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Special issue on ethanol

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What ethanol is, how it is made and its chief characteristics are described in this article.
- Ethanol and BTEX biodegradation** 3
This article describes BTEX biodegradation and how the presence of ethanol affects it.
- Ethanol influence on gasoline movement** 8
The presence of oxygenate chemicals such as ethanol can potentially influence gasoline fate and migration. Processes affected include gasoline infiltration through the unsaturated zone, gasoline spread at the water table, dissolution of slightly soluble species from gasoline into water and transport of these chemicals with the groundwater.
- Ethanol detection methods** 12
At present, ethanol is not a federally regulated compound, nor is it regulated in many states; regulators, however, are studying ethanol more closely because of its greater potential use in gasoline. Extensive data on the fate and transport of ethanol does not exist. However, researchers are identifying the criteria for ethanol characterization in the subsurface.
- Ethanol study conclusions** 14
This article summarizes data gaps in the ethanol study, including life cycle analyses, fate and transport processes and biodegradation. Conclusions and recommendations for further study are also given.

UTTU is on the Web

<http://epd.engr.wisc.edu/uttu/>

Special issue on ethanol

This special issue of *UTTU* focuses on the 12/99 report to the California Environmental Policy Council: *Ethanol Research Draft Documents: Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*. Governor Davis issued Executive Order D-5-99 on 3/25/99 calling for the removal of methyl tertiary butyl ether (MTBE) from gasoline at the earliest possible date, but no later than 12/31/02. Task 10 of the Executive Order states "the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by 12/31/99 for its consideration." The following reports can be found at <http://www-erd.llnl.gov/ethanol/>.

Vol. I	Executive Summary
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Chp 4	Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths
Chp 5	Potential Impact of Ethanol-Containing Gasoline on Surface Water Resources
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Chp 8	Comparison of Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE
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Chp 10	Response to Comments
Vol. V	Potential Health Risks of Ethanol in Gasoline Acronyms, Glossary, and Authors

In this issue of *UTTU*, the reader will find summaries of some, but not all, of these chapters. For instance, Volume 5, *Potential Health Risks of Ethanol in Gasoline*, was not reviewed because the potential health effects were not significant.

In addition, Dave Rice and Allan Patton would be interested in hearing from anyone who has field data or knows of studies concerning ethanol releases from USTs. Please contact Dave Rice at 925-423-5059 (rice4@llnl.gov) or Allan Patton at 916-227-4360 (fax 916-227-4530; apatton@cwpswrcb.ca.gov).

For additional information on MTBE and reformulated gasoline, see *UTTU* Vol. 13, No. 6 and Vol. 13, No. 4. An article on ethanol, "Ethanol as a substitute for MTBE", appears in Vol. 14, No. 1.

*UTTU thanks David Rice, Project Manager, Environmental Restoration Division, Lawrence Livermore National Laboratory, Livermore, California (rice4@llnl.gov) and Susan Powers, Associate Professor, Clarkson University, Potsdam, New York (sep@clarkson.edu), for their help on this issue of *UTTU*.*



Background on ethanol

Ethanol is a flammable, colorless liquid with a sweet alcohol odor. A short chain molecule (C₂H₅OH), 34.7 percent oxygen by weight, it is infinitely soluble in water. Polar in nature, ethanol is hydrophilic, making it difficult to extract from water.

Ethanol facts

Ethanol is made primarily from grains or other renewable agricultural and forestry feedstocks. In the U.S., most ethanol is made from corn. Production follows these seven steps:

- 1) grain milled into a fine powder called meal
- 2) meal liquefied with water, enzymes and heat (120°-150°C)
- 3) liquefied starch converted to fermentable sugars, dextrose, in a process called saccharification
- 4) yeast added to ferment sugars to ethanol and CO₂
- 5) the alcohol is distilled to increase the ethanol content from 10 percent alcohol by volume to about 96 percent
- 6) remaining water removed from the alcohol; most distillers use a molecular sieve to produce anhydrous ethanol
- 7) ethanol is denatured with 2 to 5 percent of a product to make it unfit for human consumption

We also know the following:

- ethanol is lighter than water; if released rapidly in bulk onto water, it tends to remain near the water surface
- if gasoline with a high concentration of ethanol comes in contact with even small quantities of water, it will separate from the gasoline into the water
- ethanol-containing gasoline is denser than unblended gasoline
- ethanol is very volatile and evaporates from gasoline into air approximately five times faster than MTBE; like gasoline vapors, ethanol vapors are denser than air and tend to settle near the ground in low areas; in open-air areas, these vapors disperse rapidly (Table 1)
- when burned, ethanol releases less heat than gasoline; one-and-a-half gallons of ethanol have approximately the same fuel combustion as one gallon of gasoline
- ethanol has a higher ignition temperature than gasoline (approximately 850°F vs. 495°F)
- when pure ethanol is burned, the flame is less bright than a gasoline flame, but it is easily visible in daylight
- at 110, ethanol has an octane rating similar to MTBE's; thus, when added to gasoline, ethanol increases the octane rating (the long chain, branched hydrocarbon known as octane is used as a standard and is equal to a rating of 100)

- though poisonous, ethanol is much less acutely toxic than the BTEX compounds
- ethanol is present in pharmaceuticals, mouthwash products, alcoholic beverages, cleaning products, solvents, dyes and explosives; humans frequently ingest fermented beverages containing about 12 percent by volume ethanol
- ethanol can be used by many indigenous microorganisms within the environment as an energy source; such microorganisms will preferentially utilize ethanol over other gasoline hydrocarbons, such as benzene

Property	Chemical	
	MTBE	Ethanol
Molecular weight (g/mol)	88.15	46.07
Density as a liquid (g/ml) at 20°C	0.740	0.789
K _{OW} (dimensionless)	8.71	0.50
Vapor pressure (Pa) at 25°C	32,664	7,869
Solubility (mol/m ³)	476 (-20°C)	Miscible in water
Henry's law (Pa·m ³ /mol) at 25°C	53.5	0.64
Henry's law (dimensionless = H/RT)	0.0216	0.00026

Table 1. Comparison of MTBE and ethanol properties (Rice, 1999).

Ethanol compatibility with metals and nonmetals

Ethanol and ethanol blends of gasoline conduct electricity whereas unblended gasoline is an electrical insulator. Thus, pure ethanol is more corrosive than gasoline, and materials-compatibility is an issue. Pure ethanol and gasoline with high percentages of ethanol should not be used with aluminum, zinc, tin, lead-based solder, or brass fittings. Nonmetallic materials that will degrade in the presence of ethanol include:

- natural rubber
- polyurethane
- cork-gasket materials
- leather, polyester-bonded fiberglass laminate
- polyvinyl chloride, polyamides
- methyl-methacrylate plastics

Reference

Rice, D.W.; G. Cannon, editor and R. Depue, contributor, "Background Information on the Use of Ethanol as a Fuel Oxygenate," Volume 2, in *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*, December 1999, University of California, Lawrence Livermore National Laboratory, Environmental Restoration Division, UCRL-AR-135949, Livermore, California; <http://www-erd.llnl.gov/ethanol/>.



Ethanol and BTEX biodegradation

This article is taken nearly verbatim from the report, "The Effect of Ethanol on BTEX Biodegradation and Natural Attenuation" (Alvarez and others, 1999).

By virtue of its short chain and miscibility in water, ethanol is highly biodegradable by microbial enzymes under both aerobic and anaerobic conditions. In addition, many ethanol-degraders are expected to exist in the subsurface (Alvarez and others, 1999).

Biodegradability factors

"A common limitation of natural degradative processes is the lack of adequate contact between pollutants and microorganisms. Availability of many pollutants to microorganisms can be affected by a series of ill-defined, often uncharacterized processes." Mechanisms that reduce contaminant bioavailability include

- adsorption or complexation onto solid surfaces
- sequestration in soil nanopores
- partitioning into non-aqueous phase liquids (NAPLs)

"In such cases, biodegradation rate can be controlled by desorption or dissolution rate. If biodegradation is mediated by extracellular enzymes, the bonds requiring cleavage must be exposed and not occluded by sorption to solid surfaces, or sterically blocked by large atoms, such as chlorine. Most priority pollutants, however, are degraded by intracellular enzymes. Therefore, bioavailability also implies the ability of the pollutant to pass through the cellular membrane. In regard to ethanol and BTEX compounds, all of these bioavailability requirements are generally met easily because of their relatively high aqueous solubility. However, when (hydrophobic) polycyclic aromatic hydrocarbons (PAHs) are a contaminant of concern, the characteristically high sorption to soil with PAHs makes bioavailability a significant factor limiting the success of bioremediation" (Alvarez and others, 1999).

Degradative enzymes

An enzyme is "a protein that acts as a catalyst in biochemical reactions. Each enzyme is specific to a particular reaction or group of similar reactions. Many require the association of certain nonprotein cofactors to function. The molecule undergoing reaction (the substrate) binds to a specific active site on the enzyme molecule to form a short-lived intermediate: this greatly increases (by a factor of up to 10²⁰) the rate at which the reaction proceeds to form the product.

Enzyme activity is influenced by substrate concentration and by temperature and pH, which must lie within a certain range. Other molecules may compete for the active site, causing inhibition of the enzyme or even irreversible destruction of its catalytic properties" (Daintith, 1990).

"The names of most enzymes end in -ase, which is added to the names of the substrates on which they act; thus, lactase is the enzyme that acts to break down lactose" (Daintith, 1990).

"Some enzymes, such as those participating in central metabolic pathways, are always produced (at some level) regardless of environmental conditions. These are known as constitutive enzymes. The enzymes that initiate BTEX degradation, however, are generally inducible, that is, these enzymes are produced only when an inducer (for example, toluene) is present at a higher concentration than the minimum threshold for induction, which is generally very low, usually a few $\mu\text{g/L}$. Toluene is generally a good inducer of oxygenase enzymes with relaxed specificity. Observations indicate that its presence enhances BTEX degradation. In contrast, the presence of easily degradable substrates, such as ethanol, could repress production of BTEX-degrading enzymes and result in preferential ethanol degradation" (Alvarez and others, 1999).

Enzyme induction could be hindered by a lack of bioavailability. Specifically, the presence of a compound in a NAPL or its sequestration in nanopores might result in insufficient sub-threshold concentrations in the aqueous phase to trigger enzyme induction and/or sustain a viable microbial population.

Electron acceptors

Biodegradation of a compound is a function of not only its chemical structure and physiological limitation but also its environmental properties. To function properly, microorganisms need "recognizable" substrates that serve as energy and carbon sources (for example, the target organic pollutants) and favorable environmental conditions to sustain life functions, including nutrients, pH, temperature and moisture (Alvarez and others, 1999).

Thermodynamically, oxidation of BTEX and ethanol (aerobic conditions) is favored over anaerobic reactions; thus in terms of reactivity, ethanol and BTEX will prefer molecular oxygen as the electron acceptor. Microbes use electron acceptors during "respiration" as electrons are removed from biodegradable contaminants. "This transfer of electrons releases energy to drive microbial life functions." Under anaerobic conditions, nitrate, sulfate, manganese (iv), ferric iron, sulfate and carbon dioxide serve as electron acceptors (Table 2 and Figure 1).

Electron acceptor	k / day	Half-life (days)
O_2	0.23-0.35	2-3
NO_3^-	0.53	1.3
Fe^{3+}	0.17	4
SO_4^{-2}	0.1	7
CO_2	0.12	6

Table 2. First-order rate coefficients (k) and half-lives for anaerobic and aerobic ethanol degradation (Alvarez and others, 1999).

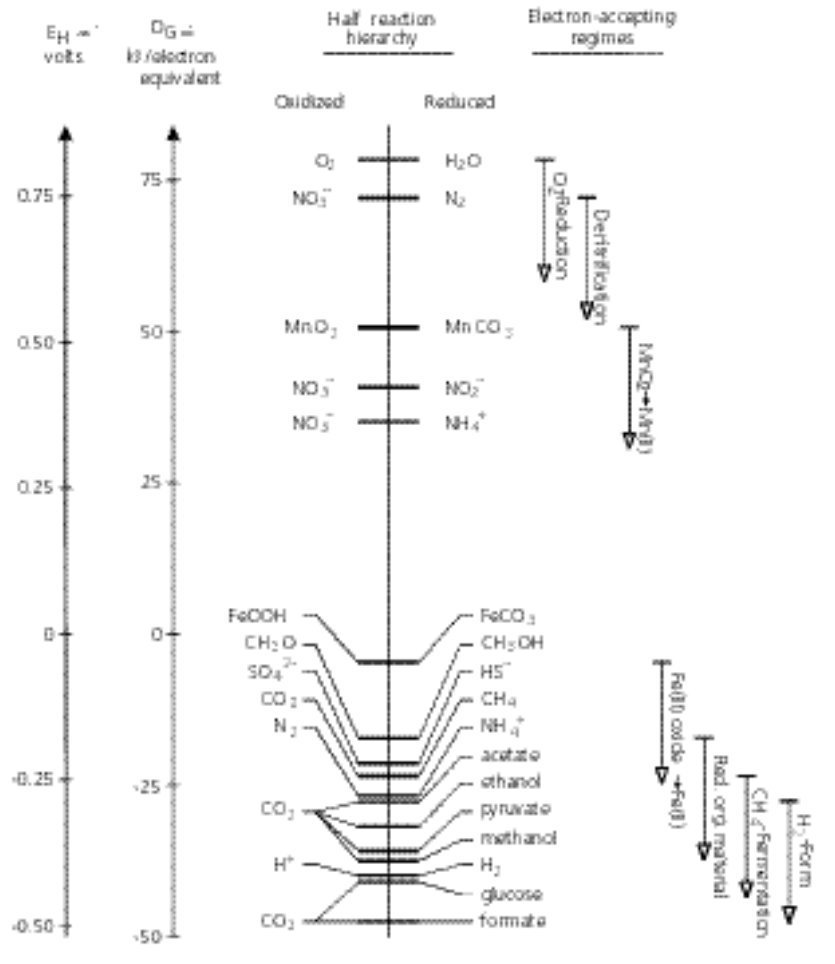


Figure 1. Hierarchy of common electron acceptors and donors, which integrates factors of thermodynamics, microbiology, and physiology of oxidation-reduction reactions (Alvarez and others, 1999).

Redox conditions

Redox refers to oxidation-reduction where oxidation is a chemical reaction involving gain of oxygen; loss of oxygen is reduction. Redox conditions are highly site-dependent. For instance, oxygen is usually present near groundwater recharge areas where rainwater infiltrates. The available oxygen within the contaminant plume, however, is often exceeded by the biochemical oxygen demand exerted by the contaminants; thus, anaerobic conditions often dominate highly contaminated areas. BTEX degradation rates are slower in oxygen-depleted zones.

Macronutrients

"Microorganisms need macronutrients to synthesize cellular components, such as nitrogen for amino acids and enzymes, phosphorus for ATP and DNA, sulfur for some coenzymes, calcium for stabilizing the cell wall and magnesium for stabilizing ribosomes. In general, however, microbial growth in subsoils is not limited by nitrogen and phosphorus as long as contaminant concentrations range in the sub ppm. A carbon: nitrogen: phosphorus ratio of 30:5:1 is generally sufficient to

ensure unrestricted growth in aquifers. Microbes also need micronutrients to perform certain metabolic functions. For example, trace metals, such as iron, nickel, cobalt, molybdenum and zinc, are needed for some enzymatic activities. Nevertheless, geochemical analysis and laboratory biodegradation assays should be performed to verify that the presence of inorganic nutrients is sufficient for natural bioremediation" (*Alvarez and others, 1999*).

pH

pH can hinder or promote microorganism growth. Growth is best around neutrality, a pH of 6 to 8, although microorganisms can perform well between pH of 5 to 9, a range which generally reflects the buffering capacity of carbonates or silicates. As polymers of amino acids, enzymes (catalysts in biochemical reactions) require the proper degree of amino acid protonation, i.e., pH conditions. Aquifers contaminated by sources such as landfill leachates may contain high concentrations of volatile fatty acids (VFAs, such as acetic acid) which can lower pH to 3, suppressing microbial activity. "... the potential accumulation of VFAs during anaerobic degradation of ethanol is a potential mechanism that could decrease the pH below the optimum range of common bacteria that degrade BTEX" (*Alvarez and others, 1999*).

Temperature

"Microbial metabolism accelerates with increasing temperature up to an optimum value at which growth is maximal. Most bacteria in subsurface environments operate most effectively at 20° to 40°C, which is a little higher than typical groundwater temperatures in the U.S. Low temperatures reduce the fluidity and permeability of the cellular membrane, which hinders nutrient (and contaminant) uptake. Higher temperatures promote greater enzymatic activity and faster biodegradation rates, up to an optimum, species-specific value. BTEX degradation rates can double or triple at temperature increases of 10°C. If the temperature rises much beyond the optimum value, proteins, enzymes and nucleic acids become denatured and inactive. The temperature of the upper 10 m of the subsurface may vary seasonally; however, between 10 and 100 m, subsurface temperatures approximate the mean annual air temperature of a particular region" (*Alvarez and others, 1999*).

Inhibitory substances such as heavy metals and other toxic substances

Microorganisms in aquifers require heavy metals in trace quantities for nutritional purposes; however, if present in soluble form at concentrations greater than 1 mg/L, heavy metals can be bacteriostatic or bactericidal. "High pollutant concentrations can also have toxic effects, such as gross physical disruption (for example, membrane dissolution) or competitive binding of critical enzymes." In addition, easily degradable substrates that are preferentially used can hinder contaminant degradation.

Moisture and salinity

Lack of moisture is a concern only in the vadose zone. Optimum conditions include a moisture content of about 80 percent field capacity or 15 percent water on a weight basis; moisture under 40 percent can significantly reduce biodegradation rates. High salinity can exert osmotic stress on microorganisms, which would hinder biodegradative processes.

Degradation pathways

In gasoline-contaminated aquifers, oxygen is often quickly depleted by microbial respiration; therefore, ethanol is likely to be degraded under predominantly anaerobic conditions. Microbial aerobic degradation of ethanol usually generates a variety of metabolic intermediates and end products (Table 3), none of which are toxic and rarely accumulate in significant amounts in groundwater. One intermediate is an aldehyde, which through the Krebs cycle is oxidized to carbon dioxide (CO₂). Some aerobic/anaerobic degradation products such as butyrate and propionate could adversely affect the taste and odor of groundwater supplies. Anaerobic degradation produces non-toxic products such as acetate, CO₂, methane, hydrogen gas and carbon dioxide. For more detail on the metabolic pathways and specific microorganisms involved, see Alvarez and others (1999).

Aerobic	Anaerobic
Acetaldehyde	Acetaldehyde
Acetate	Acetate
Acetyl-CoA	Butyric acid
Carbon dioxide (CO ₂)	Propionic acid
	Hydrogen gas
	n-propanol
	Acetone
	Carbon dioxide (CO ₂)
	Methane

Table 3. Metabolites and end products of ethanol biodegradation (*Alvarez and others, 1999*).

Biodegradation kinetics

BTEX and ethanol degradation can be described by a first-order decay regime, with contaminant concentration C and first-order decay coefficient lambda, :

$$dC/dt = -\lambda C$$

Contaminant half-life ($t_{1/2}$) is the time required to reduce its concentration by one half (that is $C_0/C = 2$):

$$T_{1/2} = \ln[2]/\lambda$$

These equations apply only to batch, completely mixed systems that assume an absence of dilution and advection. Thus, the value of λ will depend on the following:

- k, the maximum specific substrate utilization rate, which in turn depends primarily on prevailing electron-acceptor conditions and microbe type
- K_s, the half-saturation coefficient, related to enzyme affinity, bioavailability and mass transport limitations

- X, the active biomass concentration, which may not be constant and depends on environmental conditions and aquifer chemistry, including available substrates

Thus, k is not necessarily a constant but a coefficient that varies in time and space, shifting with microbial population resulting from aquifer chemistry changes. This accounts for the wide range of benzene decay rates—0.0001 to 0.0870/day—found in the literature, which suggests that extrapolation of decay rates should be done with care.

Ethanol degradation rates

In terms of degradation:

- ethanol degrades aerobically and anaerobically
- ethanol degrades faster than gasoline constituents and oxygenates; microorganisms that degrade simple alcohols are more common in nature than those that degrade BTEX compounds; thermodynamics also favor ethanol degradation
- with typical pH, temperature and nutrient levels, ethanol is expected to undergo rapid biodegradation in the subsurface
- ethanol has definite degradation rate coefficients, measured from aquifer microcosm studies
- because of its toxicity to most microorganisms, ethanol is not biodegradable in concentrations over 100,000 mg/L; such concentrations might be encountered near the source of neat ethanol releases; because the maximum allowable ethanol content in gasoline is 10 percent by volume, such high concentrations are unlikely to be encountered at sites contaminated with ethanol-gasoline blends, except near fuel/water interfaces
- ethanol concentrations should become exponentially more dilute with increasing distance from the source; thus, indigenous microbes located a sufficient distance from the source should degrade ethanol plumes
- ethanol has had no field-scale studies; field studies of methanol show concentrations of 1,000 mg/L being removed in three different soils in less than one year; pHs were 4.5 and 7.8 and temperatures 10° to 11°C; a similar study with fuel of 85 percent methanol and 15 percent gasoline (M85) in a shallow, sandy aquifer indicated all methanol degraded below 1 mg/L in 476 days—a half-life of about 40 days
- ethanol has no known field-scale studies on fate or transport
- in anaerobic aquifer slurries (in the laboratory) at initial concentrations of 50 mg/L, ethanol showed acclimation periods of 25 to 30 days; anaerobic biodegradation rate was 17.9 ± 0.6 mg/L-day; later findings indicate that initial results could be extrapolated to other redox conditions
- under various redox conditions, in aquifer microcosms at 20° to 35°C, ethanol exhibited longer degradation rates
 - at lower microbial concentrations and colder temperatures
 - due to mass transfer limitations

Ethanol degradation in surface water:

- is expected to proceed by biodegradation
- has a half-life of 6.5 to 26 hours under aerobic conditions
- is not limited by oxygen concentration

Ethanol biodegradation, even in anaerobic environments such as bottom layers of stratified lakes, is expected to be rapid; half-lives range from 1 to 4.3 days. Nutrient supply in rivers and lakes is not expected to restrict biochemical transformations because nutrients are supplied by rainfall recharge.

Ethanol effect on BTEX biodegradation

Ethanol will preferentially degrade over benzene. Evidence of ethanol's effect on BTEX biodegradation includes:

- at a concentration of 20 mg/L, ethanol was preferentially degraded under aerobic conditions over benzene because of enzyme synthesis repression
- microcosm studies suggest that preferential utilization of ethanol might increase the lag time before BTEX degradation begins; for instance, no BTEX degradation occurred in aerobic, denitrifying, iron-reducing, sulfate-reducing and methanogenic microcosms while ethanol was present; therefore, ethanol may prevent the bacteria subpopulation capable of degrading BTEX from fully expressing its catabolic potential, hindering BTEX degradation
- carbon-limiting conditions are conducive to simultaneous utilization of multiple substrates; this suggests that simultaneous ethanol and BTEX degradation is likely to occur when these compounds exist in low concentrations
- a pure culture of *Pseudomonas putida* F1 simultaneously degraded ethanol and toluene with no apparent inhibitory effect up to 500 mg/L of ethanol; toxicity thresholds of this microorganism are 6,500 mg/L for ethanol, 92 mg/L for benzene and 29 mg/L for toluene
- proliferate BTEX degraders (stimulated by ethanol) promote faster degradation rates; however, this effect might be offset by the preferential degradation of ethanol and associated depletion of electron acceptors
- using a thermodynamic model:
 - BTEX degraders were likely to grow faster on ethanol than on BTEX under a given set of conditions
 - predicted maximum specific growth rate on ethanol was 45 percent greater than the predicted maximum specific growth rate with benzene
 - the effect of ethanol on relative abundance of BTEX degraders has not been investigated
- exceptions to the detrimental effect of ethanol on BTEX degradation may be related to ethanol-induced microbial population shifts:
 - specifically, ethanol was degraded over BTEX during all electron-acceptor conditions tested
 - ethanol, however, enhanced toluene degradation in three sulfate-reducing microcosms, perhaps due to incidental growth of toluene degraders during ethanol degradation

Ethanol toxicity

Studies on ethanol toxicity indicate that ethanol:

- is very polar and partitions poorly into the hydrophobic cell membrane
- can exert biophysical effects on microorganisms
- is not mutagenic; but acetaldehyde, a metabolite of aerobic ethanol degradation, increases cell mutation rates
- can adversely affect the activity of some critical enzymes
- was toxic to microorganisms, as shown by complete lack of oxygen consumption in microcosm experiment (ethanol concentration of greater than 40,000 mg/L (4 percent wt/wt)
- allows soil microbial activity at 100,000 mg/L (10 percent wt/wt) , but not at 200,000 mg/L (21 percent wt/wt)
- will inactivate most vegetative organisms at concentrations above 100,000 mg/L
- in high concentrations, may kill bacteria by disrupting the cellular permeability barrier
- toxicity is related to chain length and hydrophobicity
- addition at 3,350 mg/L did not cause a significant inhibition of the Na⁺, K⁺-dependent ATPase, NADH oxidase or D-lactate oxidase; however, 8,500 mg/L ethanol did inhibit these enzymes

Based on results from a cell multiplication test, indigenous microorganisms are more resistant to high ethanol than to high BTEX and other fuel constituent concentrations.

Indirect environmental effects

The presence of ethanol indirectly affects the environment by

- exerting a significant biochemical oxygen demand compared to that exerted by other soluble gasoline components; thus, ethanol presence is likely to accelerate depletion of dissolved oxygen
- consuming dissolved common electron acceptors needed for anaerobic BTEX biodegradation, such as ferric iron and sulfate, potentially impeding BTEX natural attenuation
- depleting nutrient and electron acceptor store, but this has not been evaluated at the field scale
- possibly inhibiting gasoline biodegradation; field testing showed that a gasoline plume with methanol degraded slower than one with only gasoline, likely because of high methanol concentrations inhibiting microbes
- producing VFAs (volatile fatty acids) in mixed anaerobic cultures, which can accumulate and decrease the pH; this could be detrimental to methanogens that mediate anaerobic BTEX mineralization; methanogens are not significantly inhibited by VFAs in well-buffered systems; thus, such effects are likely to be system specific; however, VFAs are likely to be easily degraded and would be unlikely to accumulate in great concentrations

BTEX bioavailability and hydrodynamic properties

In addition, researchers suggest that ethanol

- could affect the availability of critical nutrients and co-substrates, although BTEX bioavailability is rarely a limiting factor in terms of biodegradation
- could decrease the extent to which BTEX compounds are retarded by sorption; evidence suggests that ethanol can affect the sorptive properties of soil organic matter
- could stimulate microbial processes that affect the aquifer's hydrodynamic properties
 - formation of cell aggregates and biofilms could clog available pore space
 - some microorganisms could contribute to mineral dissolution (CaCO₃) or precipitation (FeS) and cause porosity or permeability reduction
- could produce methane bubbles by methanogenesis, thus reducing effective porosity

Benzene plume lengths

Several studies are currently evaluating the effect of ethanol on benzene groundwater plumes. Thus far indications are that plumes are likely to increase, but the magnitude of increase is not known.

Impact to water resources

Based on the overall estimates of increased plume lengths, researchers expect about a 20 percent relative increase in the number of public drinking water wells impacted by benzene if ethanol replaces benzene (in California); this relative increase would decline at about 10 years after initiating ethanol use. The future impact of MTBE on water wells, however, would increase by as much as 45 percent. Researchers caution that because they are examining an absolute probability, these results should be used only for relative comparison.

Studies of watercraft discharges and accidental tank-car releases to surface water concluded that "aside from the acute-toxicity for aquatic species that might be associated with a spill and their associated recovery, it is unlikely that there would be any long-term toxic effects because the ethanol will not persist in water due to its rapid degradation. However, we were able to identify only one study of the biodegradation kinetics of ethanol in a surface water sample. The key uncertainty with regard to assessments of the impacts of ethanol releases to surface waters is the magnitude of the range of ethanol biodegradation rates" (*Rice and others, 1999*).

Ethanol's potential for rainout will be 40 times greater than for MTBE (based on their Henry's law constants); however, researchers acknowledge a need for laboratory studies of more accurate ethanol levels in rain and temperature-dependent values of Henry's law constant.

References

Alvarez, P.J.J. and C.H. Hunt with editors G. Cannon and D. Rice, and contributors R. Depue and B. Clark, "The Effect of Ethanol on BTEX Biodegradation and Natural Attenuation," Chapter 3, Volume 4, "Potential Ground and Surface Water Impacts," in *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*, December 1999, UCRL-AR-135949, Department of Civil and Environmental Engineering and Iowa Institute of Hydraulic Research, University of Iowa, Iowa City, Iowa 52242; <http://www-erd.llnl.gov/ethanol/>.

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Ethanol influence on gasoline movement

The presence of oxygenate chemicals, such as ethanol, in gasolines can potentially impact the migration and fate of gasoline in the subsurface (*Powers and others, 1999*). Processes potentially affected include the following:

- infiltration of gasoline through the unsaturated zone
- spreading of the gasoline pool at the water table
- dissolution of slightly soluble species from the gasoline into the water
- transport of these chemicals with the groundwater

Ethanol and BTEX concentrations in groundwater vary because of the cosolvent effect. Equilibrium concentrations of BTEX increase in the presence of ethanol, and losses due to adsorption and biodegradation decrease. The significance of these impacts in the subsurface as well as the potential impacts of mechanisms and variables (listed in Table 4) are poorly understood. "Essentially the presence of the organic ethanol molecules in the aqueous phase makes this phase less polar and therefore more compatible with organic molecules" (*Powers and others, 1999*).

Consider that following a gasoline release, "gasoline flows predominantly downward in response to gravitational forces. A fraction of the gasoline is retained as lenses or films between the air and water in the unsaturated zone. Once the bulk volume of gasoline reaches the capillary fringe, gasoline spreads laterally under a combination of gravitational and capillary forces, forming a body typically characterized by a lensoidal geometry. The capillary fringe is not completely saturated with gasoline but shares the zone with residual water and possibly air" (*Powers and others, 1999*). Where air, water and gasoline coexist at a given elevation:

- air predominantly fills the largest pores
- water fills the smallest pores
- gasoline fills the pores of intermediate diameter

Ethanol in gasoline could affect migration/distribution by:

- reducing the capillary forces, thereby changing the multiphase flow characteristics
- altering the pore structure of some mineral types

Capillary force and multiphase flow

The net impact of ethanol gasolines in the subsurface has not yet been quantified. Some observations follow:

- ethanol reduces the surface and interfacial tensions (IFT) between phases, thereby changing the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table
 - a reduced capillary force translates to a reduced capillary fringe height, thus altering gasoline pool depth; gasoline can enter smaller pore spaces; gasoline pool thickness decreases while areal extent increases
- a University of Waterloo study (*Donaldson and others, 1994* in *Powers and others, 1999*) using a gasoline with a methanol (85 percent, M85) vs. a regular formulated gasoline indicated
 - less lateral spreading in the unsaturated zone
 - a decrease in the capillary fringe height (after methanol was flushed from the system, the capillary fringe returned to its original height)
 - formation of a gasoline pool at the water table with a smooth and regular geometry and smaller lateral extent
 - formation of air bubbles where the M-85 displaced water due to non-ideal mixing of the methanol and water, causing a volume reduction
 - formation of a "halo" of droplets of gasoline around the periphery of the gasoline pool and infiltration zone due to reduced methanol concentrations and reduction in the effective solubility of the gasoline constituents; this substantially increased the NAPL-water contact area for dissolution
- reduction of IFT from 40 to 10 dynes/cm by adding isopropyl alcohol reduced hydrocarbon volume trapped in the saturated zone from 11 to 6 percent of total pore space
- a miscible displacement study of ethanol-water solutions (injected) to displace pure water in a sandbox found:
 - the ethanol solution preferentially stayed near the sandbox top because of its lower density
 - capillary fringe height was reduced by 50 percent, the same percentage as the decrease in the air-water surface tension of the ethanol solution
- another study showed that IFT reduction of water in the unsaturated zone resulted in a reduction of field capacity: drainage of water from the unsaturated zone increased contaminant transport from the vadose zone to saturated zone

How the effects described above would pertain to a spill of gasoline with 10 percent ethanol is difficult to predict. "If the mass transfer of the ethanol to the aqueous phase is rapid relative to the rate of gasoline infiltration, it is possible that some miscible displacement dynamics could dominate the

overall behavior of the infiltrating gasoline. Most of the ethanol in this case could partition into the aqueous phase, causing a change in the relative permeability of fluids in the vadose zone as the aqueous phase swells. Drainage of the ethanol-laden aqueous phase at a later time could dissolve BTEX compounds from the gasoline in a manner different than anticipated from a pool of gasohol" (*Powers and others, 1999*). Changes in gas-ohol retention in the vadose zone, and changes in a gasoline pool's size and shape at the water table would occur as

- ethanol partitions into the aqueous phase
- surface tensions and IFT reduce the capillary fringe height

The extent of these effects is not known.

Pore structure changes

Ethanol can change the pore structure of clay lenses by cracking and dehydrating the lenses. The findings of two studies follow:

- Measuring hydraulic conductivity changes of compacted, naturally occurring silty clays indicated that ethanol increased hydraulic conductivity by two orders of magnitude; experiments with ethanol displacing pore water, followed by the introduction of a non-polar hydrocarbon, resulted in a four-order-of-magnitude increase in hydrocarbon hydraulic conductivity, either from cosolvent effects or pore structure changes (*Fernandez and Quigley, 1985* in *Powers and others, 1999*)

- Gasoline containing 10 percent ethanol displaced water in kaolinitic clay soils, giving the clay a permeability 20 times greater than it would have been with water (*Stallard and others, 1997* in *Powers and others, 1999*)
 - magnetic resonance imaging revealed that the clay dehydrated on contact with ethanol and that vertical cracks formed
 - some regions of the clay became more dense because clay particles flocculate; thus, other areas of increased porosity developed

Conclusions

Ethanol can affect subsurface hydrocarbon movement by

- reducing the capillary fringe height; possible recovery of the original height could trap gasoline droplets below the water table
- reducing gasoline entrapment in the unsaturated zone
- changing direction/extent of size/shape of the gasoline pool due to reduced capillary forces around pool periphery
- potentially changing permeability of gasoline and altering migration pathways during infiltration due to significant partitioning of ethanol into the aqueous phase in the unsaturated zone
- changing permeability by dehydrating and cracking clay strata, allowing gasoline to penetrate previously impene-trable aquitards; movement of ethanol and BTEX from cracks in a clay lens would still be slower than from an unconsolidated medium

Process	Properties/mechanisms affected	Potential impact	Variables of importance
In the unsaturated zone			
Infiltration	Capillary forces	Size and shape of gasoline pool	Spill volume/duration 1) Gasoline composition 2) Heterogeneity in mineral type, grain size and water content
Spreading at the capillary fringe	Effective permeabilities 1) Volume changes as ethanol partitions into water	Distribution of gasoline residuals in the unsaturated zone and pool periphery	
	2) Dehydration and cracking of clay strata		
At gasoline source			
Leaching of chemicals into groundwater	Equilibrium composition of the two phases	Concentrations of BTEX and ethanol at the source	Gasoline composition 1) Groundwater velocities 2) Presence of residual droplets of gasoline in pool vicinity
	Mechanisms of transport of chemical species through the gasoline pools	Lifespan of the source	
	Mass-transfer rates across gasoline-water interface		
In the aqueous phase			
Transport of BTEX and ethanol to down-gradient receptors	Adsorption equilibria	Size and shape of contaminated groundwater plume	All variables affecting groundwater flow
	Precipitation of gasoline droplets		Concentration of species at the source 1) Concentration of electron acceptors 2) Organic content of mineral matrix 3) Ethanol concentration
	Biodegradation rates/mechanisms		

Table 4. Potential impacts of ethanol on fate and transport (*Powers and others, 1999*).

Cosolvency

"The addition of oxygenates to gasoline affects the ideal equilibrium partitioning relationships by the 'cosolvent effect', which is caused by the presence of a high concentration of organic compounds, such as alcohols, in the aqueous phase. These cosolvents reduce the polarity of the aqueous phase, causing a reduction in the aqueous-phase activity coefficient and allowing higher concentrations of hydrophobic organic compounds in the aqueous phase. This effect can also be explained in terms of changes in the Gibbs excess free energy associated with molecules of hydrophobic organic compounds (HOCs) in water being surrounded by cosolvent molecules as well as water molecules" (*Powers and others, 1999*).

Observations from studies on ethanol cosolvency indicate:

- alcohols in gasoline will preferentially partition into the aqueous phase
- ethanol and MTBE, which are polar oxygenates and hydrophilic, can occur in high concentrations and be highly mobile in water
- the equilibrium concentrations of gasoline constituents in water show that the alcohols increase solubility of aromatic hydrocarbons, whereas ethers, such as MTBE, have little effect on the solubility
- the significance of a cosolvent effect depends on the aqueous-phase solubility of the cosolvent
- the cosolvent effect from alcohols in gasoline would not be significant at the concentrations and residual saturations expected in the subsurface
- significant aqueous-phase concentrations of BTEX would be present during the early stages of dissolution of a gasoline release containing as little as 15 percent methanol
- for a given volume of gasoline, increases in the BTEX concentrations from a cosolvent effect were balanced by the reduced mass of these species in the gasoline because of the initial presence of the oxygenate; significant increases in aqueous benzene concentrations occurred only when the volume of gasoline-to-water was high
- batch experiments that varied volume ratios of water to gasoline (20:1 to 1:1) indicated that the maximum volume fraction of ethanol in the aqueous phase was about 15 percent; results showed that even a small concentration of ethanol in the aqueous phase (equivalent to 1 percent) increased BTX solubility somewhat
- experiments that quantified the extent of BTEX partitioning from RFGs (reformulated gasolines) with ethanol indicated that at low ethanol volumes:
 - aqueous-phase concentrations indicated an approximate linear trend, but at lower concentrations a distinctly different trend was attributed to hydration of cosolvent molecules
 - the cosolvency effect results in greater percent increases in the concentrations of the more hydrophobic xylene vs. the less hydrophobic benzene

- the extent of the cosolvency effect is often quantified by a cosolvency factor: the slope of the logarithm of the concentration vs. the volume fraction of solvent

Powers and others (*1999*) and Heermann and Powers (*1998*) in *Powers and others, 1999* describe how effects are modeled.

Interfacial mass transfer and cosolvency

The interphase mass transfer of ethanol and hydrocarbons between gasoline and groundwater is expressed as a product of a mass transfer coefficient and a concentration difference between the two phases. "The mass-transfer coefficient, k , reflects rate limitations to interphase mass transfer resulting from the non-instantaneous transport of compounds to and away from the phase boundary. Thus, for a gasoline pool, ethanol and hydrocarbons must be transported through the gasoline to the phase boundary separating the gasoline and groundwater and transported away from the boundary with the groundwater" (*Powers and others, 1999*).

"The rate at which ethanol is transported from gasoline to groundwater will largely determine the magnitude and the duration of the cosolvency effect. Very rapid rates of ethanol mass transfer would lead to greater ethanol concentrations in groundwater that would further lead to increased hydrocarbon concentrations because of cosolvency. The rate of mass transfer would govern the duration of the cosolvency effect as a result of a more rapid depletion of ethanol" (*Powers and others, 1999*).

Transport processes

The authors report the following:

- for sufficiently slow ethanol transport to the gasoline/water boundary, the net interphase mass-transfer rate will about equal the rate of ethanol transport through the gasoline
- for very rapid rates of ethanol transport, concentration gradients will be small, but ethanol will be rapidly depleted from the gasoline, invalidating the assumption used in most NAPL-groundwater models that NAPL phase is homogeneous and constant
- for sufficiently fast ethanol transport through gasoline, transport via groundwater will define the mass-transfer, rate-limiting process
- two transport processes, molecular diffusion and free convection, contribute to ethanol and hydrocarbon transport through gasoline

"Molecular diffusion describes the net movement that occurs when molecules undergoing random motion are subjected to a concentration gradient. Free convection occurs when a density gradient exists within a single fluid. If the gradient is such that the fluid is less dense near the bottom, a physically unstable fluid profile is created and convective flow occurs, typically manifested as fingers" (*Powers and others, 1999*).

Gasoline is usually less dense than ethanol, therefore gasoline with ethanol will be denser than gasoline without ethanol. As ethanol moves downward to a gasoline-groundwater interface, high and low-density gasoline regions are created and

become unstable; gasoline with higher ethanol content and greater density flows downward to the boundary, while the less dense, ethanol-depleted gasoline moves upward. This free-convective flow has been shown to greatly increase the rate of ethanol transport to the boundary, with respect to diffusional transport. "The higher rate of interphase mass transfer resulting from free convection will likely lead to greater ethanol concentrations in groundwater and, therefore, to a greater cosolvency effect. However, the higher mass-transfer rate will yield a more rapid depletion of the ethanol in the gasoline" (*Powers and others, 1999*).

In terms of transport rate in groundwater:

- mass transport is largely controlled by advection and hydrodynamic dispersion
 - advection is the principal means of transporting hydrocarbons horizontally away from the gasoline-pool boundary with flowing groundwater
 - hydrodynamic dispersion is the principal means for vertical transport away from the gasoline pool
 - as groundwater flow rates increase, these processes reduce solute concentration near the interface
 - in comparison to advection and dispersion, molecular diffusion is very slow
 - free convection is a more rapid transport process
 - here, ethanol and BTEX species would be higher in groundwater (rather than transported by diffusion)
 - ethanol, however, will be depleted from gasoline more rapidly, reducing the period of time that ethanol influences BTEX dissolution
- following ethanol depletion from gasoline, the remaining pool behaves as a standard blend gasoline
- researchers do not know whether free convection or advective/dispersion transport via groundwater is the rate-limiting step

Factors impacting transport

Adsorption is most simply described as a formation of a layer of molecules on the surface of a solid or, less frequently, of a liquid. "One of the chief effects of adsorption is the retardation of hydrocarbons in such way that their effective velocities become less than the groundwater transporting them." A one-dimensional modeling study with BTEX and M85 gasoline (*Rixey, 1994 in Powers and others, 2000*) showed that

- when cosolvent-dependent adsorption was incorporated into the model, BTEX compounds moved more rapidly through the porous medium
- methanol and BTEX were assumed to be added instantaneously, so the downgradient concentrations appeared as discrete peaks
- benzene, the least hydrophobic of the BTEX compounds, moved through the porous medium with nearly the same velocity as the methanol and water
- the cosolvency effect of the methanol on toluene was less than that for benzene

- cosolvency effects were significant only where the downgradient aqueous methanol concentrations exceed 10-13 weight percent

Studies on phase separation for M85 alcohol gasolines (*Rixey and Dortch, 1992; and Donaldson and others, 1994 in Powers and others, 2000*), indicated the following:

- a release of M85 to the subsurface showed the gasoline to be completely miscible with water; NAPL did not form
- as the fraction of water decreased, the gasoline became immiscible with water, which led to a separate phase
- pore-scale visualization studies indicated formation of NAPL droplets on sand grains that became trapped in the pore structure, consequently reducing permeability of the porous medium to water
- droplets acted as a latent hydrocarbon source

Most gasohols have ethanol concentrations that are much lower than the methanol concentration in M85. It is not expected that phase separation will occur for gasohols with 10 percent by volume ethanol. Neat ethanol's effect on subsurface processes are expected to be similar to those of alcohol's, except for two differences:

- ethanol quantities and concentrations will be greater
- the rate-limiting interphase mass transfer of ethanol from gasoline to vadose-zone water or groundwater is eliminated

Releases of neat ethanol would be expected to

- increase the aqueous solubility and dissolution rates of NAPL compounds
- reduce the mass of organic compounds sorbed to the solid phase
- reduce IFT (interfacial tension) between the NAPL and the aqueous phase and, in effect, allowing NAPL migration

Powers and others (1999) report on other studies that involved injecting ethanol into the subsurface to dissolve and mobilize NAPL.

Observations from a modeling study

Researchers used a solute transport model (MOCDENSE) to assess the potential impacts of cosolvency and dissolution rates on groundwater concentrations. Biodegradation and adsorption were not considered in these simulations. The model simulated aqueous-phase ethanol and m-xylene concentrations (gasoline had 10 percent ethanol, 13.5 percent m-xylene and 85 percent iso-octane by volume) over a period of 180 days. Groundwater flow was 0.1 m/day, aquifer effective porosity was 0.25 and the horizontal and transverse dispersivities were 1.0 m and 0.1 m respectively. The gasoline pool at the water table was 10 m by 0.5 m thick. *Power and others (1999)* give more details on the model in their text. Modeling indicated the following:

- ethanol caused a 10 percent increase in the distance to the leading edge of the m-xylene plume at 180 days

- when smaller interphase mass-transfer coefficients were used, ethanol did not affect size and extent of the m-xylene plume
- ethanol was more than 90 percent depleted from the gasoline within several days, and 99 percent depleted in less than 90 days; values were a specific function of the mass transfer coefficient

The authors concluded the following:

- inclusion of adsorption and biodegradation in the model would have shown a smaller plume size, but the plume would be larger in the presence of ethanol than for standard gasoline
- a thicker gasoline pool at the pool/groundwater phase boundary will cause greater concentrations of ethanol to dissolve because of the greater ethanol mass
- higher ethanol concentrations will produce a much greater cosolvency effect, increasing BTEX plume length

Reference

Powers, S.E. and S.E. Heermann with editors G. Cannon and D. Rice, contributors R. Depue and B. Clark, "A Critical Review: The Effect of Ethanol in Gasoline on the Fate and Transport of BTEX in the Subsurface," Chapter 2 in Volume 4, "Potential Ground and Surface Water Impacts," in *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*, December 1999, Clarkson University, Department of Civil and Environmental Engineering, W.J. Rowley Laboratories, Potsdam, New York 13699 and Lawrence Livermore Laboratory, Livermore, California, UCRL-AR-135949; <http://www-erd.llnl.gov/ethanol/>.



Ethanol detection methods

At present, ethanol is not a federally regulated compound, nor is it regulated in many states. Regulators, however, are studying ethanol more closely because of its greater potential use in gasoline. Extensive data on the fate and transport of ethanol does not yet exist, yet researchers are identifying the criteria for ethanol characterization in the subsurface. Because ethanol is a small polar molecule with an affinity for water, the most difficult step in analyzing ethanol may be extracting the molecule from water. This is especially true for small concentrations of ethanol (*Koester and others, 1999*).

Selection of an analytical method will depend on the method's

- detection level (DL)
- precision
- accuracy
- ease of performance
- data reproducibility by different laboratories
- ability to screen out false positives or negative detections

- adherence to quality assurance/quality control (QA/QC) protocols
- practicality
- cost effectiveness; current analyses for organic compounds range from \$100 to \$400

"The appropriate analytical methods to analyze (that is extract, separate, identify and measure) ethanol or any other environmental contaminant are dictated by the intended use of data." Koester and others (*1999*) studied ethanol analytical methods, and specifically detection levels (DLs), with respect to three scenarios:

- assessment of ethanol concentrations at a spill site
- documentation to meet regulatory requirements
- environmental fate and transport

Assessment of ethanol concentrations at a spill site. "The expected concentration of ethanol in contaminated groundwater near a spill site is likely to range between 400 to 4,000 ppm. Thus, to monitor an ethanol-contaminated water associated with fuel spills would require methods with DLs of 400 ppm . . . In addition, the selected analytical method must detect ethanol in the presence of high concentrations of hydrocarbons . . ."

Documentation to meet regulatory requirements. "The taste and odor thresholds of ethanol in drinking water are 50 ppm and greater than 100 ppm, respectively. If we assume that no adverse health effects are associated with consuming trace quantities of ethanol, we would predict that a drinking-water standard would be set at the taste threshold of ethanol (50 ppm). Thus, a method detection of at least 50 ppm would be sufficient to ensure water quality. This DL is approximately a factor of ten lower than required to characterize ethanol contamination at a spill site" (*Koester and others, 1999*).

Environmental fate and transport. "To determine the movement of ethanol through the environment, researchers must assess the environmental background levels of ethanol at uncontaminated sites. Parts-per-billion concentrations of ethanol, possibly produced by 'natural' chemical and biological processes, might be present in environmental surface and groundwaters. It is possible that surface and groundwaters will be indirectly impacted by the use of blended fuels. To understand the native background of ethanol in the environment and to understand impact of ethanol from blended fuels, the lowest DLs achievable (ppb or better) would be needed."

Ethanol analysis methods

Because ethanol has not been considered to be a contaminant of environmental concern, ethanol analysis has not been a great concern. "The alcoholic beverage industry performs many ethanol analyses to ensure the quality of its products. Ethanol DLs for the analyses of beer and wine cited in Table 5 range from 1 to 50,000 ppm. Many of these methods, however, do not have sufficient DLs to be applied to the analysis of ethanol in environmental samples. The method using an oxygen-electrode sensor (5–10 ppm DLs)

lacks a large dynamic range and would not be applicable to environmental analysis." Gas-diffusion membranes coupled with amperometric detection (1-ppm DL) might be useful for analysis of environmental samples.

Researchers suggested various U.S. EPA methods for ethanol analysis. Appropriate methods include azeotropic distillation (Method 5031) and vacuum distillation (Method 5032) to extract and concentrate ethanol. "These methods suggested that direct aqueous injection of water into a GC/FID (gas chromatography with flame-ionization detection) or the use of a gas chromatograph coupled with a mass spectrometer (GC/MS) were appropriate for ethanol analysis. Again, because ethanol is not a regulated compound, the U.S. EPA methods contained no information regarding DL, linear range, precision or accuracy" (Koester and others, 1999).

Several methods successfully use the purge-and-trap technique for extraction of ethanol:

- ASTM (American Society of Testing and Materials) Method D4815, developed to measure 0.1 percent concentrations of ethanol in gasoline; the method uses two-dimensional gas chromatography (2D-GC) to remove interferences; the sample is injected directly into the gas chromatograph and first eluted through a polar, capillary gas-chromatograph column that retains all oxygenates, including ethanol; then oxygenates are backflushed into a nonpolar, capillary gas-chromatograph column for final separation and detection by a flame-ionization or thermal-conductivity detector

- a method that combines purge-and-trap extraction with two-dimensional chromatography coupled with a flame-ionization detector; DLs for ethanol in clean water and in water contaminated with 5 percent nonaqueous phase liquid (NAPL) are 200 ppb and 100 ppm, respectively
- a method modified from U.S. EPA Method 8260B to obtain 50 ppb DLs for ethanol in water; the method uses purge-and-trap extraction at ambient temperature and cryofocusing prior to final analysis by GC/MS
- a method using solid-phase microextraction (SPME) coupled with GC/MS; a small fiber (~ 0.3 mm in diameter) coated with 85 mm of a carboxen/polydimethylsiloxane polymer extracts ethanol from water; after soaking in the sample for about 30 minutes, the fiber, which contains ethanol, is removed and directly injected into a GC/MS; this represents the best DL that has been reported to date for the determination of ethanol in water; although SPME can be automated easily, this technique requires a greater level of expertise to perform than purge-and-trap methods

Sample handling and preservation

Samples not properly collected, preserved and stored may be of questionable quality and not scientifically or legally defensible. Although optimal conditions for ethanol preservation and storage have yet to be determined, Koester and others (1999) recommend the following:

- collect water samples in 40-ml vials with Teflon^R-lined septum caps and no headspace

Technique	Sample	DL (ppm)	Useful for environmental analysis
Headspace GC/FID	Plasma	1,000	No
Derivatization to ethyl dithiocarbonate; differential-pulse polarography	Beer	200	No
Oxygen electrode based on NSDH oxidase from <i>Bacillus licheniformis</i> and alcohol dehydrogenases	Wine	5-10	No
Online membrane inlet ion mobility spectrometry	Beer	500	No
Heated (75°C) headspace GC/FID	Biological fluids	10	Maybe
Flow injection analysis coupled with gas-diffusion membrane and immobilized alcohol oxidase amperometric detection	Beer, wine	1	Maybe
Micellar electrokinetic capillary chromatography; diode-array detection	Wine	50,000	No
Solid-phase extraction cleanup; flow injection analysis; amperometric detection	Wine	500	No
Heated (75°C) headspace GC/FID	Blood	0.3	Yes
10-ml direct injection, GC/FID	Biological fluids	0.1	Yes
5-ml direct injection, GC/FID	Water	3	Yes
5-ml direct injection, GC/FID	Water	1	Yes
Modified ASTM Method D4815	Soil, water	0.2	Yes
Modified U.S. EPA Method 8260B with cryofocusing	Water	0.05	Yes
Solid-phase microextraction coupled with GC/MS	Water	0.015	Yes

Table 5. Ethanol analysis methods (from Koester and others, 1999).

- store aqueous samples at 4°C for up to 14 days prior to analysis
- possibly store samples for up to two years if frozen
- to help preserve water samples and to minimize potentially degrading bacterial growth, add four drops of concentrated hydrochloric acid

Recommendations to improve sampling analyses

Researchers recommended the following:

- rigorously study sample preservation methods
- improve extraction of ethanol from aqueous samples:
 - use either direct injection of an aqueous solution or injection of the headspace above an aqueous liquid to obtain DLs of 10 ppm or less; both techniques are easy and inexpensive to perform
 - investigate purge-and-trap, azeotropic distillation or vacuum distillation for producing lower DLs (the last two are more expensive and labor-intensive)
 - investigate microextraction as to possibility of producing lower DLs
- use GC separation in all future ethanol analyses to eliminate interferences
 - first use the best possible GC procedure to separate ethanol from interferences
 - then use the FID to detect ethanol
 - or perform a less rigorous GC separation coupled with a detector that would respond only to ethanol
- use 2-D chromatography if an FID detector is used to minimize interferences
- investigate GC coupling with an analyte-specific detector (atomic-emission detector (AED) or mass spectrometer (MS)
 - the AED, operated in the oxygen-specific mode, can be “blinded” to potentially interfering hydrocarbons
 - the MS can provide a mass spectral “fingerprint” unique to each compound
 - neither machine would be cost-prohibitive; they would simplify the chromatographic requirements because only one GC column would be required to separate ethanol from potential interferences
- modify existing methods slightly to improve ethanol detection in water
- use cryofocusing in combination with gas chromatography

Reference

Koester, C., with editors D. Rice and G. Cannon, and contributor R. Depue, “Evaluation of Analytical Methods for the Detection of Ethanol in Ground and Surface Water,” Chapter 7 in Volume 4: “Potential Ground and Surface Water Impacts,” in *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*, December 1999, UCRL-AR-135949, University of California, Lawrence Livermore National Laboratory, <http://www-erd.llnl.gov/ethanol/>.



Ethanol study conclusions

Rice and others (1999) identified these data gaps in the LLNL study:

- life-cycle analysis
- fate and transport processes
- biodegradation

Life-cycle analysis

Researchers developed a life-cycle model that systematically addressed “impacts from fugitive and accidental releases associated with the production, distribution and use of gasoline containing ethanol.” The assessment focused only on scenarios of chronic or accidental releases most likely to impact ground and surface waters. Not considered were

- releases of substances as a consequence of the transportation and use of feedstocks required for ethanol production
- releases of substances at centralized blending centers
- additional implications of agricultural-related impacts from ethanol-fuel production that might involve, for instance, application of additional herbicides/pesticides

Researchers found limited information on alkylates (complex solutions of isoalkanes), non-oxygenated compounds that are likely to be used in greater amounts after the MTBE phaseout. Surface releases of alkylates would likely result in evaporation and not cause dramatic changes in the way gasoline behaves in the environment. Issues not addressed include:

- an integrated life-cycle analysis concerning alkylate production, storage and use
- alkylate biodegradability, which in general is slow compared to organic compounds
- toxicity or chronic effects of alkylate in humans
- alkylate cancer risk, reproductive and developmental effects

Fate-and-transport processes

In the unsaturated zone, a critical knowledge gap exists concerning the “nature of the interaction of groundwater and air (multiphase flow) with ethanol-containing gasoline.” Ethanol affects gasoline migration and distribution in two ways:

- capillary forces are reduced, changing multiphase flow characteristics
- pore structure of some mineral types is altered by chemical interactions with ethanol

“In the presence of ethanol, hydrocarbons can enter smaller pore spaces and drain more easily from unsaturated zone soils. This may impact the distributions of residual fuel hydrocarbons in the unsaturated zone and the periphery of free-product pools that may exist. Among the impacts may be the mobilization of existing unsaturated zone contamination. As a result of reduction in capillary forces, the height of the capillary fringe may also be reduced. The depth and area of hydrocarbon pool on top of the water table may be altered,

although 10 percent ethanol in gasoline is expected to have a very minor effect. Further, the dehydration of clays and formation of microfractures will increase permeability. The importance of these factors in multiphase flow has not been quantified . . . knowledge gaps about the early stages of the overall flow and transport make adequate prediction of the important impacts of ethanol on BTEX contamination difficult" (Rice and others, 1999).

Ethanol impacts on BTEX concentrations in the saturated zone include the following:

- dissolved equilibrium concentrations of benzene, toluene, ethylbenzene and xylenes will increase with high ethanol concentrations; however, 10 percent, which is anticipated in gasoline, should have only a minor effect; this effect will be greater on hydrophobic compounds, such as xylenes
- ethanol may alter sorption and retardation and contribute to increased benzene plume lengths, which will be a function of the percentage of ethanol present

To assess plume length, researchers need "a better understanding of the significance of the size, shape and composition of free-product gasoline in contact with the water table. A thorough modeling effort to assess the sensitivity of the overall predictions to these unknown parameters would be an appropriate first step."

Biodegradation

Current hydrocarbon bioremediation and risk assessment may have to be adapted to reflect the influence of ethanol. Researchers recognize the following:

- biodegradation of fuel alcohols contributes to depletion of electron acceptors
- depletion of electron acceptors affects BTEX degradation and migration rates
- changes in electron acceptors could affect catabolic diversity and relative abundance of bacteria

- an effect of ethanol on microbial population shifts could be, for instance:
 - enrichment of ethanol-degrading bacteria in relation to BTEX-degrading bacteria
 - fortuitous enrichment of bacteria that degrade both ethanol and BTEX compounds
 - decreases in populations of certain bacteria due to ethanol toxicity
- the co-occurrence of BTEX and ethanol may be a short-lived phenomenon relative to duration of a gasoline plume; thus, oxygen and electron acceptor depletion (from ethanol degradation) may be more important than substrate interactions between ethanol and BTEX
- releases of pure ethanol at distribution terminals could magnify any negative effects of ethanol introduction into the environment (as little as 1 percent water can cause "phase separation" of an ethanol-gasoline mixture)
- it is expected that ethanol may increase BTEX plume length by hindering BTEX biodegradation, enhancing light nonaqueous phase liquid (LNAPL) dissolution, and facilitating BTEX migration due to a decrease in sorption-related retardation during transport

Researchers recommend studying the following:

- in the laboratory and field, the applicability and limitations of natural attenuation for different release scenarios of BTEX-ethanol mixtures
- the microbial ecology of aquifers contaminated with gasoline-ethanol mixtures
- substrate interactions between BTEX and ethanol; preferential substrate degradation appears to be concentration-dependent and related to repression of enzymes needed to degrade target compounds
- the concentration-dependent effect that ethanol may have on the induction or repression of enzymes that catalyze BTEX degradation

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- holistic approaches that consider transport and degradation processes interactively; much work has been focused on individual processes that oversimplify the complex conditions encountered in the field; for instance, batch studies will often eliminate the confounding effects from other variables such as BTEX and electron-acceptor concentration gradients
- ethanol influence on stimulating microbial processes that affect aquifer porosity and hydraulic conductivity, such as biofilm growth, mineral precipitation or dissolution and nitrogen and methane gas formation
- conditions that lead to a significant accumulation of volatile fatty acids (VFA, potential degradation of ethanol) that could decrease pH and inhibit bioremediation
- potential for ethanol-produced methane production to restrict groundwater flow (thus, hindering nutrient/ electron acceptor replenishment) and pose an explosion hazard (possibly requiring unique corrective measures)
- effect of neat-alcohol releases on the natural attenuation of BTEX and MTBE contamination at distribution terminals
- any available information about gasohol leak sites

General conclusions

Rice and Cannon (1999) make these general conclusions:

- models of benzene and ethanol interaction indicate that benzene plumes are likely to increase in length in the presence of ethanol; the amount of increase is uncertain
- in terms of the potential health risks of ethanol:
 - there were no substantial differences between the various fuel types with regard to the resulting levels of irritant air pollutants
 - although replacement of MTBE by either ethanol or nonoxygenated fuel is expected to have some benefits in terms of water contamination, these cannot be

quantified at present; the researchers' analyses indicated that these substitutions had no substantial effects on public-health impacts of air pollution

In conclusion, Rice and Cannon (1999) recommend the following research efforts:

- expanded life-cycle analysis of the use of ethanol and nonoxygenated fuel compounds
- detailed field studies to refine conceptual models
- microcosm and aquifer column studies using field study materials
- historical case studies to develop statistical analyses
- laboratory studies to improve estimates of Henry's law constants
- development of laboratory analytical methods
- development of a central database

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Rice, D.W., Alvarez, P.J.J., Powers, S.E., Beller, H., Kane, S.R., Daniels, J.I., Layton, D.W. and B. Doohar, "Knowledge Gaps Regarding the Surface Water and Groundwater Impacts of Ethanol-Containing Gasoline and Recommendations for Future Research," Chapter 9 in Volume 4: "Potential Ground and Surface Water Impacts" in *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*, December 1999, UCRL-AR-135949, University of California, Lawrence Livermore National Laboratory, Environmental Restoration Division, Livermore, California 94550; <http://www-erd.llnl.gov/ethanol/>.

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