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# **EVALUATION OF THE FATE AND TRANSPORT OF ETHANOL IN THE ENVIRONMENT**

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## EXECUTIVE SUMMARY

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In order to comply with federal Clean Air Act requirements for attainment of carbon monoxide and ozone standards, 17 states have opted to use oxygenated fuels. Currently, oxygenated fuels account for more than 34% of all gasoline sold in the United States (USEPA, 1998). These states are using either federal Reformulated Gasoline (RFG) or oxygenated fuel (oxyfuel) containing 2.0% and 2.7% minimum oxygen by weight, respectively. Approximately 80% of these fuels contain methyl tert-butyl ether (MTBE) to meet oxygen requirements, 15% contain ethanol, and 5% contain other oxygenates, such as tert-amyl methyl ether (TAME), diiso-propyl ether (DIPE), ethyl tert-butyl ether (ETBE), and tert-butyl alcohol (TBA). While the impact of MTBE-containing gasoline releases into the environment is currently being studied, few studies exist on the potential impact of ethanol-blended gasoline releases into the environment. The purpose of this paper is to describe the fate and transport of ethanol once released into the environment under a variety of release scenarios: atmospheric release, underground storage tank (UST) release, or pure product spill.

Ethanol is a highly soluble, mobile, short-chained hydrocarbon which does not readily volatilize from water or adsorb onto soil or sediment material. However, it does not seem to accumulate in the environment. Once released to the atmosphere, ethanol concentrations quickly become dilute and rapidly diminish due to photodegradation (half-life = 2.4 days). Therefore, significant removal by precipitation (rain or snow) is unlikely. If released to the soil and groundwater and allowed to equilibrate, ethanol is expected to partition into the aqueous phase due to its low Henry's constant ( $<0.0003$  [dimensionless] at 25°C) and soil/water partition coefficient. However, ethanol will quickly biodegrade (half-life between 1 and 5 days) and is not likely to impact drinking water wells. Based on realistic LUST release scenarios, maximum ethanol concentrations in groundwater in the vicinity of the release can be expected to be between 400 and 4,000 mg/L. Higher concentrations may be encountered in groundwater in close proximity to the source area of a pure product spill. However, in both scenarios, ethanol is not likely to increase the mobility of other gasoline constituents encountered; i.e., the cosolvency exhibited by ethanol is negligible.

One of the primary disadvantages of using ethanol-blended fuels is the reported increase in vehicle emissions. Ethanol blended gasoline decreases carbon monoxide levels more than MTBE blended gasoline; however, ethanol increases the total hydrocarbon (e.g., acetaldehyde, formaldehyde, and other short chained hydrocarbons) and NO<sub>x</sub> emissions levels—all of which are precursors to ozone formation. Acetaldehyde emissions are reported to increase by at least 100% compared to conventional gasoline, resulting in an increase in the formation of peroxyacetyl nitrate (PAN).

A second disadvantage of adding ethanol to gasoline is the potential impact of ethanol biodegradation on the natural biodegradation of other gasoline constituents present in the groundwater. Ethanol is known to readily biodegrade under a variety of aerobic and anaerobic conditions. Under these conditions, ethanol is a preferred substrate and will be preferentially utilized in the presence of BTEX (benzene, toluene, ethylbenzene and xylenes). However, as ethanol is aerobically biodegraded, oxygen and other electron acceptors, as well as nutrients will become depleted in the subsurface. As a result, BTEX plumes may be lengthened due to the resistance to biodegradation in the presence of ethanol. In 1995, the Lawrence Livermore National Laboratory in Livermore, California released a report which concluded that the median length of BTEX plumes in shallow groundwater was approximately 250 feet and that in most cases, these plumes were stable. The presence of ethanol is expected to increase BTEX plume lengths by approximately 27% under typical California groundwater conditions (ranging from 16% to 34% increase in BTEX plume length). The potential impact of increasing BTEX plume lengths is either a greater probability that drinking water well fields could be impacted by BTEX or higher BTEX concentrations at wells that are already contaminated. Both of these impacts would result in higher cleanup costs for BTEX plumes, if cleanup is warranted.

If well fields were located sufficiently near an ethanol-blended gasoline release and ethanol were to migrate to the drinking water well, the removal of ethanol could pose significant problems. However, if ethanol does impact drinking water, likely concentrations of ethanol will fall well below its toxicity limits and below its high taste and odor threshold. Consequently, treatment will not be required unless maximum allowable drinking water concentrations of ethanol are established based on some other criteria. If treatment is required, the properties of ethanol will make it difficult to easily remove from water, compared to BTEX. Due to its low Henry's constant and low soil/water partition coefficient, ethanol can not be easily removed from water by air stripping or adsorption on activated carbon.

Biologically activated filters can be used to remove ethanol from water, but typically drinking water purveyors are reluctant to use a biological process for potable water treatment. While other emerging technologies may be effective, such as reverse osmosis or nanofiltration, the only proven technology for removal of ethanol from drinking water is advanced oxidation. However, this process raises additional concerns regarding oxidation by-products.

Finally, this report briefly summarizes the aquatic toxicity and human toxicity resulting from inhalation or ingestion of ethanol. Given realistic exposure levels of ethanol in the atmosphere, groundwater, or surface water following either a refueling atmospheric release, a pure product spill, or a release from an UST to soil and groundwater, it is unlikely that any human effect will be observed as a result of inhalation or ingestion of ethanol. However, a pure product spill of ethanol or a large UST release could cause ethanol levels to become toxic to microbial and aquatic life.

In conclusion, the fate and transport of ethanol in the air, soil, and groundwater is well understood. Ethanol released alone into the environment does not accumulate because it rapidly photodegrades or biodegrades. However, the presence of ethanol may retard the biodegradation of BTEX plumes in the groundwater. Thus, the average BTEX plume length will be increased which may lead to a higher probability of BTEX impacting drinking water wells.

# 1.0 INTRODUCTION

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## 1.1 Purpose of Report

The purpose of this report is to summarize the scientific literature on the fate, transport, treatment, and toxicity of ethanol in air, soil, groundwater, and surface water as a result of its use as a fuel oxygenate. This study addresses the environmental persistence of ethanol and the impact, if any, of ethanol on water resources. Also included in this report is a summary of the literature describing the advantages and disadvantages of using ethanol to meet fuel oxygenate requirements.

## 1.2 Scope

The fate and transport of ethanol will be analyzed by studying the life-cycle transport of ethanol through the environment. The three primary scenarios for the release of ethanol to the environment are atmospheric releases, leaking underground storage tank (LUST) releases, and spills during ethanol transport. Each scenario will be discussed in this report. Once released to the environment, the fate of ethanol is controlled by physical, chemical, and biological processes including dissolution, volatilization, adsorption, biodegradation, and abiotic chemical degradation. This report will describe the relative magnitude of these processes, as well as the effect of ethanol on other gasoline constituents that may be simultaneously released. A probabilistic ethanol plume length analysis will be used to quantify the impact of ethanol on the fate and transport of other constituents. Finally, this report will briefly summarize some of the human and aquatic toxicity data associated with elevated ethanol concentrations in groundwater or surface water.

### 2.1 History of Use

Fuel oxygenates have been used in the United States for more than two decades (Squillace et al., 1995). Oxygenates were added to gasoline initially to increase the octane rating, and more recently to reduce vehicle emissions of carbon monoxide and hydrocarbons. Ethanol is one of several gasoline additives that fulfill the gasoline oxygen content requirements of the Clean Air Act. The practice of adding ethanol to gasoline began in 1978 in the U.S. when a Nebraska group marketed gasohol, a gasoline containing 10% ethanol by volume. The purpose of this program was to increase gasoline availability during the oil embargo (Chevron, 1996; USEPA, 1998). In 1990, the Clean Air Act Amendments (CAAA) mandated the use of oxygenates in gasoline, either year-round or seasonally, in certain air quality basins not meeting federal air quality standards for carbon monoxide (CO) and ground-level ozone (O<sub>3</sub>), or “smog.” To meet the requirements of the CAAA, the EPA initiated the Oxyfuel Program in 1992 and the Reformulated Gasoline Program (RFG) in 1995. The former requires the use of gasoline with 2.7% oxygen by weight during the winter months to control carbon monoxide emissions, and the latter requires the use of gasoline with 2% oxygen throughout the year in ozone non-attainment areas. These mass oxygen contents correspond to 7.3% and 5.4% ethanol by volume, respectively. In 1992, 8% of all gasolines in the United States contained ethanol. Currently, approximately 30% of all fuel sold in the United States is oxygenated to meet RFG requirements and an additional 4% is oxygenated to meet Oxyfuel requirements (USEPA, 1998). Ethanol-blended fuels account for approximately 15% of all oxygenated fuels sold in the United States (USEPA, 1998).

### 2.2 Production

Ethanol can be synthesized from ethylene, acetylene or sulfite waste liquors; it can also be produced by the hydrolysis of ethyl sulfate, or the oxidation of methane (Chevron, 1996; Merck Index, 1989). The most common method of ethanol production is by the fermentation of carbohydrates, mainly corn (Pimentel, 1998); subsequent to carbohydrate fermentation, ethanol is distilled, dehydrated and denatured prior to its addition to fuel.

About 1 billion gallons of ethanol have been produced in the United States during each of the past few years (Pimentel, 1998). In April 1998, 100 million gallons of ethanol were produced in the U.S. compared to almost 300 million gallons of methyl tert-butyl ether (MTBE) (Energy, 1998). Ninety-four percent of the ethanol produced in 1993 was from the fermentation of corn in the Midwest (Chevron, 1996). Consequently, the production of ethanol is highly influenced by the market price of

corn, e.g., in 1996 as corn prices rose to \$5/bushel (USDA, 1997), ethanol production was dramatically curtailed (DeWitt, 1997).

### 2.3 Chemical and Physical Properties

Ethanol is a highly mobile small chain alcohol with an infinite aqueous solubility. It is hygroscopic, i.e., it has a tendency to absorb moisture when in contact with air. Relative to ether oxygenates such as MTBE, ethanol has high oxygen content and heat of vaporization, and low air/water and soil/water partition coefficients. In addition, ethanol is denatured in order to comply with the Bureau of Alcohol, Tobacco, and Firearms, resulting in a 2% to 5% addition of an approved denaturant chemical. The physical and chemical properties of ethanol and MTBE are summarized in Table 2.1.

<b>Table 2.1</b>		
<b>A Summary of Physical and Chemical Properties of Ethanol and MTBE</b>		
<i>Physical and chemical properties</i>	<i>Ethanol (reference)</i>	<i>MTBE (reference)</i>
CAS no.	64-17-5	1634-04-4
Molecular weight [g/mole]	46	88.15
Elemental composition by weight		
% Oxygen	34.7	18.2
% Carbon	52.1	68.1
% Hydrogen	13.1	13.6
Specific gravity	0.79 @ 15°F (1)	0.74 @ 25°C (8)
Boiling point [°C]	78.5 (1)	53.6 - 55.2 (8)
Water solubility [mg/L]	Infinite (1)	43,000 - 54,300 50,000 (8)
Vapor pressure		
[mm Hg] (@ 25°C)	49 - 56.5 (7)	245 - 276 (8)
[kPa] (@ 100°F)	17 (6)	
Heat of vaporization [kJ/kg]	900 (6)	
Henry's Law constant [atm m <sup>3</sup> g <sup>-1</sup> mole <sup>-1</sup> ]	6.17 x 10 <sup>-6</sup> (7) 5.13 x 10 <sup>-6</sup> (7) 6.29 x 10 <sup>-6</sup> (7)	5.9 x 10 <sup>-4</sup> (8) 1.1 x 10 <sup>-3</sup> (8) 1.2 x 10 <sup>-3</sup> (8) 3.0 x 10 <sup>-3</sup> (8)
Henry's Law constant [-]	2.10 x 10 <sup>-4</sup> (7) 2.52 x 10 <sup>-4</sup> (7) 2.57 x 10 <sup>-4</sup> (7)	2.399 x 10 <sup>-2</sup> (8) 4.496 x 10 <sup>-2</sup> (8) 5.722 x 10 <sup>-2</sup> (8) 1.226 x 10 <sup>-1</sup> (8) 2.6 x 10 <sup>-2</sup> (8) 1.8 x 10 <sup>-2</sup> @ 20°C (8)
Log K <sub>oc</sub>	1.21, 0.2 (7)	1.091, 1.035, 1.049 (8)
Log K <sub>ow</sub>	-0.16, -0.31 (7) -0.32 (4)	1.20 (8)

Maximum concentration approved by EPA for use a fuel oxygenate		
Mass % O <sub>2</sub>	3.7 (3)	2.74 (3)
Volume % Oxygenate	10.0 (3)	15.0 (3)
Octane rating number		110 (9)
Research	111 (6)	
Motor	92 (6)	
Blending research octane number -- RON	129 (3)	118 (3)
Blending RVP [psi]	15 (4)	8 (9)
Stoichiometric air/fuel ratio	9.0 (6)	
Net lower heating value		
Mass [kJ/mg]	27.0 (2)	
Volume [kJ/mL]	21.3 (2)	

(1) Merck Index; (2) Kirchstetter et al., 1996; (3) Chevron, 1996; (4) Piel and Thomas, 1990; (5) Reuter et al., 1992; (6) Rice et al., 1991 and (7) Zogorski et al., 1996, (8) OSTP Report, 1997, (9) MTBE Workshop, 1998.

## 2.4 Fate in the Environment

Once released into the environment, the mechanism of ethanol loss depends on the environmental compartment receiving the release: atmospheric release, LUST release to soil and groundwater, or spill during ethanol transport. Various reports have published estimates of the range of possible half-lives (see Table 2.2) in each of these environmental compartments. In the atmosphere, it is predicted that ethanol will be oxidized quickly; the half-life ranges between 0.5 and 5 days. In the soil or groundwater, the data presented in Table 2.2 predicts rapid biodegradation of ethanol with a half-life ranging from 0.1 to 2.1 days. Finally, in surface water following a pure ethanol spill, ethanol is predicted to quickly biodegrade; estimated half-lives range from 0.25 to 1 days. Table 2.2 implies that regardless of the release scenario, ethanol is unlikely to accumulate in the soil, air, surface water, or groundwater due to its rapid photooxidation (air) and biodegradation (water/soil) rates. However, it is unclear whether these estimated rates were developed under realistic field conditions. Consequently, the reported values in Table 2.2 represent generic order-of-magnitude half-lives and may not be accurate for a site-specific assessment of the fate and transport of ethanol. In Section 4, these rates will be better defined as a function of the specific atmospheric, hydrogeologic (subsurface), and limnologic (lake) conditions.

<b>Table 2.2</b> <b>Estimated Half-Lives of Ethanol in the Environment.</b> <b>Adapted from Handbook of Environmental Degradation Rates (1991)</b>	
<b>Environmental Medium</b>	<b>Half-life (hours)</b>
<b>Soil</b> <i>(Based upon soil die-away test data)</i>	2.6 - 24
<b>Air</b> <i>(Based on photooxidation half-life)</i>	12.2 - 122
<b>Surface water</b> <i>(Based upon unacclimated aqueous aerobic biodegradation)</i>	6.5 - 26
<b>Groundwater</b> <i>(Based upon unacclimated aqueous aerobic biodegradation)</i>	13 - 52

## 2.5 Advantages/Disadvantages of Ethanol

The main advantages associated with the use of ethanol as a fuel oxygenate is its high oxygen content and short half-life in the environment (Table 2.2) relative to other oxygenates. Furthermore, ethanol exhibits low human toxicity at the estimated exposure levels from the accidental releases of ethanol-gasolines into the environment. Ethanol is heavily used by the drinking alcohol industry; as a result, the human body is generally tolerant to ethanol levels much higher than would be encountered in environments contaminated with ethanol-blended gasolines.

Ethanol has several disadvantages as a blending component. The addition of 10% ethanol by volume can increase the Reid vapor pressure (RVP) of a conventional gasoline by 1 psi (Chevron 1996). This increased volatility limits the feasibility of using ethanol as an additive during warm weather months (EPA, 1998). Also, ethanol-blended fuels cannot be shipped by pipeline because of ethanol's high affinity for water (Williams, 1995). This causes ethanol to be transported by barge, rail car, or truck. If an ethanol-blended gasoline comes in contact with water or water vapor (as in pipelines), ethanol will bring the water into solution which leads to the phase separation of the ethanol-water-gasoline component mixture. To prevent phase separation, ethanol is splash blended with the gasoline at terminals (i.e., in the tank truck which will deliver the blend to the service station). Ethanol terminal blending involves more operating and capital expenses than the refinery blending of MTBE and other oxygenates (Chevron, 1996; Newenham, 1997).

## 3.0 PARTITIONING OF ETHANOL IN THE ENVIRONMENT

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### 3.1 Ethanol Partitioning Between Environmental Compartments

The purpose of this section is to describe the relative proportion of ethanol that partitions into the air, water, and soil phases once equilibrium is established between these compartments. The following sections describe this partitioning between air, water, and soil compartments, as well as the physiochemical interactions between ethanol and other gasoline constituents in groundwater.

### 3.2 Air/Water Partitioning

The air to water partitioning behavior of ethanol is governed by Henry's Law. A dimensionless Henry's Law constant represents the equilibrium ratio of a contaminant's concentration in the air to its concentration in the water. For the most part, a compound with a dimensionless Henry's Law constant less than 0.05 will tend to partition strongly from the gas phase into the water phase if contaminated air is brought into contact with clean water (Zogorski et al., 1996). Values of Henry's Law constant for ethanol are given in Table 2.1 and range from  $2.1 \times 10^{-4}$  to  $2.6 \times 10^{-4}$  [-] at 25°C. Since this range is quite low, atmospheric ethanol is likely to partition into water vapor droplets, and similarly, ethanol in water bodies is likely to remain in the aqueous phase. Therefore, volatilization from surface water or off-gassing from groundwater are not likely to be significant mechanisms for ethanol mass loss from water.

### 3.3 Soil/Water Partitioning

The soil/water partition coefficient,  $K_d$ , specifies the equilibrium ratio of a contaminant's concentration in/on the solid phase to that in the aqueous phase. The soil/water partition coefficient determines a contaminant's relative rate of movement in groundwater due to adsorption to a solid surface. For non-ionic compounds such as ethanol,  $K_d$  values are a function of the organic carbon content of the soil and the organic carbon based partition coefficient,  $K_{oc}$ .  $K_d$  is the product of  $K_{oc}$  and the fraction of organic carbon in the soil,  $f_{oc}$ , i.e.,  $K_d = K_{oc} \cdot f_{oc}$ . Although values of  $f_{oc}$  are site-dependent, they are typically low in most subsurface environments (~0.005) (Zogorski et al., 1996). Additionally,  $K_{oc}$  values for ethanol are low (Table 1) relative to values of other gasoline oxygenates and aromatics. Therefore,  $K_d$  values are low which results in a retardation factor for ethanol and other short-chain alcohols very close to unity (Wood et al., 1990; Zogorski et al., 1996). Thus, under most conditions, dissolved ethanol will migrate at the velocity of the groundwater. Adsorption to aquifer materials in the subsurface or to sediments in surface water is not likely to affect the fate of ethanol in the

environment. Ethanol is expected to remain predominantly (>99%) in the water phase under most conditions.

### **3.4 Dissolution from Gasoline**

The dissolution of hydrocarbons from gasoline into groundwater occurs as ethanol leaches from the light gasoline-ethanol mixture. The aqueous concentrations of gasoline hydrocarbons and ether oxygenates in contact with water can be estimated from the hydrocarbon's solubility in water multiplied by its mole fraction in the gasoline (maximum theoretical solubility of MTBE = 48,000 ppm x 11% by volume = 5,280 ppm) (Poulsen et al., 1992). However, because ethanol is infinitely soluble, this simple equation breaks down and the concentration must be estimated based on mixing conditions, assuming a fuel/groundwater mixing ratio and a dilution factor. For estimating purposes, the fuel/groundwater mixing ratio is approximated to be 2 and the subsurface dilution factors are between 10 and 100. If >99% of the released ethanol from ethanol-blended fuel dissolves in the water, the maximum volume concentration of ethanol in the water would be 5% (50,000 ppmv) based on the volume percent of ethanol required to meet minimum oxygenate requirements (10%). After taking into consideration the range of subsurface dilution factors specified above, the maximum range of ethanol concentrations would be 0.05% to 0.5% by volume or about 400 to 4,000 ppm by mass. However, these concentrations can only be expected at gasoline/water interfaces or near pure ethanol releases because much lower concentrations are anticipated further from the source due to ethanol plume dilution.

Heermann and Powers (1997 & 1998) studied the partitioning behavior of ethanol and BTEX compounds from an ethanol-blended gasoline. According to Heermann (1998), the aqueous concentration of ethanol from the dissolution of ethanol-blended gasolines is dependent on the concentration of ethanol in the gasoline and on mass transfer limitations in subsurface systems. Heermann was able to show that when the concentration of ethanol was 10% (by volume) in a gasoline, greater than 99% of the ethanol partitioned into the water phase. Heermann did not investigate the dissolution rate of the dissolved ethanol and determined that it is limited by ethanol molecular diffusion to the gasoline/groundwater boundary which may result in longer dissolution times (> 1 year). Poulsen et al. (1992) looked at the dissolution of methanol from an M-85 gasoline (85% methanol by volume) into the aqueous phase. Poulsen experimentally determined that approximately 99% of the methanol leached into the aqueous phase in the time required for three volumes of water, each equal to the initial volume, to pass by the floating product (1992). These researchers concluded that this dissolution rate would result in a short discrete plume.

In conclusion, all of the ethanol present in a gasoline will likely be released into the groundwater, but the time frame for this process is site specific. A large, thick gasoline source could result in long

molecular diffusion paths which would limit the speed of dissolution and create long, attached ethanol plumes; whereas, a small thin gasoline source could facilitate dissolution and create a short, detached ethanol plume. Both of these scenarios are not only specific to the gasoline plume shape, but are also dependent on the subsurface groundwater flow conditions.

### **3.5 Cosolvency Effects**

Cosolvency is a chemical phenomenon whereby one chemical dissolved in water increases the solubility of a second chemical due to the high solubility of the second chemical in the first chemical. Due to the infinite miscibility of ethanol in the water phase, it may act as a cosolvent for other gasoline constituents when it is present at high concentrations (Cline et al., 1991; El-Zoobi et al., 1990; Groves, 1988; Pinal et al., 1990 & 1991). As a result, the presence of ethanol may significantly increase the aqueous solubility of other hydrocarbons by effectively reducing the retardation factors and sorption coefficients of these gasoline components in subsurface systems (Chen, 1997). However, recent research has shown that at the currently used ethanol concentrations (up to 7.3% by volume), the presence of oxygenates in gasoline does not cause cosolvency in gasoline-water mixtures. Even at higher concentrations of oxygenates, no cosolvency effects have been observed. For example, up to 85% methanol in gasoline and a gasoline/water mixing ratio of 10 has been shown to produce no enhanced BTEX solubility.

## **4.0 FATE AND TRANSPORT OF ETHANOL IN THE ENVIRONMENT**

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Using the chemical and physical properties of ethanol (Table 2.1) and the partitioning factors discussed in Section 3, it is possible to describe the movement and reactions of ethanol in the environment. The following three subsections discuss the fate and transport of ethanol in the atmosphere, subsurface (i.e., soil and groundwater), and surface water. Each subsection describes the potential source of ethanol into the respective compartment and the ensuing loss mechanisms from that compartment.

### **4.1 Atmosphere**

#### **4.1.1 Sources of Ethanol in the Atmosphere**

Although the 1990 Clean Air Act Amendments mandated the use of oxygenates in fuels, these amendments did not require that these compounds be monitored in the environment. As a result, there is a limited number of peer-reviewed documents in the scientific literature reporting either measured or estimated atmospheric levels of ethanol in the United States. Most of the available data is for sites in Brazil where ethanol is used heavily both as a fuel and a fuel additive, and where ambient levels of ethanol in urban areas have received considerable attention (Grosjean et al., 1998a & 1998b).

Several processes are responsible for ethanol releases to the atmosphere as a result of its widespread use by the fuel industry. Such releases may occur from leakage or spills during the industrial and commercial processes responsible for ethanol production, transport and storage. Data from industrial releases of ethanol are not currently available. Methanol industry releases are reported in the Toxics Release Inventory (TRI); however, ethanol estimates are not included (Zogorski et al., 1996) since ethanol is not currently considered a hazardous air pollutant. Other ethanol releases are primarily from motor vehicles and include emissions during refueling, hot soak evaporative emissions, and tail-pipe emissions of unburned gasoline (Harley et al., 1992).

Ethanol emissions during refueling result from displaced vapor as the tank is filled, or from vapors due to overfill and accidental spills (Backer et al., 1997). These evaporative emissions may be a considerable source of ethanol into the atmosphere, especially during hot weather, particularly because the use of ethanol has been shown to increase the Reid vapor pressure (RVP) of gasoline (Piel and Thomas, 1990) which is a good indicator of a fuel's volatility (Chevron, 1996). An experimental study was recently performed in order to compare evaporative emissions from an ethanol-blended gasoline, E-10 (10% ethanol by volume), to those from a non-oxygenated gasoline (Aulich et al., 1994). The

results of this study indicated that more total fuel evaporated from E-10, but that ethanol accounted for 13% by weight of the total material evaporated. This suggests that evaporative emissions from ethanol-blended fuels are probably a significant source of ethanol in the ambient air.

Tail-pipe emissions of ethanol result from its incomplete combustion in vehicle engines. A study was performed to measure ambient levels of ethanol during the period of March 1996 - April 1997 in Porto Alegre, Brazil, where 17% of light duty vehicles run on hydrated ethanol (Grosjean, et al., 1998a). Ambient levels of ethanol were found to range from 0.4 to 68.2 ppbv with an average of  $12.1 \pm 13.3$  ppbv. These values are higher than those reported in some urban areas in the United States (Table 4.1) but are consistent with the fleet data in Porto Alegre, Brazil. This study also estimated a fleet emission rate for ethanol in Porto Alegre of  $2338 \pm 393$  tons per year. The results of this study suggest that evaporative emissions of ethanol may be accompanied by substantial releases of unburned ethanol in the exhaust.

## **4.1.2 Losses of Ethanol from the Atmosphere**

### **4.1.2.1 Chemical Oxidation**

Once emitted into air, ethanol molecules may be oxidized by reactions with ozone, nitrate radicals or hydroxyl radicals. The dominant mechanism controlling the fate of alcohols in the atmosphere is their reaction with hydroxyl radicals (Zogorski et al., 1996). The oxidation of ethanol via the hydroxyl radical leads to the formation of acetaldehyde, which in turn may produce peroxyacetyl nitrate (PAN) and formaldehyde, both of which are precursors of ozone formation (Grosjean et al., 1998a; Kirchstetter, 1998).

Grosjean et al. (1997) evaluated the impact of ethanol (and MTBE) on ambient air quality using laboratory and field measurements. These researchers reported an ethanol reaction rate constant with the hydroxyl radical of  $3.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This value is comparable to others reported in the literature; for example, Piel and Thomas (1990) and Kirchstetter (1998) reported rate constants of  $3.4 \times 10^{-12}$  and  $3.05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Grosjean et al. (1997) also calculated the half-life of ethanol based on its reaction rate with hydroxyl radical and found it to be 2.4 days (Table 4.2).

**Table 4.1**  
**Levels of Ethanol in Urban Air (and in a tunnel) as Reported in Relevant Peer-Reviewed Papers**

<b>Concentration (ppbv)</b>	<b>Location</b>	<b>Date Comments</b>	<b>Reference</b>
0.7	Downtown Los Angeles	1993 Prior to the introduction of reformulated gasoline	Grosjean et al., 1998b
2.9 - 4.9	Houston and Boston	1993 At two former USEPA Toxic Air Monitoring Study sites	Kelly et al., 1993
3 - 5	Four Southern CA locations	1996 After introduction of CA Phase II RFG which contains MTBE	Grosjean et al., 1998b
0.4 - 68.2	Porto Alegre, Brazil	1996 - 1997 17% of light duty vehicles run on hydrated ethanol	Grosjean et al., 1998b
180 - 310	Mooca, Sao Paulo, Brazil	1990 28% of vehicles run on ethanol	Grosjean et al., 1998b
1900, 2260 <sup>a</sup>	Cerqueiro Cesar, Sao Paulo, Brazil	1990 28% of vehicles run on ethanol	Grosjean et al., 1998b
1080 - 1440	Tunnel, Sao Paulo, Brazil	1990 28% of vehicles run on ethanol	Grosjean et al., 1998a Grosjean et al., 1998b

<sup>a</sup>Two highest concentrations measured in Cerqueiro Cesar

This value is comparable to other atmospheric oxidation half-lives for ethanol reported in the literature (Handbook of Environmental Degradation Rates, 1991).

<b>Table 4.2</b> <b>Atmospheric Persistence of Ethanol</b> <b>Compared to MTBE Based on Reactions with the Hydroxyl Radical</b> <b>(Adapted from Grosjean et al. (1997))</b>		
Oxygenate	•OH reaction rate constant cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Half life (days) •OH = 1.0 x 10 <sup>6</sup> molecule cm <sup>-3</sup>
Ethanol	3.33 ± 0.23 x 10 <sup>-12</sup>	2.4
MTBE	3.24 ± 0.8 x 10 <sup>-12</sup>	2.3

#### 4.1.2.2 Precipitation

Like other volatile organic compounds in the atmosphere with a low Henry's constant, ethanol can be expected to partition from air into water vapor. Precipitation of ethanol from the atmosphere can directly introduce ethanol to surface water. Precipitation falling on land can also contribute to surface water contamination from overland runoff and storm-water recharge, in addition to contaminating groundwater by infiltration and diffusion through the unsaturated zone.

Since the Henry's constant for ethanol is extremely low (Table 2.1), ethanol favors the water phase and will partition into water vapor droplets in the atmosphere. However, while precipitation may contribute to atmospheric loss of ethanol, the rapid oxidation rate of ethanol and the predicted low ethanol concentrations in the atmosphere may limit the amount of ethanol which is available to partition into water during precipitation events.

#### 4.1.3 Impact of Ethanol Use on Air Quality

While the use of oxygenated fuels may decrease air pollution, ethanol-blended gasoline has been implicated in reductions in air quality due to increases in acetaldehyde, PAN, ozone (O<sub>3</sub>) and NO<sub>x</sub> levels in urban air.

Several studies have been conducted in order to evaluate the impact of ethanol-blended gasolines on exhaust and evaporative emissions relative to other oxygenated and non-oxygenated gasolines. Reuter et al. (1992) measured emissions from twenty 1989 vehicles as a function of gasoline composition. They determined that additions of ethanol (10% by volume), MTBE (15%) or ethyl tert-butyl ether (ETBE) (17%) to gasoline reduced exhaust total hydrocarbon and carbon monoxide emissions, but increased NO<sub>x</sub> emissions (Table 4.3 and Table 4.4). Several researchers have studied the atmospheric impact of ethanol-blended gasolines and have confirmed the general trends shown in

Table 4.3 compared to non-oxygenated fuels (Akutsu et. al., 1991; Anderson et. al., 1996; Gaffney et. al., 1997).

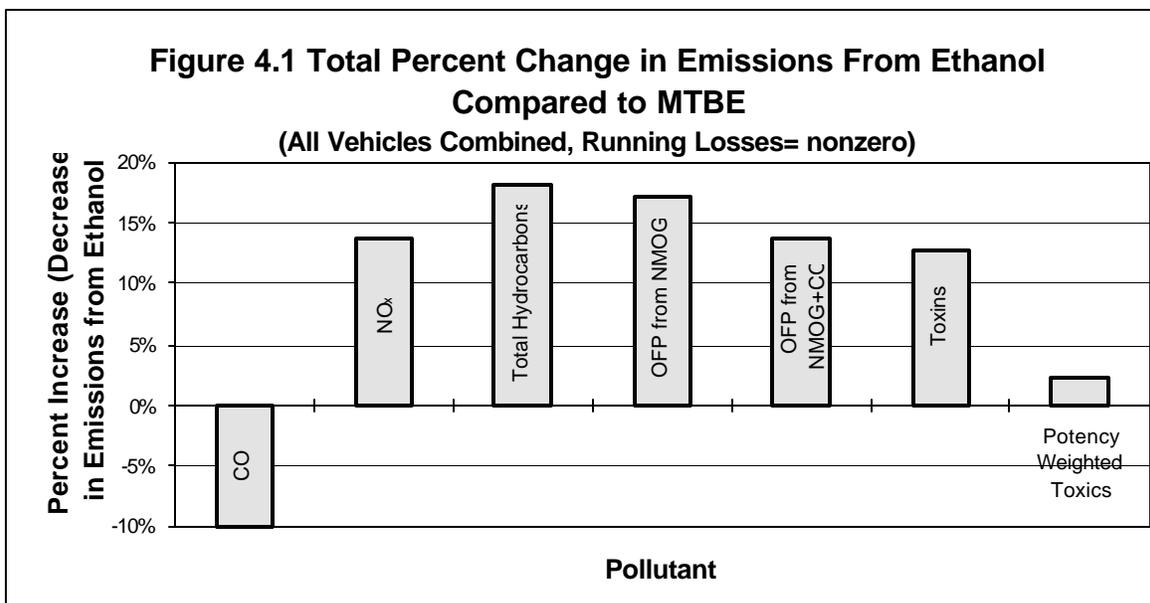
<b>Table 4.3</b> <b>Percent Changes in Vehicle Emissions</b> <b>from the Use of Several Oxygenated Blends</b> <b>Compared to Non-Oxygenated Fuels</b> <b>Adapted from Reuter et al. (1992)</b>			
<b>Emissions</b>	<b>Ethanol</b> <b>(10% v/v)</b>	<b>MTBE</b> <b>(15% v/v)</b>	<b>ETBE</b> <b>(17% v/v)</b>
Exhaust: Total HC	-4.9	-6.5	-5.2
Exhaust: CO	-13.4	-9.3	-14.6
Exhaust: Acetaldehyde	<b>159</b>	-0.9	254.2
Exhaust: NO <sub>x</sub>	<b>5.1</b>	3.6	5.5
Evaporative: Diurnal HC	<b>30.3</b>	-5.8	-5.0
Evaporative: Hot Soak HC*	<b>50.1</b>	13.0	9.5

\* Hot Soak emissions are releases of gasoline vapors from hot parked cars due to expansion of the gasoline.

The California Air Resource Board (CARB, 1998) has recently completed a series of tests evaluating evaporative and exhaust emissions from an ethanol-oxygenated gasoline compared to those from an MTBE-oxygenated gasoline. As Figure 4.1 illustrates, the use of ethanol blends decreased the amount of carbon monoxide emitted into the atmosphere compared to the use of MTBE blends, but significantly increased the amount of NO<sub>x</sub>, total hydrocarbons, ozone forming potential (e.g., PAN), and toxins, in addition to the overall potency weighted average of all emissions combined.

**Table 4.4**  
**Selected Reports from the Literature on the Impacts of Ethanol-Blended Fuels on Motor Vehicle Emissions**  
**Relative to a Non-Oxygenated Fuels**

Study description	Atmospheric impacts	Reference
Fuel: 10% ethanol Emissions measured: exhaust and evaporative Fleet of twenty 1989 light duty vehicles	Decrease (13%) in exhaust CO Decrease (5%) in exhaust hydrocarbons Increase (159%) in exhaust acetaldehyde Increase (30-50%) in evaporative hydrocarbons	Reuter et al., 1992
Fuel: 8.1% ethanol Emissions measured: CO and acetaldehyde Fleet of three pre-1985 light duty vehicles	Decrease in CO Increase (120-190%) in exhaust acetaldehyde	Stump et al., 1994
Fuel: 10% ethanol Emissions measured: O <sub>3</sub> , NO <sub>x</sub> , CO, PAN, aldehydes, organic acids Field study, ambient air, Albuquerque, NM	Increase in PAN Increase in aldehydes (>25 ppb acetaldehyde) Increase in NO <sub>x</sub>	Gaffney et al., 1997
Fuel: hydrated ethanol or E22G78 Three urban areas, Brazil	Increase in acetaldehyde (1-35 ppb ambient air, 240 ppb in a tunnel)	Grosjean et al., 1990



OFP is Ozone Forming Potential; NMOG is Non-Methane Organic Gas (CARB, 1998)

The increases in emissions using ethanol blends have been shown to be most significant for acetaldehyde (a constituent of OFP in Figure 4.1), total evaporative hydrocarbons, and NO<sub>x</sub>. The increase in acetaldehyde emissions is a result of the incomplete combustion of ethanol and has been shown in many studies to increase by an average of 171% compared to conventional gasoline (OSTP, 1997; Stump et al., 1990; Knapp et al., 1998; Reuter et al., 1992; Warner-Selph et al., 1990). Gaffney (1997) states that acetaldehyde reacts in the atmosphere to form PAN, a hazardous air pollutant and precursor to ozone. The increases in diurnal and hot soak emissions are primarily due to the higher RVP of ethanol-blended gasolines. The increase in NO<sub>x</sub> is likely because ethanol has a greater oxygen content by weight (3.5%) than MTBE (2.0%) which increases the oxygen concentrations in the combustion chamber of motor vehicles.

## 4.2 Soil and Groundwater

### 4.2.1 Sources of Ethanol in Soil and Groundwater

Very few data sets are available on reported levels of oxygenates in aquatic systems and subsurface environments in the United States. Most of the available information in the scientific literature focuses on MTBE with little or no monitoring data available for ethanol and other fuel oxygenates (Zogorski et al., 1996). The apparent lack of monitoring for ethanol, particularly in aqueous systems, is likely a result of (1) the level of difficulty associated with ethanol analysis in the water phase, (2) its short half-life due to its high biodegradation potential and (3) the lack of governmental monitoring and control

requirement mandates for groundwater, surface water and drinking water (Clean Water Act, Safe Drinking Water Act). Monitoring data is also not available in countries like Brazil where ethanol has been used extensively in the last two decades as both a fuel and a fuel additive, even though some of these locations rely heavily on groundwater aquifers for drinking water. For example, Sao Paulo, Brazil derives 70% of its potable water from aquifers (Corseuil et al., 1998).

There are several processes related to the use of ethanol as a fuel additive which are directly responsible for ethanol releases to soils and groundwater. The dominant source is the direct release of ethanol-blended fuels into the subsurface from fuel spills or leaking underground storage tanks. A minor source is precipitation from the atmosphere onto land which introduces ethanol into the subsurface either by diffusion through the unsaturated zone or by infiltration. Precipitation has been shown to be a minor source of other oxygenates such as MTBE (OSTP, 1997) into groundwater, and therefore, it is very unlikely that precipitation will be a major source of ethanol into the groundwater.

#### **4.2.2 Losses of Ethanol from Soil and Groundwater**

Due to the physiochemical properties of ethanol as discussed in Section 2, ethanol will remain primarily in the aqueous phase. In addition, alcohols, such as ethanol, are ubiquitous in nature, and widely produced in the environment by both chemical and biological processes (Ingram and Buttke, 1984). As a result of ethanol's high solubility, low retardation, and natural occurrence, the dominant mechanism of ethanol loss from the subsurface is expected to be biodegradation.

##### **4.2.2.1 Biodegradation**

In general, microorganisms have been shown to play a prominent role in governing the fate of hydrocarbons in subsurface aquatic and soil systems (NRC, 1993). When environmental conditions are amenable to microbial activity, aerobic microbial populations oxidize organic contaminants and consume oxygen in the process. Once the localized area has been depleted of the oxygen necessary for aerobic respiration, anaerobic conditions develop and anaerobic biodegradation proceeds. While it is well known that ethanol will biodegrade readily in the subsurface, three factors are required for successful ethanol biodegradation: the presence of indigenous ethanol-degrading microbial populations, the availability of electron acceptors and nutrients, and adequate pH and temperature levels.

##### **4.2.2.1.1 Presence of Indigenous Ethanol-Degrading Microbes**

The ease of alcohol biodegradability is well established in the microbiological literature. A short chain alcohol such as ethanol can be easily degraded under both aerobic and anaerobic conditions (Chapelle, 1992). Ethanol can be oxidized by enzymes of central microbial metabolic pathways (Hunt and Alvarez, 1997). Because most indigenous microbes use these pathways to degrade other substrates, a wide distribution of ethanol-degraders in the environment can be expected. Additionally, the bioavailability of ethanol to the microorganisms is anticipated due to ethanol's infinite solubility in water.

#### 4.2.2.1.2 Availability of Electron Acceptors

Microorganisms obtain energy by transferring electrons from electron donors (in this case, ethanol) to electron acceptors. Electron acceptors are compounds that have a lower oxidation state than the electron donors; they include molecular oxygen, nitrate, Fe(III), sulfate and carbon dioxide. The most energetically favored mechanism by which microorganisms oxidize organic compounds is aerobic metabolism (Table 4.5).

<b>Table 4.5</b> <b>Selected Types of Aerobic and Anaerobic Respiration</b> <b>Involved in Microbial Metabolism of Organic Matter.</b> <b>Taken from Suflita and Sewell (1991)</b>			
<b>Process</b>	<b>Electron Acceptor</b>	<b>Metabolic Products</b>	<b>Relative Potential Energy</b>
<b>Aerobic Respiration</b>	O <sub>2</sub>	CO <sub>2</sub> , H <sub>2</sub> O	High
<b>Denitrification</b>	NO <sub>3</sub> <sup>-</sup>	CO <sub>2</sub> , N <sub>2</sub>	
<b>Iron reduction</b>	Fe <sup>3+</sup>	CO <sub>2</sub> , Fe <sup>2+</sup>	
<b>Sulfate reduction</b>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>2</sub> , H <sub>2</sub> S	
<b>Methanogenesis</b>	CO <sub>2</sub>	CO <sub>2</sub> , CH <sub>4</sub>	Low

When oxygen is not available, the following electron acceptors reflect the preferential utilization by microbes: nitrate > Fe(III) > sulfate > carbon dioxide (Brock and Madigan, 1991). The redox potential in subsurface environments is highly site-dependent. Oxygen is usually present in and around groundwater recharge areas as a result of infiltrating rainwater.

The presence of oxygen is a requirement for obligate aerobic microorganisms. Facultative aerobic and anaerobic microorganisms are able to use other electron acceptors when oxygen is not available.

#### **4.2.2.1.3 Availability of Nutrients**

Most microorganisms require life-sustaining growth factors such as nitrogen and phosphorus for cell growth. In general, microbial growth in most sub-soils is not limited by nitrogen and phosphorus as long as the contaminant concentrations are in the sub part per million (ppm) range (Tiedje, 1993).

#### **4.2.2.1.4 Adequate pH and Temperature Levels**

Most microorganisms grow best in a relatively narrow range of pH around neutrality (6 - 8) (LaGrega et al., 1994). The relatively characteristic range of pH values found in groundwater systems (5 - 9) generally reflects the buffering capacity of the framework carbonate or silicate minerals that make up groundwater aquifers (Chapelle, 1992; King et al., 1992). This characteristic range of pH values in aquifers is unlikely to pose a significant problem for the biodegradation of ethanol by indigenous subsurface microorganisms.

The temperature of an environment is also an important factor for the growth and activity of microorganisms. Metabolism of subsurface populations accelerates with increased temperatures up to an optimum value at which growth is maximum. Most of the bacteria present in subsurface environments operate most effectively at 20 - 40°C. This is the temperature range of many natural environments (Chapelle, 1992) since subsurface temperature within 100 meters are typically within 2°C of the mean annual surface temperature.

#### **4.2.2.1.5 Reports of Ethanol Biodegradation Under Various Redox Conditions**

A simple alcohol such as ethanol can be degraded in both aerobic and anaerobic environments (Chapelle, 1992) at rates much faster than MTBE (see Table 4.6). Only large concentrations (> 100,000 ppm) of alcohols are generally considered to be toxic to most microorganisms, and are therefore not biodegradable (Brusseau, 1993; Hunt 1997a). However, such high concentrations are rarely encountered at sites contaminated with ethanol-gasoline blends since the maximum allowable ethanol content in gasoline is 10% by volume in the United States. High concentrations of ethanol may occur at fuel/water interfaces or near pure ethanol spills. Such concentrations may inhibit microbial activity near the source, but will become exponentially more dilute as the distance from the source increases. Consequently,

ethanol plumes will be degraded by indigenous microbes located a sufficient distance beyond the source where ethanol concentrations are not inhibiting.

<b>Table 4.6 Comparative Rate Constants for Anaerobic and Aerobic Degradation</b>			
	<b>Anaerobic Pseudo First Order Rate Constant</b>		<b>Aerobic Pseudo First Order Rate Constant</b>
<b>Compound</b>	<b>Electron Acceptor</b>	<b>Range of Rates (day<sup>-1</sup>)</b>	<b>Range of Rates (day<sup>-1</sup>)</b>
<b>Ethanol</b>	NO <sub>3</sub> <sup>-</sup>	0.53 <sup>(1)(7)</sup>	0.23 <sup>(1)(7)</sup>
	Fe <sup>3+</sup>	0.17 <sup>(1)(7)</sup>	0.35 <sup>(1)(7)</sup>
	SO <sub>4</sub> <sup>-2</sup>	0.1 <sup>(1)(7)</sup>	
<b>Methanol</b>	NO <sub>3</sub> <sup>-</sup>	0.02-0.052 <sup>(3)(7)</sup>	0.019 <sup>(4)(8)</sup>
	SO <sub>4</sub> <sup>-2</sup>	0.016-0.010 <sup>(3)(7)</sup>	
<b>MTBE</b>	Anaerobic Range	0.0062 - 0.00096 <sup>(5)(9)</sup>	0.0012 <sup>(6)(7)</sup>
<b>Benzene</b>	NO <sub>3</sub> <sup>-</sup>	0-0.045 <sup>(3)(7)</sup>	0.043 <sup>(5)(7)</sup>
	Fe <sup>3+</sup>	0-0.024 <sup>(3)(7)</sup>	0.14 <sup>(5)(7)</sup>
	SO <sub>4</sub> <sup>-2</sup>	0-0.047 <sup>(3)(7)</sup>	
	Methanogenic	0-0.052 <sup>(3)(7)</sup>	
	General	0.0062-0.00096 <sup>(5)(9)</sup>	

1) Estimated from Corseuil et. al., 1997; 2) Suflita et. al., 1993; 3) Aronson et. al., 1997; 4) Hubbard et al, 1994; 5) USGS, 1998; 6) Barker et. al., 1998; 7) Determined in a laboratory; 8) Determined from field data; 9) Estimated from first principles.

No known studies of ethanol biodegradation under field conditions were located for this report. However, Table 4.6 summarizes the reported ethanol, benzene, and MTBE laboratory data and the methanol laboratory and field data. Comparing the biodegradation rate constants, it is clear that in the laboratory, ethanol degrades much faster than the other substrates. However, because ethanol and methanol are similar substrates, the biodegradation rate constants in the field can be assumed to be similar for both of these alcohols. One field study at the CFB Borden site in Canada reports biodegradation rates for methanol from a methanol-blended fuel (Barker et al., 1990). The objective of this study was to investigate the fate and persistence of this fuel (85% methanol, 15% gasoline) in an aerobic shallow sandy aquifer. The results of this study indicated that all of the methanol (approximately 2,400 L resulting in an initial concentration of approximately 7,000 mg/L) was essentially biodegraded in 476 days (half-life approximated to be 40 days). Another study investigating methanol biodegradation in soils from three different sites under various redox conditions revealed that methanol concentrations of 1000 ppm were removed in less than a year at temperatures of 10 - 11°C and at pH values of 4.5 - 7.8 (Butler et al., 1992). Based on the results of these two studies, and because of the similar properties of methanol and ethanol, the biodegradation of ethanol under similar conditions is expected to be equally effective.

While there are no known field scale studies, a few laboratory studies have focused on ethanol biodegradation. Suflita and Mormile (1993) measured acclimation periods (periods before degradation proceeded) and biodegradation rates of ethanol and other fuel oxygenates in anaerobic aquifer slurries at ethanol concentrations of 50 ppm (not included in Table 4.6). These researchers reported an ethanol acclimation period of 25 - 30 days and an anaerobic biodegradation rate of  $17.9 \pm 0.6$  mg/L/day. The observed acclimation period for methanol was shorter (5 days), but its biodegradation rate was slower ( $7.4 \pm 0.7$  mg/L/day) than ethanol. In a later study, these authors illustrated that their results can be extrapolated to other redox conditions and experimentally showed that various short chain alcohols were easily degraded in different sediments under a range of redox conditions (Suflita and Mormile, 1994). Corseuil et al. (1998) also examined the biodegradation of ethanol under various redox conditions. The time required to degrade ethanol (80 - 100 mg/L) in this study under different redox conditions is presented in Table 4.7.

**Table 4.7**  
**Approximated Time (in days) Required to Biodegrade 80 - 100 mg/L**

<b>of Ethanol in Aquifer Microcosms Under Various Redox Conditions.</b>	
<b>Redox Condition in Microcosm<sup>a</sup></b>	<b>Time to degrade 80 - 100 mg/L of ethanol (days)<sup>b</sup></b>
Aerobic	5
Denitrifying	3
Iron-reducing	12.5
Sulfidogenic	25
Methanogenic	12

<sup>a</sup>The sources of soil and groundwater in the microcosms were different for each of the aquifer microcosms. <sup>b</sup> Extrapolated from figures presented by Corseuil et al. (1998).

In conclusion, it is expected that ethanol will undergo rapid biodegradation in the subsurface under typical pH, temperature, and nutrient conditions, regardless of the available electron acceptors.

#### **4.2.3 Sorption and Off-Gassing**

Other ethanol loss mechanisms from the soil and groundwater include sorption, volatilization, and abiotic transformation. However, these processes do not contribute significantly to the loss of ethanol from the environment because their rates are expected to be slower than the rapid rate of biodegradation. As stated previously, little sorption is expected for compounds such as ethanol because of its polarity, low  $K_d$  values and infinite aqueous solubility. Ethanol is therefore expected to travel through the subsurface at essentially the velocity of water (Brusseau, 1993). In addition, the high solubility and low Henry's constant are expected to result in minimal loss of ethanol from the groundwater due to volatilization or off-gassing. However, ethanol will volatilize from the LNAPL which may lead to significant migration of ethanol away from the source due to vapor phase diffusion-driven transport. No literature was identified which addressed the vapor phase transport of ethanol. But, regardless of the location where ethanol enters the groundwater, biodegradation will likely quickly reduce concentrations.

## **4.3 Surface Water**

### **4.3.1 Sources of Ethanol in Surface Water**

Point sources of ethanol in surface water bodies include accidental releases of ethanol either during transport or at industrial facilities. Other sources include spills and releases in lakes and reservoirs used for recreational activity during fueling and personal watercraft use. Non-point sources of ethanol include precipitation from the atmosphere as discussed previously and shown to be insignificant.

### **4.3.2 Losses of ethanol in surface water**

Several processes may contribute to ethanol losses from surface water bodies. These include biodegradation, abiotic degradation, volatilization and bioaccumulation. As with groundwater, the dominant loss mechanism in surface water is biodegradation.

#### **4.3.2.1 Biodegradation**

The dominant process responsible for the removal of ethanol in surface water bodies is biodegradation. The reported half-life of ethanol in surface waters under aerobic conditions is very short and spans the range of 6.5 to 26 hours (Handbook of Environmental Degradation Rates, 1991). In moving water bodies, oxygen concentrations are sufficient to support microbial processes and oxygen is not expected to be a limiting factor for biodegradation. Even in oxygen-limited environments such as the bottom layers of stratified lakes, anaerobic biodegradation is expected to proceed at rapid rates; the reported half-life for ethanol biodegradation under anaerobic conditions ranges from 26 to 104 hours (Handbook of Environmental Degradation Rates, 1991). The nutrient supply in rivers and lakes is generally not expected to restrict the rate of biochemical transformations because the required nutrient supplies are constantly recharged by rainfall (Alexander, 1994).

#### **4.3.2.2 Abiotic Degradation**

Abiotic degradation reactions (hydrolysis, photolysis, photooxidation) are not likely to contribute significantly to ethanol removal from surface water bodies. Hydrolysis reactions usually transform compounds into more polar products; ethanol is a very polar molecule and is relatively stable in water. Photolysis involves the transformation of a compound as a consequence of its direct absorption of light; ethanol has a very low absorption spectrum in the UV/visible light range. Photooxidation of ethanol via the hydroxyl radical is possible. Hydroxyl

radicals are formed in water by the photolysis of nitrate, nitrite and hydrogen peroxide, from reactions with excited humic materials, or from the reaction of  $H_2O_2$  with Fe(II) (Schwarzenbach, 1993). However, biodegradation rates exceed photooxidation rates in surface water. Finally, bioaccumulation of ethanol is not expected to be significant because ethanol has a low  $K_{oc}$  value (Table 2.1) which represents minimal sorption to bed sediments or suspended sediments.

#### **4.3.2.3 Volatilization**

Volatilization is not a primary source of loss for ethanol since ethanol has a low air/water partition coefficient and the rate of biodegradation most likely exceeds the rate of volatilization. In a recent study, the volatilization rates for several oxygenates and gasoline constituents were calculated based on their chemical properties and on lake conditions (Malcolm Pirnie, 1998a). Under typical California lake conditions (Temperature = 20°C; wind speed > 5 mph; epilimnion ~ 20 feet), ethanol was predicted to volatilize almost five times slower than MTBE. Under these conditions, MTBE has a half-life of ~9 days; whereas, ethanol has a half-life of ~40 days.

#### **4.3.2.4 Conclusions**

In conclusion, even though volatilization and adsorption will not significantly reduce ethanol concentrations in surface waters, ethanol will not persist due to its intrinsic tendency to be quickly biodegraded.

## 5.0 IMPACT OF ETHANOL ON OTHER GASOLINE CONSTITUENTS

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### 5.1 Preferential Biodegradation of Ethanol

BTEX compounds -- benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene -- are the most toxic group of hydrocarbons in gasoline. Bioattenuation is a major control mechanism to prevent the persistence of these compounds in subsurface environments. Due to the ease of ethanol biodegradation, researchers have found that ethanol is preferentially utilized over the BTEX components under both aerobic and anaerobic conditions (Corseuil et al., 1998). Salanitro also found that high concentrations of alcohol oxygenates can potentially impede the biodegradation of BTEX (1993). Ethanol will likely be biodegraded in preference to BTEX under both aerobic and anaerobic conditions.

### 5.2 Current Research on Effect of Ethanol

A limited amount of work has been conducted on the effect of ethanol on BTEX bioattenuation and most of it has involved experimental studies in the laboratory. Corseuil et al. (1998) reported that the presence of ethanol in aquifer microcosms retarded BTX (benzene, toluene and o-xylene) aerobic biodegradation, and exacerbated the biochemical oxygen demand. As a result, anoxic conditions developed as soon as the oxygen demand exceeded the available oxygen in the microcosms. This led to the persistence of benzene in the microcosms during the study period (~100 days); i.e., no benzene biodegradation. In anaerobic microcosms, ethanol was reported to adversely affect toluene degradation under iron-reducing and methanogenic conditions. The researchers concluded that the preferential utilization of ethanol under aerobic and anaerobic conditions, in conjunction with a corresponding depletion of electron acceptor concentrations, strongly suggests that ethanol in dissolved hydrocarbon plumes might have a negative effect on BTX bioattenuation. Such results are particularly important for the fate of benzene, a known carcinogen (Dean, 1985), and the most recalcitrant monoaromatic under anaerobic conditions.

In another study, the biodegradation of ethanol and BTX mixtures was investigated using a pure culture, *Pseudomonas putida* F1 (PpF1), in addition to aquifer microorganisms (Hunt et al., 1997). In the aquifer microcosms, the aerobic degradation of toluene was completely inhibited until all the ethanol was degraded. In the pure culture studies, the presence of ethanol did not significantly affect the biodegradation of toluene at low concentrations; however, the presence of 500 mg/L of ethanol did exhibit a slight inhibitory effect.

Information on the effect of other oxygenates on the biodegradation of gasoline hydrocarbons in the field is available. In a field experiment at the Borden site in Canada, researchers investigated the

influence of methanol and MTBE on the fate and persistence of BTEX in groundwater (Barker et al., 1990). Three gasolines (M-85, 15% MTBE, and base gasoline) were allowed to migrate in an aquifer. While methanol slowed the rate of disappearance of BTEX, MTBE had no such effect. It was concluded that the mechanism for greater BTEX persistence in the presence of methanol may be due initially to inhibition by toxic methanol concentrations but mostly by inhibition due to the removal of oxygen by preferred methanol biodegradation.

### **5.3 Conclusions**

In conclusion, while ethanol may not be persistent in the subsurface, results from several laboratory studies suggest that its preferential utilization may cause a lag time before BTEX bioattenuation begins. This lag time for BTEX biodegradation is expected to increase the average BTEX plume length by the distance traveled by the ethanol. Alkanes are expected to be less bioavailable due to their low solubility and biodegrade anaerobically at a rate similar to BTEX. Using a first order approximation for the stable length of an ethanol plume following release from a leaking underground storage tank, it is possible to determine a rough quantification of this increased plume length.

## 6.0 QUANTIFICATION OF INCREASED BTEX PLUME LENGTH RESULTING FROM PRESENCE OF ETHANOL

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### 6.1 Method of Analysis

In the following section, details are presented for a first-order approximation to evaluate the fate of benzene, toluene, ethylbenzene and *o,m,p*-xylenes (BTEX) gasoline components in groundwater in the presence of ethanol. The purpose of this effort is to determine the likely increase in BTEX plume length due to the presence of ethanol in a gasoline release. Previous researchers have stated that maximum BTEX plumes will stabilize at a distance less than 260 feet (Mace, 1997; Rice, 1995). However, this distance is highly site specific and will change significantly as groundwater velocity fluctuates and the chemical specific biodegradation rate constant changes.

As stated Section 4.0 of this report, researchers believe that indigenous subsurface microorganisms preferentially consume ethanol in the presence of other potential substrates under both aerobic and anaerobic conditions (Corseuil, 1997). Consequently, minimal biodegradation of BTEX compounds occurs until biodegradation and dispersion reduce ethanol to sufficiently low concentrations that encourage the microorganisms to switch to other available substrates such as benzene. This effective lag time prior to the on-set of BTEX biodegradation will cause an extension in the length of stable BTEX plumes because the rate of biodegradation is the primary factor determining the length of a stable BTEX plume (McNabb, 1996).

A pictorial representation of the effect of ethanol on the length of a BTEX plumes is illustrated in Figure 6.1. In the absence of ethanol, BTEX biodegradation occurs at a given biodegradation rate,  $\lambda$ . This  $\lambda$  is a volume weighted average biodegradation rate constant composed of an anaerobic biodegradation rate within the heart of the plume and an aerobic biodegradation rate at the edge of a plume. Without significant recharge or re-aeration, most BTEX plumes will quickly become anaerobic due to the limited amount of oxygen available. When both ethanol and BTEX are available substrates, Corseuil found that BTEX will not be degraded when ethanol concentrations are greater than 3 mg/L (1997). Therefore, when ethanol concentrations are above this threshold level, the BTEX biodegradation rate constant is essentially zero. However, when ethanol concentration falls below 3 mg/L, or the BTEX plume migrates past the ethanol plume, BTEX biodegradation will commence at the given  $\lambda$  (see Table 4.6). Corseuil did not conduct experiments to completely characterize the threshold ethanol concentration, nor did he attempt to extrapolate his results to field conditions. Therefore, the use of 3 mg/L as the threshold concentration and the assumption that BTEX biodegradation is zero at ethanol concentrations above this threshold represents two assumptions that should be verified in either laboratory or field investigation.

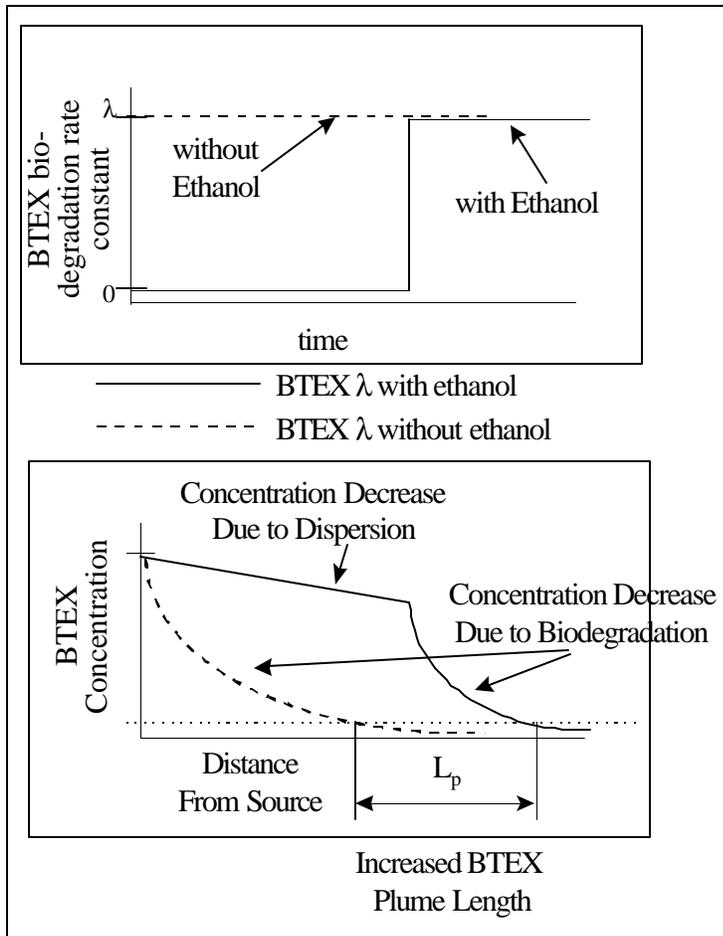


Figure 6.1 Schematic drawing of increased BTEX plume length due to the formation of a BTEX biodegradation lag time created by the presence of ethanol.

Due to the creation of the effective lag time prior to BTEX biodegradation in the presence of ethanol, the resultant change in BTEX plume length will be proportional to the length of the ethanol plume as illustrated in Figure 6.1 (where the ethanol plume is defined by the stated threshold concentration). For this modeling effort, we have assumed that there is a continuous source and, therefore, the ethanol plume will reach some stable distance down gradient from the source. Because ethanol does not adsorb on soil, it will be transported at the velocity of groundwater. Consequently, the ethanol plume will move faster than the BTEX plume. When the BTEX plume is behind the ethanol plume (defined at 3 mg/L), this model assumes that no BTEX biodegradation is occurring.

Several simplifying assumptions have been made for this first-order approximation. Most importantly, the fate of BTEX compounds was assessed through evaluation of benzene as a tracer compound. Benzene is the most toxic of the BTEX compounds and the slowest to biodegrade and, therefore, of highest priority for water purveyors with potentially contaminated drinking water wells. Toluene, ethyl-benzene and *o,m,p*-xylenes plume lengths will stabilize in the subsurface at different distances from those predicted for benzene. Secondly, alkane concentrations were assumed to be low due to the low alkane solubility and, thus, assumed not to affect the biodegradation of ethanol or BTEX. Thirdly, it was assumed that ethanol concentrations near the source are 4000 mg/L, which is based on an ethanol concentration of 5% by volume in gasoline with a 10-fold dilution factor; however, actual field source concentrations may be higher or lower than this value. Benzene was assumed to enter the water table at a concentration of 8 mg/L, which is representative of leaking underground storage tank source conditions (Weissenborn, 1998). Finally, it

is assumed that the gasoline release exists in porous media and, therefore, this evaluation does not apply to fractured bedrock aquifers.

## 6.2 Model Development and Analysis

The two dimensional fate and transport equation derived by Domenico (1987) was used to calculate the predicted concentrations of both ethanol and benzene. Use of this equation to analyze plume behavior under a variety of hydrogeologic and geochemical conditions is widespread (see e.g., McNabb and Doohar, 1996). The Domenico solution in two dimensions is given by:

$$C_{(x,y,t)} = \left(\frac{C_o}{4}\right) \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4R\lambda\alpha_x}{v}\right)^{1/2}\right]\right\} \operatorname{erfc}\left[\frac{x - \frac{v}{R}t\left(1 + \frac{4R\lambda\alpha_x}{v}\right)^{1/2}}{2\left(\alpha_x \frac{v}{R}t\right)^{1/2}}\right] \\ \cdot \left\{\operatorname{erf}\left[\frac{y + Y/2}{2(\alpha_{y,x})^{1/2}}\right] - \operatorname{erf}\left[\frac{y - Y/2}{2(\alpha_{y,x})^{1/2}}\right]\right\}$$

**Equation 6 - 1**

Where:

- $C_o$  = the source concentration [mg/L]
- $x$  = the distance from the source in the longitudinal direction [m]
- $y$  = the distance from the source in the lateral direction [m]
- $\alpha_x$  = dispersivity in the x direction [m]
- $\alpha_y$  = dispersivity in the y direction [m]
- $R$  = the retardation factor based upon the partitioning coefficient of the constituent ( $K_{oc}$ ), the organic content of the matrix ( $f_{oc}$ ), the bulk density ( $\rho$ ) of the matrix, and effective porosity ( $n_0$ ) of the aquifer material [-]
- $\lambda$  = first order decay constant of the constituent [ $\text{day}^{-1}$ ]
- $v$  = the groundwater velocity based on hydraulic conductivity ( $K$ ), hydraulic gradient ( $i$ ) and effective porosity ( $n_0$ ) of the aquifer material [m/s]
- $Y$  = the length of the source in the lateral direction [m]

From this equation it can be seen that the governing factors in the transport of a constituent are  $\lambda$ ,  $v$ ,  $R$  and dispersivity ( $\alpha_x$  and  $\alpha_y$ ). A further evaluation shows that  $\lambda$  and  $v$  are the most influential parameters for both ethanol and benzene in determining the length of a stable plume. Dispersion is a scale dependent function of the matrix and the contaminant velocity, but represents a much smaller contribution to plume stabilization than biodegradation, despite the higher benzene retardation than ethanol ( $R_{\text{BTEX}} > R_{\text{EtOH}}$ ). In the analysis, ethanol concentrations were first calculated for any given  $v$  and

ethanol  $\lambda$ . The benzene  $\lambda$  was reduced to zero (i.e., no degradation of benzene) until ethanol concentrations dropped below the threshold value (3 mg/l) determined by Corseuil et. al. (1997). The benzene and ethanol plume lengths were approximated based on iterative changes in the evenly spaced observation points along the x-axis (down the center of the plume). Consequently, the plume lengths are not exact, but are the best approximation based on the method used.

### 6.3 Biodegradation Rate Constants for Ethanol and Benzene

At the distance where the ethanol concentration dropped below the threshold value, the maximum reported value for the biodegradation rate constant of benzene under general conditions was applied to Equation 6-1 ( $0.0062 \text{ day}^{-1}$  from Table 4.6). This biodegradation rate constant was also applied for the case when no ethanol is present. The plume length of benzene was then determined to be the distance from the source where benzene concentrations fall below 0.001 mg/l (the primary MCL for benzene in California). This resulting plume length was then compared to a benzene plume length based on the maximum reported value for the biodegradation rate constant, as might be conservatively expected in the absence of ethanol. This analysis was conducted at four values of the groundwater linear velocity ranging from 0.004 feet per day to 0.4 feet per day. Each value of the velocity was tested at three values of  $f_{cc}$ : 0.2 %, 0.5 %, and 1.0 % (i.e., three different retardation factors).

The ethanol  $\lambda$  reported in the literature is based upon laboratory results and is not necessarily representative of field conditions. The average anaerobic laboratory derived  $\lambda$  for ethanol under a variety of reducing conditions is  $0.28 \text{ day}^{-1}$  (equivalent to a half-life of 2.5 days) (See Table 4.6). At this rate, anaerobic biodegradation of ethanol reduces ethanol concentrations quickly and, therefore, ethanol is not significantly transported. Ethanol plume lengths calculated based on this  $\lambda$  were on the order of 10 to 30 feet, which would not significantly elongate stable BTEX plume lengths. However, the laboratory data must be adjusted to field conditions in order to approximate a field derived  $\lambda$ . This can be done in three ways.

First, the laboratory-defined  $\lambda$  was determined for a constant temperature of 28°C during its experimentation. While this  $\lambda$  has been referred to as a first-order biodegradation rate constant, it actually represents the substrate utilization constant, as defined in the Michaelis-Menten equation. Groundwater typically exists at temperatures below 15°C. Based on the Arrhenius equation (a temperature correction to the Michaelis-Menten equation) and typical microorganisms, the biodegradation rate constant can be reduced by one half for every 10°C decrease in temperature because of diminishing biological growth and, thus, degradation activity (Gerhardt, 1994). Second, Corseuil stated that the number of bacteria in his laboratory experiments is approximately 10 times greater than typical microbial populations in the natural environment (Corseuil, 1998a). Consistent with

Michaelis-Menten kinetics, a 10-fold reduction in biomass results in a 10-fold reduction in the substrate utilization constant. This allows an order of magnitude reduction of  $\lambda$  to approximate field conditions. Finally, mass transfer limitations in the field will produce an effective reduction in the laboratory-defined  $\lambda$ ; however, this factor is very difficult to quantify without extensive testing. As a result of these three adjustments for field conditions, the ethanol  $\lambda$  used in Equation 6.1 was  $0.014 \text{ day}^{-1}$  based on a conservative  $10^\circ\text{C}$  difference in temperature between the field and the laboratory and an order of magnitude difference in the microbial population available for biodegradation in the subsurface.

#### 6.4 Results and Conclusions

The results of these analyses shown in Table 6.1 indicate that using an ethanol biodegradation rate constant of  $0.014 \text{ day}^{-1}$ , stable benzene plume lengths travel approximately 27% further than they would occur without ethanol present (ranging from 17% at  $v=0.004 \text{ ft/day}$  and  $f_{oc}=0.2 \%$  to 34% at  $v=0.4 \text{ ft/day}$  and  $f_{oc}=1\%$ ). The percentage generally increases with increasing  $v$  and  $f_{oc}$  values. However, the plume lengths were approximated based on iterative changes in observation point spacing with the lowest value observed being the reported value. As a result, the plume lengths are not exact and represent the best approximation based on the method used. Similarly, the strong scale dependency (i.e., a large  $v$  will create a longer plume) results in a larger error of the method with increasing plume length. It should be noted that groundwater velocities of 4 feet per day are rare unless there is a significant stress on the aquifer such as pumping or other large discharge boundaries.

In conclusion, the ethanol biodegradation rate constant will control the length of an ethanol plume and, therefore, controls increases in the BTEX plume length. Given a laboratory-derived first-order approximation of the ethanol biodegradation rate constant, under anaerobic conditions stable BTEX plume lengths are likely to increase by 16% to 34% in the presence of ethanol. Under typical California conditions, such as those described by McNabb and Doohar (1996) BTEX plume lengths are expected to increase approximately 27% in the presence of ethanol. Actual changes in plume length in the field could vary from this calculated figure significantly due to site specific ethanol and BTEX biodegradation rate constants varying from the published laboratory values used here. Field evaluation of the impacts of ethanol on benzene and BTEX plume lengths is recommended given the level of assumptions required for this analysis.

Table 6.1 Predicted Increases in the Benzene Plume Length				
		$f_{oc}$ 0.005		
v in ft./day	Plume Length 1 (ft.) (PL1)	Plume Length 2 (ft.) (PL2)	PL2-PL1	% difference
0.004	5	6	1	22%
0.04	26	33	7	27%
0.4	220	280	60	27%
		$f_{oc}$ 0.002		
0.004	6	7	1	17%
0.04	38	48	10	27%
0.4	330	420	90	27%
		$f_{oc}$ 0.01		
0.004	3	4	1	19%
0.04	17	22	5	27%
0.4	145	195	50	34%
<i>Plume Length 1 - Benzene with no ethanol affect</i> <i>Plume Length 2 - Benzene effected by ethanol</i> v = groundwater velocity $f_{oc}$ = organic carbon content				

## 7.0 DRINKING WATER TREATMENT

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### 7.1 Impetus for Treatment

While it is unlikely that elevated levels of ethanol will persist in groundwater due to the rapid rate of biodegradation, ethanol-blended gasoline releases near drinking water supply wells could result in drinking water impacted with ethanol. The taste and odor concentration of ethanol is relatively high. The odor threshold for ethanol as a pure substance has been reported at levels greater than 100 ppm, while the taste threshold is reported to be near 50 ppm (ECDIN, 1998). Based on currently observed MTBE concentrations in drinking water supply wells and the knowledge that ethanol biodegrades rapidly, it is unlikely that ethanol concentrations will reach the taste or odor threshold in drinking water. Therefore, the levels of ethanol allowable in drinking water would likely be based on either a health-based standard, which would also be high, or some other aesthetic criteria.

Regardless of the driving force, it is likely that drinking water containing elevated levels of ethanol will require treatment before it is delivered to the public. There are several treatment options including air stripping, activated carbon, advanced oxidation, membrane filtration, or biologically activated filtration. Each of these treatment technologies is discussed briefly below.

### 7.2 Air Stripping

The effectiveness of air stripping for removing a contaminant from water is a direct function of the contaminant's Henry's constant. As the Henry's constant increases, the contaminant is more readily removed from water. Typically, chemicals with a dimensionless Henry's constant below 0.005 (20°C) are not amenable to removal by air stripping (Roberts, 1997). Consequently, conventional air stripping will not be used to remove ethanol ( $H[-] < 0.0003$ ) from drinking water. However, increases in the water temperature will increase the Henry's constant, which will allow use of stripping for removing ethanol. This process, known as steam stripping, may be effective in removing ethanol from drinking water. However, high costs (>\$5.00/1,000 gallons) are required to raise the temperature of water from 10°C to 40°C which will likely limit the acceptability and feasibility of this technology for removal of ethanol from drinking water.

### 7.3 Activated Carbon

The effectiveness of activated carbon for removing a contaminant from water is a direct function of that contaminant's soil/water partition coefficient ( $K_d$ ). As discussed earlier, ethanol has a very low soil/water partition coefficient due to its high polarity and, hence, solubility. Therefore, ethanol is not expected to adsorb strongly to granular activated carbon (GAC) or other adsorbents. The

ineffectiveness of adsorption is also demonstrated in the Freundlich isotherm constants for ethanol which range from 0.0 to 0.4 [mg/g(L/mg)<sup>1/n</sup>]. Compared to benzene which adsorbs relatively well (isotherm constant ranges from ~20 to 117 [mg/g(L/mg)<sup>1/n</sup>]), ethanol has a very small equilibrium adsorption coefficient (Crittenden et. al., 1997). Thus, adsorption processes, such as GAC, will not be effective for removing ethanol from drinking water.

#### **7.4 Advanced Oxidation**

The factors that control the effectiveness of advanced oxidation for removing a contaminant from water include water quality (alkalinity, bromide), contact time, and contaminant oxidation potential. A major vendor of advanced oxidation processes (AOP) claims that ethanol treatment in drinking water requires energy input similar to that required for MTBE treatment. Based on a recent study by Malcolm Pirnie on treatment costs associated with removal of MTBE from drinking water, the cost to remove MTBE, and therefore ethanol, from drinking water may be as low as \$0.50/1,000 gallons for a large scale treatment system (6,000 gpm). However, AOP technologies raise additional problems regarding oxidation by-product formation. The suitability of AOP for removal of ethanol requires site specific pilot studies to resolve treatment cost and by-product formation issues.

#### **7.5 Membranes**

Reverse osmosis or nano filtration membranes can be used to remove organic compounds from water. These processes remove organic molecules by size exclusion. However, due to the small molecular size of ethanol, membranes are not expected to be effective at removing this compound. No reports have been identified which address the applicability of this technology to ethanol removal.

#### **7.6 Biologically Activated Filters**

Biologically activated filters (BAFs) can effectively remove ethanol because of its relative ease of biodegradation. However, drinking water purveyors are often reluctant to use BAFs due to the potential for microbial activity in the treated effluent water. Federal law mandates the disinfection of all groundwater used as drinking water, regardless of the groundwater quality. Therefore, disinfection with chlorine or ozone following a BAF will reduce purveyors' water quality concerns. Although this treatment option is conceptually feasible with moderate costs, there will be resistance on the part of water utilities because of the inherent limitations of biological processes in drinking water treatment applications. Consequently, the use of BAFs to remove ethanol from drinking water is likely to be limited.

## **7.7 Conclusions**

In conclusion, conventional drinking water treatment technologies for organic removal (air stripping and activated carbon) are not effective for removal of ethanol from drinking water. Advanced oxidation processes may be effective, but this technology presents several other concerns as mentioned earlier. Alternatively, biologically activated filters represent a cost-effective proven technology to remove ethanol from drinking water, but this technology may be limited by treated water quality concerns of water purveyors. Thus, technical options for ethanol removal are limited and have not yet been demonstrated at field sites using field-scale applications.

### 8.1 Health Effects of Ethanol

Human exposure to ethanol can occur via several pathways. Due to the increase in vapor pressure of ethanol-blended gasolines, the most likely exposure pathway is inhalation of volatilized ethanol during refueling. The other potential route of exposure is ingestion of ethanol-contaminated drinking water.

#### 8.1.1 Inhalation

Inhalation of ethanol vapors may cause headache, nausea, vomiting, dizziness, drowsiness and sensory irritation (Health Effects Institute, 1996; MSDS, 1998). The mechanisms of ethanol loss in the human body following inhalation are not due to metabolism as is the case with ingested ethanol (Pastino et al., 1997). Approximately sixty percent of inhaled ethanol is absorbed in humans (Kruhoffer, 1983). As ethanol gas is inhaled, it dissolves in the mucous lining of the upper respiratory tract. It then diffuses from a region of high concentrations, such as the lumen, to a region of low concentrations, such as epithelial cells and blood capillaries. As a result, some of the inhaled ethanol desorbs and is exhaled (Pastino et al., 1997).

Exposure to ethanol via inhalation can be attributed to four major processes during which ethanol is released to the atmosphere: (1) refueling, (2) evaporative emissions, (3) exhaust emissions containing ethanol from incomplete combustion processes and (4) vapors from leakage and spills during industrial and commercial processes. The legal airborne permissible exposure limit for ethanol is 1000 ppmv averaged over an 8 hour workshift period.

It has been estimated that more than 100 million people in the United States are briefly exposed to low levels of volatile organic carbons from gasoline during refueling activities. In an effort to evaluate the risk from inhalation of ethanol during refueling, a group of researchers recently measured steady-state blood ethanol concentrations during exposure of female and male mice and rats to various ethanol concentrations (Pastino et al., 1997). The results of this study suggested that inhalation of ethanol at or above the concentrations expected to occur during refueling results in minimal blood ethanol concentrations; these concentrations are too low to produce any behavioral or toxic effects in humans (Pastino et al., 1997).

#### 8.1.2 Ingestion

The toxicity and health effects from ingestion of moderate to large quantities of ethanol have been extensively investigated and will not be discussed in this study. Under these conditions, ethanol

can increase the risks of certain cancers, adversely affect the developing embryo, produce neurotoxicity, and cause various other types of damage (Health Effects Institute, 1996). However, it is unlikely that such effects occur at the very low concentrations to which most people are accidentally exposed to from the use of ethanol-blended fuels. Lethal effects of ethanol (as represented by the concentration expected to be lethal in 50% of a test population (LD<sub>50</sub>)) are presented in Table 8.1.

<b>Table 8.1</b> <b>Lethal Doses in Rats and Mice</b> Adapted from MSDS (1988)	
LD <sub>50</sub> (Oral-rat -- mg/kg)	7060
LD <sub>50</sub> (IPR-rat -- mg/kg)	4070
LD <sub>50</sub> (Oral-mouse -- mg/kg)	7800
LD <sub>50</sub> (IV-rat -- mg/kg)	1440

## 8.2 Aquatic Toxicity

Most of the toxicity studies that have been conducted for ethanol have assessed the acute toxicity of this compound in aquatic systems. Cogwill and Milazzo (1991) reported the sensitivity to ethanol for two cladocerans, *Ceriodaphnia dubia* and *Daphnia magna*. This study reported values of median lethal concentrations, LC<sub>50</sub>, and median effective concentrations, EC<sub>50</sub>, for ethanol (Table 8.2). LC<sub>50</sub> is the estimated concentration that is expected to be lethal to 50% of the test animals or plants, and EC<sub>50</sub> is the estimated concentration that is expected to cause an effect other than death to 50% of the test animals or plants (non-lethal effects include changes in behavior, growth, immobilization, reproduction and equilibrium).

<b>Table 8.2</b> <b>Reported Median Lethal and Median Effective Concentrations for Ethanol <sup>(1)</sup></b>			
Test animal or plant	LC <sub>50</sub> (mg/L)	EC <sub>50</sub> (mg/L)	Reference
<i>Daphnia magna</i> (Water flea)	9248 <sup>a</sup> (48 hours)	14 <sup>b</sup> (216 hours)	1
<i>Ceriodaphnia dubia</i> (Water flea)	8808 <sup>a</sup> (48 hours)	26 <sup>b</sup> (216 hours)	1
<i>Hyaella azteca</i> (Scud)	454	NA <sup>c</sup>	2

(1)Cogwill et al., 1991; (2) Zogorski et al., 1996 <sup>a</sup> Based on survival; <sup>b</sup> Based on progeny, brood number and mean brood size; <sup>c</sup> Not available

Using the USEPA classificatory scheme, the LC<sub>50</sub> for ethanol was found to be non-toxic, although the organisms failed to reproduce at high concentrations of ethanol. The researchers concluded that this mode of action could be viewed as only slightly toxic. This study also presented comparative response data which included a marine diatom (*Skeletonema costatum*), a green alga (*Selenastrum capricornutum*), the two cladocerans and fathead minnow (*Pimephales promelas*). The results of this study indicated that ethanol was essentially non-toxic to the species tested. Numerical results from this comparative study are presented in Table 8.3. However, Table 8.3 illustrates that the toxicity of ethanol is greater (454 ppm for scud) for aquatic life than that of MTBE (672 ppm for a fathead minnow) (OSTP, 1997).

<b>Table 8.3</b>			
<b>Comparative Data of Aquatic Toxicity for Ethanol and MTBE</b>			
<b>Adapted from Cogwill and Milazzo (1991) and OSTP (1997)</b>			
<b>Ethanol</b>		<b>MTBE</b>	
<i>Daphnia magna</i> LC <sub>50</sub> (based on survival) (mg/L) (48 hours)	9248	<i>Pimephales promelas</i> ( <i>fathead minnow</i> ) LC <sub>50</sub> (based on survival) (mg/L) (96 hours)	706
<i>Pimephales promelas</i> LC <sub>50</sub> (based on survival) (mg/L) (96 hours)	14740	<i>Pimephales promelas</i> ( <i>fathead minnow</i> ) LC <sub>50</sub> (based on survival) (mg/L) (96 hours)	672
<i>Ceriodaphnia dubia</i> LC <sub>50</sub> (based on survival) (mg/L) (48 hours)	8808	<i>Nitocra Spinipes</i> LC <sub>50</sub> (based on survival) (mg/L) (96 hours)	>1000
<i>Hyalella asteca</i> ( <i>Scud</i> ) LC <sub>50</sub> (based on survival) (mg/L) (216 hours)	454	<i>Bleak</i> ( <i>European Fish</i> ) LC <sub>50</sub> (based on survival) (mg/L) (96 hours)	>1000

In another study, Lagerspetz et al. (1993) provided a comparison of the toxicity of ethanol to *Anodonta cygnea* (mussel) and *Daphnia magna* (water flea). The authors reported EC<sub>min</sub> values of 2 mg/L (EC<sub>min</sub> is defined as the lowest concentration of ethanol which in one hour significantly affected the particle transport rate by frontal gill cilia of mussels). Ethanol concentrations of this magnitude will likely be present at the LNAPL/water interface but will quickly dilute to much lower concentrations which will present no likely aquatic toxicity effects.

### **8.2.1 Toxicity to Microbial Populations**

In general, large concentrations (10 - 15%) of alcohol are considered to be toxic to most microorganisms (Brusseau, 1993; Ingram and Buttke, 1984). Ethanol concentrations above 100,000 ppm result in the immediate inactivation of most vegetative organisms with spore-forming organisms being considerably more resistant. Most bacteria exhibit a dose-dependent inhibition of growth over the range of 1 to 10% ethanol by volume, and very few species can grow at concentrations over 10% (Ingram and Buttke, 1984).

Limited studies have been conducted to evaluate the effect of alcohols from alcohol-blended gasolines on subsurface microbial populations; most of these studies have focused on methanol. In such a study, methanol was found to degrade in soils from three different sites up to a concentration of 1000 mg/L with no apparent toxicity to the microorganisms (Butler et al, 1992). In a study using ethanol, Hunt et al. (1997) reported that ethanol concentrations in microcosm experiments higher than 40,000 mg/L were toxic to the microorganisms as evidenced by a complete stop in oxygen uptake. In a more recent study, microbial activity was measured in the presence of several concentrations of ethanol; high levels of microbial activity were observed for 5% and 10% ethanol by volume but the activity decreased significantly in the presence of 20% ethanol (Araujo et al., 1998).

## 9.0 CONCLUSIONS

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### 9.1 Fate and Transport

Ethanol is a widely used fuel oxygenate that can be directly released to the environment during its production, storage, transportation, gasoline blending, and use of gasoline containing ethanol. Ethanol is also discharged to the atmosphere during combustion in internal engines as unburned fuel. In ground water, ethanol levels depend upon the nature of the release and the magnitude of the release. Because ethanol is totally miscible in water, all of the ethanol in gasoline will partition into the water phase. Depending upon the level of dilution, ethanol levels in the ground water can exceed 50,000 mg/L (0 dilution factor). Probable levels in the vicinity of an ethanol-blended gasoline spill range from 400 to 4,000 mg/L.

### 9.2 Ethanol Impact on BTEX Plume Length

In general, ethanol is expected to biodegrade quickly regardless of what other organic substrates are available. Ethanol has been shown to degrade under both aerobic and anaerobic conditions at rates that would limit the extent of any ethanol plume to within a few hundred feet of a release site, under most conditions. In subsurface areas with very high ground water velocities (>1 ft/day), longer plumes are possible. The primary concern with the presence of ethanol in the subsurface is its impact on the natural or engineered biodegradation of other constituents in gasoline, namely BTEX. Laboratory and field data have confirmed that ethanol will be preferentially utilized in the presence of BTEX under both aerobic and anaerobic conditions. The implications of this finding in the field are not well established. Conceptually, this means that other gasoline components will continue to migrate until the ethanol has disappeared sufficiently to permit biodegradation of other constituents to occur. The length of BTEX plumes will likely be increased and the magnitude of this increase, while site specific, is expected to be approximately 27% for typical California conditions.

### 9.3 Ethanol in the Atmosphere, Soil, and Surface Water

In the atmosphere, the half life of ethanol is similar to that of other alkyl ether oxygenates, including MTBE. Ethanol undergoes rapid reactions with hydroxyl radicals, and in summer conditions, half-lives are on the order of days.

In both running and standing surface water bodies, ethanol is not expected to volatilize quickly, and under quiescent conditions in a reservoir or lake, ethanol may persist for months in the absence of biodegradation. It appears, however, that biodegradation will occur if water temperatures are above

10°C, with ethanol half lives on the order of hours to days. It is thus unlikely that ethanol would persist in surface waters.

#### **9.4 Treatment**

Ethanol is completely miscible in water, and it has a very low Henry's constant (approximately 100 times less volatile from water than MTBE). Most treatment technologies that are effective in removing benzene and MTBE from water (air stripping, granular activated carbon) are not effective in removing ethanol. Advanced oxidation processes show promise, and it appears that ethanol oxidation in water occurs at rates similar to the oxidation of MTBE. Steam stripping can effectively remove ethanol, but this process is cost prohibitive and, therefore, not suitable for drinking water applications. Biological treatment processes are effective at removing ethanol from water and can be used in a remediation context. However, use of biological treatment in drinking water situations is unlikely due to inherent concerns over process stability and treated water quality from biological processes in drinking water applications. In conclusion, if ethanol were to be found in drinking water, treatment would be expensive and difficult.

#### **9.5 Human and Aquatic Toxicity**

The literature reviewed shows that at concentrations which are likely to exist in the environment, ethanol will probably not be toxic to either aquatic life or humans. However, according to the Interagency Assessment of Oxygenated Fuels, ethanol is more toxic than MTBE to aquatic life (OSTP, 1997). While the aquatic toxicity of ethanol is high (405 ppm for scud), concentrations of this magnitude could be observed near a LUST source area or after a pure product ethanol spill. Thus, in most cases, ethanol concentrations will be benign to surrounding organisms, but in extreme circumstances, ethanol could prove toxic to indigenous microbes or aquatic life.

#### **9.6 Ethanol and Air Quality**

Based on the studies conducted to date, oxygenated fuels have been shown to significantly decrease the amount of carbon monoxide in the air. However, ethanol-blended fuels have been shown to increase the amount of NO<sub>x</sub> and total hydrocarbons, both of which are ozone precursors. Specifically, ethanol-blended fuels increase emissions of acetaldehyde by at least 100% compared to conventional fuels. Acetaldehyde reacts in the atmosphere to form PAN, a hazardous air pollutant and precursor to ozone. Ethanol produces a net increase in the ozone forming potential (e.g., increasing atmospheric concentrations of PAN, NO<sub>x</sub>, and hydrocarbons) and the overall potency weighted toxics in the atmosphere compared to MTBE, the other widely used oxygenate. Thus, the California Air

Resource Board reports that MTBE is more beneficial to the overall reduction in atmospheric toxics and ozone forming potential than ethanol.

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