making up for the octane and volume that would be lost with the removal of M*t*BE from RFG. Currently, alkylates account for 15 to 30 percent of the finished gasoline pool (Pryor, 2001). The traditional alkylation process combines light olefins and isobutane using sulfuric acid or hydrofluoric acid as catalysts. The use of these acids should be considered with regard to the potential health and environmental implications.

Highly branched alkanes (e.g., isooctane (C-8)) have a low water solubility and a high volatility, an indication that they would not pose as much a threat to surface and groundwater as M*t*BE. (See Table 7.2.) In the case of an accidental surface water release, alkylates are expected to concentrate in the air phase due to their high Henry's law constants (Lawrence Livermore, 1999). In groundwater they would bond strongly to soil particles and biodegrade slowly. Using unpolluted forest soil to incubate the gasoline solution, Solana-Serena conducted a laboratory study and identified the degradation half-life for isooctane as approximately 88 days (Marchetti, 2001). However, a field study looking at the in-situ biodegradation of isooctane identified a much slower rate of degradation and came to the conclusion that degradation is dependent on the presence of specific microorganisms (Marchetti, 2001).

Currently, there are very limited data on the human health implication of exposure to alkylates, especially concerning "cancer risk, reproductive, and developmental effects" (Lawrence Livermore, 1999). However, of the petroleum hydrocarbon class of compounds, those compounds presently recognized as carcinogenic by EPA, the World Health Organization, and the scientific community at large fall into the aromatic class and not the aliphatic class where the alkylates lie.

The Massachusetts Department of Environmental Protection's Office of Research and Standards has developed a relatively new approach to evaluating the potential toxicities of the compounds that make up complex mixtures of petroleum hydrocarbon compounds which has been embraced quite widely by other state governments (Hutcheson, et al., 1996). This methodology can be applied to alkylates to permit evaluation of their potential toxicity.

The method consists of the identification of structurally-based subgroups of compounds, further subgrouped by their sizes as determined by numbers of carbon atoms in the compound. Fraction-specific toxicity values (oral reference doses [RfDs] and inhalation reference concentrations [(RfCs]) have been identified for each subgroup. The relative potential toxicity of an alkylate mixture will depend on the relative composition of the constituent compounds. For any potential exposure scenario, the weight percent of constituent compounds can be apportioned to each fraction, a dose for that fraction from the exposure can be calculated and compared to the fraction's RfD or RfC. These ratios of hazard can be summed to give a total hazard for the mixture for the exposure scenario evaluated.

Table 7.1 Physical - chemical properties of fuel oxygenates.

Source: National Science and Technical Council Committee on Environment and Natural Resources, June 1997. Interagency Assessment of Oxygenated Fuels.

[Values are at 25°C unless otherwise stated. The ranges are from one reference and multiple listings are from multiple sources. Values in bold are values used in the narrative text. MeOH, methanol; EtOH, ethanol; TBA, *tert*-butyl alcohol; MTBE, methyl *tert*-butyl ether; ETBE, ethyl *tert*-butyl ether; TAME, *tert*-amyl methyl ether; DIPE, diisopropyl ether; TBF, *tert*-butyl formate. Sources: Budavari, 1989; Chiou *et al.*, 1979; Flick, 1991; Howard, 1990-93, 1991; Lide, 1994; Lyman *et al.*, 1990a, 1990b; Mackay *et al.*, 1991-93; McAuliffe, 1966; Montgomery and Welkom, 1990; Owen and Coley, 1990; Robbins *et al.*, 1993; Yeh, 1992]

Property	MeOH	EtOH	TBA	MTBE	ETBE	TAME	DIPE	TBF
Molecular weight (g/mole)	32.04	46.07	74.12	88.15	102.18	102.18	102.18	102.13
Specific gravity	0.796	0.794	0.791	0.744	0.73	0.77	0.736-0.7491	0.886
Boiling temp., °C	64.7	78-79	82.9	53.6-55.2	67	86	91 68-69	82
Water solubility, ($Cs_{(o)}$), mg/L	infinitely soluble	infinitely soluble	infinitely soluble	43,000-54,300 **50,000**	~26,000	~20,000	9,000 @ 20°C 2,039	~40,000
Vapor pressure @ 25°C, mm Hg	121.58	49-56.5	40-42	245-256	152	68.3	149-151@ 20°C	81@20°C
Log K_{ow}	-0.75	-0.16 -0.31	0.35	1.20	1.74		1.52	
Henry's Law constant, (H), (atm-m^3)/(g-mole)	4.42E-06	6.17E-6 5.13E-6 6.29E-6	1.175E-5 1.19E-5 1.04E-5 1.47E-5	5.87E-4 1.1E-3 1.4E-3 3E-3	2.66E-3	1.27E-3	9.97E-3 4.77E-3 5.87E-3	2.72E-4
Dimensionless Henry's Law constant (H/RT)	1.087E-4	2.522E-4 2.097E-4 2.571E-4	4.803E-4 4.864E-4 4.251E-4 5.927E-4 **4.8E-4**	2.399E-2 4.496E-2 5.722E-2 1.226E-1 2.6E-2 **0.018 @ 20°C**	1.087E-1	5.191E-2	4.075E-1 1.95E-1 2.399E-1	1.111E-2
Log Koc	0.921 0.44	1.21 0.20	1.57	1.091 1.035 1.049	2.2 0.95	2.2 1.27	1.82 1.46	1.11
CAS no.	67-56-1	64-17-5	75-65-0	1634-04-4	637-92-3	994-05-8	108-20-3	762-75-4

For the C5 to C8 alkanes subgroup, which includes isooctane, this method used n-hexane as the reference compound to give this subgroup an RfD of 0.06 mg/kg/day (Hutcheson, et al., 1996). This toxicity value was based on the potential of this compound to produce peripheral neuropathy as well as cranial neuropathy, blurred vision, and abnormal color vision (Hutcheson, et al., 1996). Toxicity values for other fraction's reference compounds were taken from established sources or were developed using available toxicity information (Hutcheson, et al., 1996).

Toluene is another nonoxygenate alternative to M*t*BE in RFG. A maximum contaminant level (MCL) for toluene in drinking water has been set by the U.S. EPA at 1 part per million (ppm). The potential health effects of toluene have been identified by the U.S. EPA and include the following (at exposure levels above the MCL):

- ▲ **Short-term** - minor nervous system disorders such as fatigue, nausea, weakness, confusion.
- ▲ **Long-term** - more pronounced nervous system disorders, such as spasms, tremors, impairment of speech, hearing, vision, memory, coordination, and liver and kidney damage. (US EPA, 1998)

Cancer-related health effects of toluene have been studied in animals. A long-term study conducted on rats and mice by the National Toxicology Program, found that toluene did not cause cancer (Agency of Toxic Substance and Disease Registry, 1989). In 1987, the U.S. EPA classified toluene in Cancer Group D: Not Classifiable as to Human Carcinogenicity, a group used for agents with inadequate human and animal evidence of carcinogenicity or for which no data are available. (US EPA, 2000) In the case of a spill, toluene will evaporate from surface soils and will leach into the groundwater, where the breakdown by microbes in the soil will be slow. In the case of a surface-water spill, evaporation will occur within a few hours and “it has little tendency to accumulate in aquatic life” (US EPA, 1998).

Methylcyclopentadienyl manganese tricarbonyl (MMT) is a manganese-based oxygen enhancer. Prior to 1996, the U.S. EPA had not approved MMT for use, based on health concerns, but was required to allow its use due to a court ruling that found the agency had no basis for making it illegal. The current state of scientific knowledge on MMT indicates that “airborne manganese at high doses are know to cause disabling neurological impairments in movement and speech with symptoms similar to Parkinson’s disease” (Environmental Defense, 1998). New Hampshire is planning to add a primary drinking water standard for manganese at 0.84 mg/L, based on the possible neurological impairments.

Adequate health testing is needed to identify the effects of chronic, low level exposure to airborne manganese. Studies identifying the behavior of MMT when leaked or spilled as well as studies evaluating the human health effects of ingested MMT must be conducted. Based on EPA statistics, it is believed that only 0.02 percent of the U.S. gasoline supply contains MMT. The United States automobile industry has been instrumental in limiting the use of MMT since it is believes that MMT may cause the failure of the emissions control systems in some vehicles.

Table 7.2 Physiochemical properties for M*t*BE, ethanol, benzene, and isooctane.

PROPERTY	M*t*BE	ETHANOL	BENZENE	ISOOCTANE
MW (g/mol)	88.15	46.07	78.11	114.23
Boiling point (°C)	55.2	78.2	80.1	99.2
Density (g/mL)	0.741	0.789	0.879	0.69
K_{ow}	8.71	0.50	135	12,200
Vapor Pressure (kPa)	33.3	7.9	12.6	6.49
Solubility (mg/L)	51,000	Miscible	1,800	2.44

Source: Marchetti, Alfredo, Environmental Transport and Fate of Alkylates. Presented at Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California. Oakland, CA., April, 2001.

OTHER ALTERNATIVES TO M*t*BE

CONCLUSIONS

In many ways, the solution to the RFG conundrum will involve tradeoffs. It is important to keep in mind, for example, that the addition of M*t*BE into gasoline decreased the percentage of benzene (a known carcinogen) in gasoline. Any solution will need to strike a delicate balance that meets both air and water quality concerns. Of the possibilities listed above, the alkylates have characteristics that suggest further investigation. However, too little is known about the alternatives discussed above to draw any conclusions as to their viability as M*t*BE alternatives without further study.

CHAPTER 7 REFERENCES

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CHAPTER 4
APPENDIX A

AQUATIC TOXICITY DATA FOR ETHANOL FROM ECOTOX DATABASE

CHAPTER 4
APPENDIX B

WATER QUALITY BENCHMARK CALCULATIONS FOR ETHANOL

CHAPTER 4
APPENDIX C

DRAFT EPA WATER QUALITY CRITERIA FOR M*t*BE

CHAPTER 4
APPENDIX D

RESULTS OF STREETER-PHELPS MODEL EVALUATIONS