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EVALUATION OF THE FATE AND TRANSPORT OF METHANOL IN THE ENVIRONMENT

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The purpose of this report is to summarize the existing information regarding methanol—its fate and transport in the environment and potential impacts, if any, on human health and the environment. Pure methanol (M100) which is expected to be used in fuel cell vehicles is the primary focus of this study, as opposed to the currently available gasoline-methanol fuel mixture which consists of 15 percent gasoline and 85 percent methanol (M85). A thorough literature review was conducted with over 100 documents reviewed as part of this study. Because neither the Clean Air Act (CAA), Clean Water Act (CWA), nor the Safe Drinking Water Act (SDWA) require methanol monitoring, a national database on occurrence of methanol in the environment is not available for evaluation. Therefore, results from laboratory and field studies documented in the literature and computer modeling were used to assess the fate and transport of methanol in the environment. A more complete summary of the findings of this study is presented in the following detailed report. This executive summary provides an overview of these findings.

BACKGROUND

Methanol has been a widely used industrial chemical since the 1800s. Methanol is produced from steam reformed natural gas and carbon dioxide using a copper-based catalyst. Current uses of methanol include use as a feed stock for a variety of widely used organic chemicals, including formaldehyde, acetic acid, chloromethane, and methyl tert-butyl ether (MTBE). It is also used as a solvent in paint strippers, paints, carburetor cleaners, plastics, plywood, and automobile windshield washer solutions. Since 1965, methanol has been used in the U.S. as a fuel in certain vehicles (e.g., race cars), either as M100 or M85. Flexible fuel vehicles (FFVs)—vehicles capable of using either conventional gasoline, M85, or any combination of the two fuels—were developed by Ford Motor Company in 1978. A program funded by the California Energy Commission in conjunction with several oil companies provided the initial refueling infrastructure. FFVs were produced primarily to reduce the U.S. dependency on crude oil and for their ability to reduce carbon monoxide and ozone forming emissions.

For a number of reasons, including an insufficient network of M85 fueling facilities, methanol FFVs have not become widespread. Therefore, other clean burning vehicles will be required to achieve even lower emission standards likely to be established in the future. Recently, researchers have turned from alternatively-fueled internal combustion engines to fuel cell technology. In 1994, Georgetown University introduced the first liquid-fueled fuel cell vehicle which derived its energy by reacting hydrogen and oxygen in the fuel cell. In 1999, the world's largest automakers are all working to commercialize fuel cell vehicles. Due to the liquid properties of methanol at room temperature, ambient pressure, the high hydrogen to carbon ratio, and the relatively low combustion temperature, methanol is considered an ideal hydrogen carrier for fuel cell vehicles. The continuing development of fuel cell vehicles is driven by the projected low cost, environmental consumer benefits, and regulations in California, New York, Massachusetts, and other areas which require 10 percent of the Model Year 2003 vehicles to be Zero Emission Vehicles (ZEV) and by concerns over global warming. Consequently, there is a significant economic incentive to develop and market fuel cell vehicles which are expected to appear in large quantities worldwide by 2004.

Methanol production worldwide is expected to increase to meet the anticipated future demand. In the U.S., annual methanol production has risen consistently over the last ten years, with 17 plants currently producing approximately 2.25 billion gallons of methanol per year (see Table ES-1). Currently the U.S. imports 25 percent of its total demand, principally from Canada. In 1993, approximately 12 million gallons of methanol were used as a direct fuel, either M100 or M85 for FFVs in California, and another 212 million gallons were used in other fuels and fuel additives. The American Methanol Institute (AMI) estimates that by the year 2010, methanol demand for fuel cell vehicles alone may reach 882 million gallons per year, which would be 8 percent of the current (1998) world capacity.

TABLE ES-1
Global Methanol Capacity and Demand (1997)

Entity	% of Capacity	% of Demand
North America	35	36
Asia/Pacific	17	22
Western Europe	11	22
South America	11	4
Other	26	16

Adapted from http://www.chemweek.com, 1998

POTENTIAL FOR RELEASE OF METHANOL TO THE ENVIRONMENT

The expected exponential growth in the demand for methanol will result in increased transportation by barge and rail, as well as an increased number of storage and distribution facilities. Given this expected increase in production, transportation, storage, and use of methanol, the potential for accidental releases to the environment will increase. In 1992, methanol ranked third amongst all chemicals reportedly released by industry to the environment as noted in annual Toxics Release Inventory (TRI) reports required by the U.S. Environmental Protection Agency (USEPA). As shown in Table ES-2, U.S. methanol releases are primarily to the atmosphere; however, approximately 20% of the methanol is directly discharged to the soil, groundwater, or surface water (total mass released represents approximately 1% of the total mass of methanol produced).

TABLE ES-2
Estimated Releases of Methanol for the United States

Reported Release to:	1992[a] (million lbs/year)	1993[b] (million lbs/year)
Atmosphere	195	171.8
Underground Injection	27	27.9
Land	3.3	1.72
Water	16.4	10
Total releases	251.7	211.4

[a]*USEPA, 1994a.* [b]*Zogorski et al., 1997.*

Three conceptual release models or scenarios were considered as part of this study. These include: tank truck or rail car release, barge release, and release from underground storage tanks (USTs) at a refueling facility. A release from a tank truck or rail car could take place in a variety of settings. A rail tank car accident could potentially release up to 34,500 gallons of methanol. In addition to transport of methanol in the U.S. by rail, the U.S. obtains some of its methanol demand from overseas, all of which is transported by ships or barges. Thus, releases to ocean, estuary, or river environments are possible. A typical barge tanker carries 45,000 tons of product (13.6 million gallons) and in 1999, a 96,000 ton (29.1 million gallons) vessel will be introduced for dedicated methanol transport. The third release scenario involves methanol losses at a fueling or storage facility from an UST. A typical UST could allow a fuel release into the subsurface at a rate of 0.5 gallons per minute (gpm) before the leak detection devices are activated. Although continuous releases of this size are uncommon, the potential for significant methanol losses from USTs cannot be overlooked.

Because the CAA, CWA, and SDWA do not require monitoring of methanol in groundwater, surface water, or the atmosphere, national monitoring data sets on methanol occurrence in air or water are not available. However, the behavior of methanol within environmental compartments—soil, air, surface water, and ground water—can be predicted based on its chemical and physical properties. Methanol is a clear, colorless, volatile liquid with a faint alcohol-like odor, though it is difficult to detect in the air at low concentrations (<10 part per million by volume (ppm_v)). Methanol is the simplest alcohol, having only one carbon atom, and is capable of being completely mixed in water. It easily dissolves in other alcohols and chlorinated hydrocarbons, but has limited solubility in diesel fuel, vegetables oils, and aliphatic hydrocarbons. The chemical and physical properties of methanol have been used to describe the fate and transport of methanol in the environment in the event that an accidental release were to occur.

FATE AND TRANSPORT

Although methanol occurs naturally in the environment as a result of various biological processes in vegetation, microorganisms, and other living species, a large release of concentrated methanol to ground water, surface water, or soil has the potential to adversely impact the affected environment. Once released, the half-life of methanol (the time required for 50% reduction in the mass released or present) depends on numerous factors including: the nature of the release, quantity of the release, and physical, chemical and microbiological characteristics of the impacted media. Table ES-3 is a summary of the estimates of the range of probable methanol half-lives in various environmental media as documented from various reports, in comparison with the probable half-lives of benzene, a common gasoline constituent. Based on these data, regardless of the release scenario, methanol appears unlikely to accumulate in the groundwater, surface water, air, or soil.

TABLE ES-3
Estimated Half-Lives of Methanol and Benzene in the Environment

Environmental Medium	Methanol Half-life (days)	Benzene Half-life (days)
Soil *(Based upon unacclimated grab sample of aerobic/water suspension from groundwater aquifers)*	1 - 7	5 - 16
Air *(Based on photooxidation half-life)*	3 - 30	2 - 20
Surface water *(Based upon unacclimated aqueous aerobic biodegradation)*	1 - 7	5 - 16
Groundwater *(Based upon unacclimated grab sample of aerobic/water suspension from groundwater aquifers)*	1 - 7	10 - 730

Adapted from Howard et al. (1991).

The physical and chemical properties of methanol help to further define the fate and transport of this chemical in the various environmental media in the context of each of the conceptual release scenarios. The dominant mechanisms of methanol loss from subsurface soil and groundwater are expected to be biodegradation and advection (dispersion and diffusion) with little loss from adsorption on soils due to its high solubility and low retardation factor. In surface water, the infinite solubility of methanol will result in rapid wave-, wind-, and tide-enhanced dilution to low concentrations (< 1%). Once concentrations have been diluted below toxic levels the dominant mechanism of methanol loss is expected to be biodegradation. Compared to other loss mechanisms identified, including volatilization and chemical degradation, biodegradation is expected to be the dominant process controlling the fate of methanol in the soil, groundwater, and surface water environments. In addition, the biodegradation of methanol can occur under both aerobic (oxygen present) and anaerobic (oxygen absent) conditions.

Therefore, following any of the three conceptual release scenarios presented, methanol is not likely to persist in soil or water due to its rapid biodegradation. Methanol is miscible in water and consequently will dissolve quickly and be diluted to low concentrations in the event of a surface water spill. In groundwater, methanol concentrations are highly dependent on the nature and the magnitude of the release, but will likely fall to low concentrations once complete dissolution has occurred. In both surface and ground waters, methanol will likely be easily biodegraded under a wide range of possible water quality conditions.

Relative to conventional gasoline and diesel fuel (and many of their constituent elements such as benzene), methanol is a safer and more environmentally benign fuel. Thus, hazards caused by gasoline releases will be more serious than those due to methanol releases, and these hazards will persist longer in the environment.

TREATMENT

Following a release of methanol to the subsurface as a result of any of the three release scenarios, remediation of soil and ground water may be required if natural biodegradation is not sufficient to meet potential clean up standards in a reasonable time frame. Methanol will quickly biodegrade and, therefore, natural attenuation is likely to be an effective and inexpensive remediation strategy for both soil and water. If biodegradation is not sufficient to meet cleanup objectives and an alternative remediation strategy is required, the high vapor pressure of methanol suggests that soil vapor extraction will effectively remove any residual methanol from the soil. Once extracted from the subsurface, the methanol vapors can be biodegraded using appropriate technologies such as vapor phase biofilters.

It is unlikely that elevated levels of methanol will persist in either groundwater or surface water due to the rapid rate of biodegradation. However, if drinking water sources experienced a methanol release, treatment would likely be required before distribution to the public. Most treatment technologies that remove gasoline components from water, including air stripping and granular activated carbon, are not effective at removing methanol due to its low volatility and high solubility. Reverse osmosis or nanofiltration are also ineffective at removing methanol because of its small size and low molecular weight.

Advance oxidation processes such as ozonation with ultraviolet light are expected to be effective, but the feasibility and cost of treatment is site specific. Biological treatment processes are effective at removing methanol from drinking water, and are increasingly being accepted by the drinking water community for drinking water applications. However, biological treatment in drinking water applications is still not extensively used and, therefore, would require broader regulatory acceptance. In conclusion, in the unlikely event that methanol contaminates source waters, methanol can be removed in both a remediation and drinking water treatment context using biological processes. However, the effectiveness, cost and public acceptance will be site specific.

HUMAN AND AQUATIC TOXICITY

Methanol's properties and toxicity are well understood. According to the extensive literature reviewed for this study, methanol is neither mutagenic nor carcinogenic. Human exposure to methanol can occur via the inhalation, ingestion, or dermal contact pathways. Inhalation of methanol vapors can cause irritation of the mucus membranes, dizziness, nausea, headaches, and blurred vision if exposure at high levels occurs. While inhalation is the most common route of exposure to the body, ingestion represents the most serious acute health hazard due to the much higher volume of methanol which can be ingested relative to the volume which can be inhaled. The effects of ingestion follow the same pattern described for inhalation. With respect to dermal contact, methanol readily absorbs into the dermal layer with repeated exposure causing eczema, redness, and scaling. However, the current evidence shows that acute toxic effects on humans and some animals from methanol only occur at high doses (> 10 mg/l). The U.S. Department of Energy considers gasoline to be "overall" more hazardous to human health than neat (i.e., pure) methanol.

Methanol is significantly less toxic to marine life than crude oil or gasoline, and many of the effects of short term exposure are temporary and reversible. The Office of Pollution Prevention and Toxics indicated that methanol is essentially non-toxic to the four aquatic fish species that were tested. A large methanol spill into a surface water would have some immediate impacts to the biota in the direct vicinity of the spill. However, because of its properties (i.e., methanol readily mixes with water and evaporates quickly in the atmosphere) methanol would rapidly dissipate into the environment, and within fairly short distances from the spill would reach levels where biodegradation would rapidly occur.

RECOMMENDED RESEARCH

The detailed report which follows this executive summary contains a comprehensive evaluation of the fate and transport of methanol in the environment. As previously stated and supported by this comprehensive evaluation, if methanol is released into the soil, groundwater or surface water, it will rapidly biodegrade. However, there are several fate and transport issues where available literature is incomplete and additional research is warranted to fill apparent data and information gaps. Three areas of future research are recommended:

- Similar to other fuels, methanol may contain additives to address performance, pollution, or health issues. If additives are required, a thorough evaluation of the fate and transport of these additives is recommended.

- The literature reviewed for the comprehensive report suggests that methanol will rapidly degrade once released into soil, groundwater, or surface water. However, if high concentrations of methanol exist near the point of release, the concentration of methanol may be toxic to microorganisms in the immediate area resulting in limited or no biodegradation. An analysis of methanol releases that have occurred at methanol fueling areas, storage areas, production locations, or during transport should be conducted to verify that methanol does behave as predicted.

- The fate and transport of a methanol plume that becomes commingled with a gasoline plume is briefly addressed in this report; however, there remain several uncertainties. The effect of the presence of methanol on the fate and transport of conventional gasoline plumes needs to be better understood, including an evaluation of methanol impacts on the solubility and biodegradation rates of benzene and other gasoline constituents.

1.1 Purpose and Scope of Report

One of the main industrial strategies for reducing carbon emissions to the atmosphere from mobile sources is the development of near zero emissions vehicles, such as those powered by fuel cells. Use of these vehicles is expected to increase dramatically over the next decade and beyond. One promising technology for fuel cell powered vehicles is the use of methanol as the fuel source.

As fuel cell powered vehicles proliferate, dramatic increases in worldwide use of methanol are anticipated. Increased use of methanol as a fuel source will increase the potential for releases of methanol to the environment during production, transport, storage, distribution and consumption. As a consequence, questions regarding the potential impacts of unintentional methanol releases to the environment, its subsequent transport and fate, and its possible impacts on human health and the environment can be expected.

The purpose of this study, requested by the American Methanol Institute, is to summarize existing knowledge on the fate and transport of methanol in the environment, and to identify potential impacts, if any, on human health and the environment. This report will focus primarily on fate and transport issues arising from the use of pure methanol as expected in fuel cell vehicles, also known as M100, as opposed to the currently available gasoline-methanol fuel mixture, which consists of 85 percent methanol and 15 percent gasoline (M85). Available literature will be reviewed on: 1) fate and transport processes that can affect the distribution of methanol in the environment; 2) fate and transport of methanol in the context of potential release scenarios; 3) human and aquatic toxicity of methanol; and 4) treatment processes for removing methanol from soil or water. In addition, available information will be reviewed on the characteristics of additives that may be considered for use in methanol. Finally, data gaps will be identified and research needs recommended as appropriate to reduce uncertainties regarding the fate and transport of methanol.

1.2 Introduction and History of Use

Methanol is a widely used industrial chemical that has been in commercial use since the 1800's. Methanol is produced from steam reformed natural gas and carbon dioxide using a copper-based catalyst. Current uses of methanol include a feed stock for formaldehyde, acetic acid, chloromethane, and methyl tert-butyl ether (MTBE), and a solvent in paint strippers, paints, carburetor cleaners, plastics, plywood, and car windshield washer fluids.

Since 1965, methanol has been used as a fuel in certain vehicles, either as a pure compound (M100) or as a mixture of methanol and conventional gasoline, in an 85/15 mix, (M85). For example, methanol has been used as a fuel source in Indy race cars for more than 30 years (CEC, 1998). In 1987, the first prototype flexible fuel vehicles (i.e., vehicles capable of running on conventional gasoline, M85, or any combination of the two fuels) were developed by Ford Motor Company (CEC, 1998). A program funded by the California Energy Commission in conjunction with several oil companies provided the initial refueling infrastructure. Emerging from this program, Ford built 2,500 Taurus FFVs (2,137 in California) in 1993 (CEC, 1998). FFVs were primarily produced because they could decrease the nation's dependency on crude oil and because of their ability to reduce carbon monoxide and ozone forming emissions to levels below those mandated by the Clean Air Act Amendments (CAAA) of 1990.

California currently leads the nation in the number of operating FFVs (light and heavy duty): 10,000 light duty FFVs and 485 heavy duty FFVs as of 1994 (CEC, 1994) and approximately 15,000 light duty FFVs in 1998. To facilitate these FFVs, California installed over 110 public and private methanol fueling facilities; however, this network is not sufficient to supply M85 conveniently to all individual consumers requiring fuel (http: www.energy.ca.gov/). For this reason and others, methanol FFVs have not become widespread and are no longer being produced; the advantages and disadvantages of FFVs have not been investigated in this report.

In recent years, researchers have turned from alternatively-fueled internal combustion engines to fuel cell technology. Georgetown University introduced the first liquid-powered fuel cell vehicle in 1994. A fuel cell combines hydrogen and oxygen electrochemically to form water, electricity, and heat. The purpose of any fuel in a fuel cell vehicle is to serve as a source of hydrogen. Due to the liquid properties of methanol at room temperature, and ambient pressure, the high hydrogen to carbon ratio, and the relatively low combustion temperature, methanol is considered an ideal hydrogen carrier for fuel cell vehicles (Nowell, 1998). The continuing development of fuel cell vehicles by several auto manufacturers is driven by the projected low cost of the vehicles and regulations in California, New York, Massachusetts, and other states which require 10% of the Model Year 2003 vehicles to be Zero Emission Vehicles

(ZEV). A ZEV is a vehicle which does not emit carbon monoxide, volatile organic compounds (VOC), non-methane organic gases (NMOG), formaldehyde, nitrous oxides (NOx), or particulate matter. Methanol-powered vehicles will only receive a partial emissions credit (i.e., a 0.7 credit where a ZEV credit of 1 implies no emissions) (CARB, 1998) because there are some evaporative emissions associated with the use of methanol fuel falling in the category of NMOG; however, running emissions of all chemicals except carbon dioxide and water vapor are substantially reduced. Consequently, there is significant economic and environmental incentives to develop and market fuel cell vehicles which are expected to appear in large quantities worldwide by 2004 (Nowell, 1998).

1.3 Methanol Production

Methanol is produced in 17 plants across the United States, which accounted for 35% of the total global methanol production capacity in 1997 (see Table 1-1). The total annual production of methanol in the US has risen consistently over the last ten years and continues to grow as a result of methanol's use in the manufacture of MTBE, a widely used gasoline oxygenate. Due to the demand for methanol from MTBE manufacturers, methanol prices reached a peak in 1994. Since then, capacity has been steadily added and demand from MTBE manufacturers has decreased resulting in a significant drop in methanol prices. Approximately 1.3 billion gallons of methanol were produced in the U.S. in 1992, 2.2 billion gallons in 1995, and 2.25 billion gallons in 1998. In 1993, approximately 12 million gallons of methanol were used as a direct fuel, as either M100 or M85, for FFVs in California, while another 212 million gallons were used in other fuels (e.g., Indy race car) and to produce fuel additives (MTBE).

TABLE 1-1
Global Methanol Capacity and Demand (1997)

Entity	% of Capacity	% of Demand
North America	35	36
Asia/Pacific	17	22
Western Europe	11	22
South America	11	4
Other	26	16

Adapted from http://www.chemweek.com, 1998

The American Methanol Institute (AMI) estimates that by the year 2010, methanol demand for fuel cell vehicles could reach 882 million gallons per year, which is 8% of current (1998) world capacity. By 2020, AMI estimates that this demand may increase to 135% of current world capacity (Nowell, 1998). This exponential growth in the methanol industry will result in increased transportation by barge and train, as well as an increased number of storage and distribution facilities.

1.4 Chemical and Physical Properties

The behavior of an organic chemical within environmental compartments—air, groundwater, surface water, and soil—can be predicted by that compound's chemical and physical properties. Methanol is a clear, colorless, volatile liquid with a faint alcohol-like odor, though it is difficult to detect at concentrations below 10 ppm. Methanol is the simplest of the alcohols, having only one carbon atom, and is completely miscible in water. Methanol easily dissolves in other alcohols and chlorinated hydrocarbons, but has limited solubility in diesel fuel, vegetable oils, and aliphatic hydrocarbons (USDOE, 1991). The properties of methanol are compared to the properties of conventional gasoline in Table 1-2. Benzene is included in the Table as a representative gasoline constituent where the properties of gasoline are not available. Many of these properties will be referred to throughout the text to describe the fate and transport of methanol in the environment.

Table 1-2
A Summary of Physical and Chemical Properties of Methanol, Gasoline (BTEX), and Benzene

Physical and chemical properties	***Methanol***	***Gasoline***	***Benzene***
Molecular weight [g/mole]	32.04	~100 (c)	78.11 (c)
Elemental composition by weight			
% Oxygen	50%	(mix of C4 to C14 hydrocarbons)	0%
% Carbon	37.5%		92%
% Hydrogen	12.5%		8%
Specific gravity	0.7915 @ 60°F (f)	0.72-0.78 (c)	0.88(c)
Boiling point [°C]	64.7	27-225 (b)	80.1(c)
Water solubility [mg/L]	miscible	100-200(c)	1,780
Vapor pressure			
[mm Hg] (@ 25°C)	126	--	76, 95 (c)
[psi] (@ 100°F) (e)	4.63	7-15	--
Heat of combustion [kJ/kg] (b)	19,930	43,030	---
Henry's Law constant [atm m^3 g^{-1} $mole^{-1}$]	4.55×10^{-6} 4.42×10^{-6}(c)	---	5.43×10^{-3} (c)
Henry's Law constant [-] @ 25 ^{o}C	1.087×10^{-4}	---	0.22
Liquid Dispersion Coefficient @ [m^2/s] 25^{o}C	1.65×10^{-9}	---	9.95×10^{-10}
Log K_{oc}	0.921 0.44 (c)	---	1.8-1.99 1.50-2.16 (c)
Log K_{ow}	-0.77 -0.75(c)	---	2.13 1.56-2.15 (c)
Flammability Limits (b):			
Lower (LFL)			---
Volume percent	6.0	1.4	
Temperature (°C)	7	-43	
Upper (UFL)			---
Volume percent	36.5	7.6	
Temperature (°C)	43	-30 to-12	
Flash Point (°C)	12°C (54°F) (a)	-43 (°F)	---
Vapor Density @ 1 atm; 10 ^{o}C (b)	1.4	2-5	3.4

(a) Merck Index, 1989; (b) Machiele, 1989; (c)Zogorski et al., 1997; (d) Bauman, 1989; (e) USDOE, 1991;

1.5 Release Scenarios

In 1992, methanol ranked third among all chemicals reportedly released by industry to the environment as noted in annual Toxics Release Inventory (TRI)—reports required by the U.S. Environmental Protection Agency (USEPA) (USEPA OPPT, 1994). These releases are primarily from glue manufacturers, MTBE formulators, pulp and paper manufacturers, and other chemical producers (AMI, 1998). As shown in Table 1-3, US methanol releases in 1992 and

1993 were primarily to the atmosphere; however, approximately 20% of the methanol is directly discharged to soil, groundwater or surface water. The total volume of methanol released to the environment represents approximately 1% of the total production volume. The Clean Air Act (CAA), Clean Water Act (CWA), and Safe Drinking Water Act (SDWA) do not require monitoring of methanol in surface water, groundwater, or the atmosphere. Thus, national monitoring data sets and information on methanol occurrence in air or water are not available (Zogorski et al., 1997).

Given the limited data on releases and occurrences of methanol, this report will evaluate the fate and transport of methanol in soil and water in the context of three methanol release scenarios. The three scenarios are as follows:

TABLE 1-3
Estimated Releases of Methanol in the United States

Reported Release to:	**1992[a] (million lbs/year)**	**1993[b] (million lbs/year)**
Atmosphere	195	171.8
Underground Injection	27	27.9
Land	3.3	1.72
Water	16.4	10
Total releases	251.7	211.4

[a]USEPA, 1994a. [b]Zogorski et al., 1997.

Scenario 1: Tank truck or rail car release. Currently, the most of the imported methanol to the U.S. is transported by rail car from Canada. A release from a rail car or tank truck could take place in a variety of settings, including the desert, the coast, or near a drinking water source. A tank car may release as much as 34,500 gallons of methanol (Perry et al., 1984). Approximately 1,400 truckloads are delivered each year throughout California (CEC, 1994).

Scenario 2: Barge release. Ocean and river releases could occur since the U.S. imports some methanol from overseas by barge or ship. A typical ship carries 45,000 tons (13.6 million gallons) of product, and in 1999, a 96,000 ton (29.1 million gallons) vessel for methanol transport will be introduced.

Scenario 3: Storage / Fueling facility Release. The third conceptual scenario involves the release of methanol at a fueling or storage facility. Currently, a gasoline underground storage tank (UST) can release fuel into the subsurface at a leak rate as high as 0.5 gpm before the leak detection devices are activated; methanol USTs are expected to have a similar detection sensitivity. Consequently, it is conceivable that methanol releases will occur at methanol fueling facilities at a rate similar to gasoline UST releases. If methanol USTs are located at a gasoline dispensing location, subsurface methanol releases may encounter existing gasoline contaminant plumes. The 1998 federal UST upgrade requirements will significantly reduce the number of new releases; however, impacts of methanol releases on the fate of existing plumes needs to be considered. This scenario represents an important potential route of methanol release to groundwater.

1.6 Fate in the Environment

Methanol occurs naturally in the environment due to various biological processes in vegetation, microorganisms, and other living species (ENVIRON, 1996). However, a large release of methanol to the surface water, soil, or groundwater has the potential to adversely impact the surrounding environment.

Once released into surface waters or the subsurface environment, the fate of methanol depends on numerous environmental factors including: the nature and quantity of the release, and physical, chemical and biological characteristics of the impacted media. Various reports summarize estimates of possible methanol half-lives (the time required for 50% reduction in concentration) (see Table 1-4) in various environmental media. In the atmosphere, methanol will be photo-oxidized relatively quickly; the half-life ranges between 3 and 30 days. In soil or groundwater, rapid biodegradation is expected with the half-life ranging from 1 to 7 days. Finally, in surface water following a pure methanol spill, methanol is expected to disappear quickly; half-lives are reported between 1 and 7 days. The half lives are compared to reported half lives for benzene to illustrate the relatively rapid degradation of methanol.

TABLE 1-4
Estimated Half-Lives of Methanol and Benzene in the Environment

Environmental Medium	Methanol Half-life (days)	Benzene Half-life (days)
Soil *(Based upon unacclimated grab sample of aerobic/water suspension from groundwater aquifers)*	1- 7	5 - 16
Air *(Based on photooxidation half-life)*	3 - 30	2 - 20
Surface water *(Based upon unacclimated aqueous aerobic biodegradation)*	1 - 7	5 - 16
Groundwater *(Based upon unacclimated grab sample of aerobic/water suspension from groundwater aquifers)*	1 - 7	10 - 730

Adapted from Howard et al. (1991).

Based on data summarized in Table 1-4, regardless of the release scenario, methanol appears unlikely to accumulate in the soil, air, surface water, or groundwater. However, it is unclear whether these reported rates were developed under realistic field conditions. Consequently, these values represent generic order-of-magnitude half-lives and should be used with caution for a site-specific assessment of the fate and transport of methanol. In Section 3, these rates will be further evaluated as a function of specific hydrogeologic (subsurface), and limnologic (lake) conditions.

2.0 PARTITIONING OF METHANOL IN THE ENVIRONMENT

2.1 Methanol Partitioning Between Environmental Compartments

The purpose of this section is to describe the equilibrium partitioning of methanol between air, water, and soil phases. Partitioning is directly related to the physiochemical properties of methanol including solubility, vapor pressure and adsorptivity and the physical and chemical characteristics of the environmental compartment.

When any chemical is released to an environment consisting of more than one medium (e.g., air and water), the chemical will tend to distribute itself between these two phases, a process that has been well described by the science of chemical thermodynamics (see e.g., Thibodeaux, 1996; Schwarzenbach et al., 1993). In an enclosed system, the concentrations of the chemical in each phase can be predicted assuming that an equilibrium is achieved. In an open system, which is undergoing dynamic changes, continual transfer between phases is likely. The rate of these changes is important for predicting the fate and transport of the chemical of interest. For purposes of this analysis, however, the simple equilibrium model provides a basis for assessing the relative distribution of a compound such as methanol between environmental media.

2.2 Air/Water Partitioning

The air/water equilibrium partitioning behavior of methanol can be predicted using Henry's Law when methanol concentrations are less than 100,000 ppm (i.e., less than 10% by weight). The Henry's Law constant represents the ratio of a contaminant's concentration in the air to its concentration in the water at equilibrium. A compound with a dimensionless Henry's Law constant less than 0.05 will partition strongly from the gas phase into the water phase when contaminated air is brought into contact with clean water (Zogorski et al., 1997). The value of Henry's Law constant for methanol given in Table 3-6 is 1.09×10^{-4} [-] at 25^{o}C. Since this value is quite low, atmospheric methanol will partition into water droplets. Conversely, methanol in water bodies is likely to remain in the aqueous phase. Therefore, once in water, methanol will be difficult to remove by volatilization.

2.3 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, thus, determining the distribution of a chemical between soil and water. In addition, the K_d value can be used to estimate the rate of movement of a chemical in groundwater compared to the rate of groundwater flow. For non-ionic organic compounds such as methanol, K_d values are a function of the organic carbon content of the soil (f_{oc}) and the organic carbon based partition coefficient (K_{oc} [L/kg]). It can be shown that $K_d = K_{oc} \bullet f_{oc}$ (Schwarzenbach et al., 1993). Values of f_{oc} are site-dependent and are typically low in most subsurface environments (on the order of 0.5% or $f_{oc} = 0.005$) (Zogorski et al., 1997). K_{oc} values for methanol are low (~8) (Table 1-2) relative to values of other gasoline oxygenates (~12 for MTBE) and aromatics (~100 for benzene). Consequently, in a soil/water environment, methanol will be present primarily in the water phase.

For the listed K_{oc} values, it can be shown that retardation due to adsorption will be negligible (Wood et al., 1990; Zogorski et al., 1997). The retardation factor for methanol and other short-chain alcohols is usually one. Thus, dissolved methanol will migrate at the velocity of groundwater except in soils with organic carbon fraction greater than 10 percent (i.e., for $f_{oc} = 0.1$ the K_d is approximately 0.8 signifying nearly equivalent concentrations of methanol adsorbed on soil and dissolved in water). Consequently, methanol will generally travel through the groundwater at rates significantly higher than constituents in gasoline, including benzene, toluene, ethylbenzene, or xylenes (BTEX). However, due to rapid dissolution and biodegradation, ultimate methanol plume lengths will likely be shorter than BTEX plumes.

2.4 Methanol Dissolution

The dissolution of methanol into groundwater involves dissolution from a pure methanol pool (M100). Under this scenario, methanol is likely to leach quickly from the release area into the groundwater. For gasoline releases, 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 methanol is completely miscible in water, this relation breaks down and the concentration must be estimated based on presumed mixing conditions using a fuel/groundwater mixing ratio and a dilution factor.

Assuming that subsurface mixing ratios are between 10 and 100, the maximum range of methanol concentrations would be 0.9% to 9.1% by volume (7,000 to 70,000 ppm by mass) for a M100 release. However, these high concentrations will only occur in the immediate vicinity of pure methanol releases. Much lower concentrations are anticipated further from the source due to methanol plume dilution.

Alternatively, the concentration of methanol in the groundwater can be approximated by taking the ratio of the release flow rate and the groundwater velocity and assuming a source area width and vertical mixing ratio. For example, if methanol is released from an underground storage tank at approximately 0.5 gpm, and groundwater is moving at 1 ft/day, the source area width is 1 meter and the vertical mixing ratio is 10 to 100, the resulting methanol concentration in the groundwater will be between 70 ppm and 700 ppm. These concentrations would be much larger in the immediate vicinity of a catastrophic underground storage tank release (i.e., complete tank failure) or barge release. However, in most cases, the infinite solubility of methanol will cause methanol concentrations to rapidly decrease as a result of mixing, dispersion, and diffusion.

Poulsen et al. (1992) evaluated the rate of dissolution of methanol from a M85 into water. Poulsen et al. (1992) experimentally determined that approximately 99% of the methanol would leach into the water phase in the time required for three volumes of water, each equal to the initial gasoline volume, to move past the gasoline. They concluded that this would result in a short discrete plume.

The rate of methanol dissolution into the subsurface following a release is similar to the rate of ethanol dissolution because methanol and ethanol have similar properties. 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 due to dissolution of ethanol-blended gasolines is dependent on the concentration of ethanol in the gasoline and on mass transfer limitations in subsurface systems. Heermann showed 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 quantify the time required for dissolution but determined that it is limited by the rate of ethanol liquid molecular diffusion to the gasoline/groundwater boundary which may result in longer dissolution times (> 1 year).

In conclusion, pure methanol will quickly dissolve into the groundwater and disperse at a rate directly proportional to the velocity of the local groundwater. All of the methanol present in an M85 gasoline will likely be released into the groundwater, but the time for complete dissolution is site specific. It is unlikely that either M85 or M100 will exhibit a slow dissolution time (>1 year) because of the large quantities of methanol in contact with the water phase, methanol's infinite solubility in water, and methanol's affinity for the water relative to soil, thus, reducing the effects of diffusion-controlled dissolution. However, the time required for dissolution is highly dependent on the source area shape and the types of soils in the subsurface. Therefore, if methanol enters a low permeable soil horizon with minimal groundwater contact, dissolution could proceed slowly.

2.5 Commingling/Cosolvency Effects

Cosolvency is a chemical-phenomenon whereby one chemical dissolved in water increases the aqueous solubility of a second chemical. For example, BTEX compounds tend to be more soluble in concentrated aqueous methanol solutions than in water alone. This preferential solubility is referred to as the cosolubility effect. The possibility of enhanced aqueous solubility of BTEX due to a neat or pure methanol plume that encounters existing subsurface BTEX contamination is an issue for methanol releases from underground storage tanks at existing gasoline stations (Scenario 3) (Donbaldson et al., 1993).

The majority of studies on the effects of methanol cosolvency have focused on increased BTEX solubility within methanol/gasoline mixtures such as M85. Results show that M85 releases into the subsurface may produce high concentrations of aqueous methanol as well as elevated aqueous BTEX concentrations near the front of the plume. However, the BTEX distribution in the plume will change as a function of the aqueous/gasoline phase volume ratios (Poulsen et al., 1992; Chen et al., 1997; Beck, 1991). In 1991, the American Petroleum Institute published a study that evaluated the effect of methanol on the cosolubility of BTEX compounds for M85 (Barker, et al., 1990). API concluded that for aqueous methanol concentrations below 8.5% (v/v) (i.e., about a 10-fold dilution factor), BTEX solubility was not increased. As the concentration of methanol increased from 8% to 25%, the BTEX solubility increased linearly

TABLE 2-1
Effects of Methanol on Aqueous BTEX Solubility

Equilibrium Methanol Conc.	Observed BTEX Solubility (ppm)
8%	120
17%	174
44%	933

(Barker, et al., 1990)

with the methanol concentration. Above a 25% (v/v) concentration of methanol, the BTEX solubility increased exponentially with the methanol concentration (see Table 2-1). In conclusion, the magnitude of BTEX cosolubility is controlled by the concentration of the methanol plume at the point of BTEX/methanol plume interaction which is a function of the dilution factor (Barker, et al., 1991).

Cosolvency experimentation with M85 was also conducted at the Canadian Forces Base in Borden, Ontario. Similar to previous studies, the Borden study concluded that for methanol concentrations below 0.7% (i.e., 7,000 ppm), there was no distinguishable change in the mobility or solubility of the BTEX components. However, this study concluded that enhanced mobility will likely occur for methanol concentrations greater than 25% (i.e., 250,000 ppm) (Barker, et al, 1990; Hubbard et al., 1994). While these concentrations are unlikely in the plume area, they can be anticipated in the source area of an M100 or M85 plume with a low dilution factor.

3.0 FATE AND TRANSPORT OF METHANOL IN THE ENVIRONMENT

The chemical and physical properties of methanol are described in Section 1 and Section 2 and summarized in Table 1-3. The following three subsections discuss the fate and transport of methanol following a release, as presented in the three scenarios, namely: 1) tank truck or rail car spill to soil and/or groundwater; 2) barge spill to surface water; and 3) underground storage tank release to soil and groundwater. Each subsection further describes the sources of methanol into the respective environmental compartment and the ensuing loss mechanisms from that compartment.

3.1 Soil and/or Groundwater Release

Very few data sets are available on reported levels of methanol in aquatic systems and subsurface environments in the United States. The apparent lack of monitoring for methanol, particularly in aqueous systems, is likely a result of (1) the level of difficulty associated with methanol analysis in the water phase, (2) its short half-life due to its high biodegradation potential and (3) the lack of governmental monitoring requirements and control mandates for groundwater, surface water and drinking water (Clean Water Act, Safe Drinking Water Act).

3.1.1 Sources of Methanol in Soil and Groundwater

There are several processes related to the use of methanol as a fuel which would be directly responsible for methanol releases to soil and groundwater. The dominant sources are those discussed in Scenarios 1 and 3—release from a tank truck or rail car and release from an underground methanol storage tank. Precipitation may also serve as a transport mechanism which introduces methanol into the subsurface by infiltration through the unsaturated zone. Precipitation, however, has been shown to be a minor source of contaminant transport into the soil and groundwater for other highly water-soluble chemicals, such as MTBE, (Zogorski et al., 1997) and is therefore expected to be a minor contributing source of methanol into groundwater.

3.1.2 Losses of Methanol from Soil and Groundwater

As a result of its high solubility, low retardation factor and ease of biodegradability, the dominant mechanisms of methanol loss from subsurface soil and groundwater are expected to be biodegradation and advection (i.e., transport from the source area by groundwater flow), with little loss due to adsorption.

3.1.2.1 Biodegradation

In general, microorganisms have been shown to play a prominent role in governing the fate of fuel 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 established in the scientific literature that methanol will biodegrade readily in the subsurface under both aerobic and anaerobic conditions, three factors are required for successful methanol biodegradation: the presence of indigenous methanol-degrading microbial populations, the availability of electron acceptors and nutrients, and adequate pH and temperature levels.

3.1.2.1.1 Presence of Indigenous Methanol-Degrading Microbes

Methanol is widely produced in nature by anaerobic microorganisms responsible for complex aromatic hydrocarbon biodegradation (Heijthuijsen and Hansen, 1990; Oremland et al., 1982). As a result, methanol molecules are ubiquitous in nature. Furthermore, due to methanol's high solubility in water, methanol molecules are bioavailable to microorganisms which can utilize them as a source of carbon and energy. A wide distribution of methanol-degraders in the environment can therefore be expected (Brock and Madigan, 1991).

Systematics of methanol oxidation: Methylotrophs, organisms that can grow using only one-carbon compounds such as methanol, are known to use both methane and methanol as their sole carbon and energy source under both aerobic and microaerobic (low oxygen) conditions (Brock and Madigan, 1991). Methylotrophs are of commercial interest in the bacterial metabolism of C_1 compounds (Heijthuijsen and Hansen, 1990; Komagata, 1990). Consequently, a large number of methanol-utilizing bacteria have been isolated from a wide variety of natural sources, and most of these isolates have been identified as aerobic, Gram-negative bacteria (Komagata, 1990).

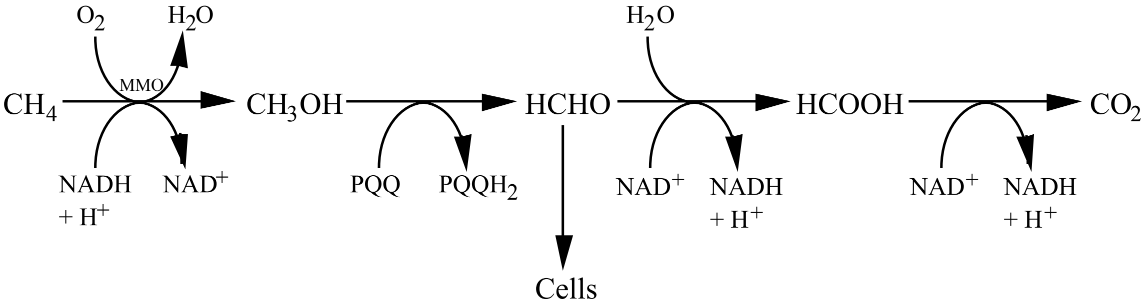

Figure 3-1. Methane oxidation pathway of methanotrophic microorganisms. Adapted from (Chang, 1995).

Methanol is also an intermediate of the methane oxidation pathway used by methanotrophic organisms (see Figure 3-1); methanotrophs are ubiquitous in nature. Methanotrophs oxidize methane to methanol by the enzyme methane monooxygenase. Methanol is then oxidized to formaldehyde by methanol dehydrogenase (Lehninger et al., 1993; Smeraldi et al., 1994) which is then assimilated into cell material by the activity of either of two pathways, one involving the formation of the amino acid serine and the other proceeding through the synthesis of sugars (Prescott et al. 1996).

Table 3-1
Selected types of aerobic and anaerobic respiration involved in microbial metabolism of organic matter

Process	**Electron Acceptor**	**Metabolic Products**	**Relative Potential Energy**
Aerobic Respiration	O_2	CO_2, H_2O	High
Denitrification	NO^{3}-	CO_2, N_2	
Iron reduction	Fe^{3+}	CO_2, Fe^{2+}	
Sulfate reduction	SO_4^{2-}	CO_2, H_2S	
Methanogenesis	CO_2	CO_2, CH_4	Low

Taken from Suflita and Sewell (1991)

3.1.2.1.2 Availability of Electron Acceptors

Microorganisms obtain energy by transferring electrons from electron donors (in this case, methanol) to electron acceptors. Electron acceptors are compounds that have a lower oxidization state than electron donors and 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 (i.e., the use of oxygen as the electron acceptor) (see Table 3-1).

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

Methanol biodegradation has been shown to take place under both aerobic (oxygen as the electron acceptor) and anaerobic (all electron acceptors besides oxygen) conditions. The aerobic biodegradation of methanol is the most energetically favored mechanism for methanol-degraders and leads to the mineralization of methanol.

Microbial growth on methanol with nitrate as the electron acceptor by facultatively anaerobic nitrate-reducing bacteria is the second most energetically favored mode of methanol metabolism (Metcalf and Eddy, Inc., 1979). There are over 100 wastewater treatment plants in the United States that currently use methanol as a carbon source to remove nitrate (NO_3^-) from water by anaerobic denitrification. Other modes of anaerobic biodegradation of methanol have been studied extensively, resulting in the identification of at least 11 species of methanogenic bacteria that can grow on methanol (Brock and Madigan, 1991).

Other types of anaerobic metabolism include acidogenesis (resulting in the production of acetate or butyrate) (Florencio et al., 1995) and sulfidogenesis (Heijthuijsen and Hansen, 1990). The ability of sulfate-reducing bacteria to oxidize methanol was rarely reported in early studies (Esnault et al., 1988; Ward and Winfrey, 1985). However, in the past few years, evidence has accumulated which suggests that sulfate-reducing bacteria are involved in anaerobic degradation of methanol in sediments, particularly in marine environments. Sulfidogenic methanol-utilizing microorganisms have been shown to oxidize methanol by reducing sulfate to hydrogen sulfide (Heijthuijsen and Hansen, 1990). Finally, some methanol-degrading strains have been shown to utilize hydrogen (Heijthuijsen and Hansen, 1990).

3.1.2.1.3 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 ppm range (Tiedje, 1993). As stated previously, for M100 releases into the subsurface, methanol concentrations will often exceed 1 ppm, resulting in potentially nutrient-limited conditions. However, as methanol is advected away from the source area, concentrations will decrease and microbial activity is not likely to be nutrient-limited.

3.1.2.1.4 Adequate pH and Temperature Levels

Most microorganisms grow best in a relatively narrow pH range around neutrality (6 to 8) (LaGrega et al., 1994). The characteristic range of pH's found in groundwater systems (5 to 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 range of pH values in aquifers is unlikely to pose a significant problem for the biodegradation of methanol by indigenous subsurface microorganisms since most of the methanol-utilizing bacteria which have been isolated from natural sources have been shown to grow in the neutral pH range (Komagata, 1990). Even if the pH of groundwater were to deviate significantly from the neutral pH range, some strains of methanol-utilizing microorganisms have been shown to prefer acidic pH values ranging from 2.0 to 5.5, while others have been shown to prefer alkaline pH values of 7.0 to 9.5 (Komagata, 1990).

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 maximized. Most of the bacteria present in subsurface environments operate most effectively between a temperature range of 20°C to 40°C. This is the range of many natural environments (Chapelle, 1992) since subsurface temperatures within 100 meters of the surface are typically within 2°C of the mean annual surface temperature. Temperature should therefore not pose a significant problem for the biodegradation of methanol by indigenous subsurface microorganisms even at temperatures as lows as 10°C.

3.1.2.1.5 Reports of Methanol Biodegradation Under Various Redox Conditions

Simple alcohols such as methanol and ethanol can be degraded in both aerobic and anaerobic environments at rates much faster than gasoline components, such as benzene (see Table 3-2). It is important to note in Table 3-2 the difference between laboratory-derived and field-derived degradation rates. Laboratory rates are often higher (an order of magnitude or more) than field-derived rates due to a combination of elevated laboratory temperature and a larger microbial density in the laboratory growth medium. For example, note that all the reported benzene rates are laboratory-derived and, thus, likely represent faster degradation rates than would be observed in the field.

Table 3-2
Comparative Rate Constants for Anaerobic and Aerobic Degradation

	Anaerobic Pseudo First Order Rate Constant		**Aerobic Pseudo First Order Rate Constant**
Compound	**Electron Acceptor**	**Range of Rates (day^{-1})**	**Range of Rates (day^{-1})**
Ethanol	NO_3^-	0.53 (1)(11)	0.23 (1) (11)
	Fe^{3+}	0.17 (1) (11)	0.35 (1) (11)
	SO_4^{-2}	0.1 (1) (11)	
Methanol	NO_3^-	0.0051-0.88 (3) (11)	0.019 (4) (12)
	SO_4^{-2}	0.016-0.34 (3) (11)	0.011 (10) (12)
	Anaerobic	0.0059-0.017 (7) (11)	
	Methanogenic	0.030 (8) (11), 0.35 (9) (11)	
Benzene	NO_3^-	0.0095-0.045 (3) (11)	0.043 (5) (11)
	Fe^{3+}	0.0065-0.024 (3) (11)	0.14 (5) (11)
	SO_4^{-2}	0.0022-0.047 (3) (11)	
	Methanogenic	0.0039-0.052 (3) (11)	
	General	0.0062-0.00096 (5) (13)	

1) Estimated from Corseuil and Alvarez 1996b; Corseuil et al. 1996c and 1998; 2) Suflita et. al., 1993; 3) Aronson et. al., 1997; 4) Hubbard et al, 1994; 5) Rathbun, 1998; 6) Barker et. al., 1998; 7) Novak et. al., 1985; 8) Bagley and Gossett, 1995; 9) Florencia et al., 1995; 10) Barker et al., 1990; 11) Determined in a laboratory; 12) Determined from field data; 13) Estimated from first principles.

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 et al, 1997a,b). High concentrations of methanol may occur near pure methanol spills and may inhibit microbial activity near the source; however, these concentrations will become more dilute with time and with increasing distance from the source (Katsumata and Kastenburg, 1996).

The biodegradation of methanol has been measured both in the field and in laboratory studies. In an extensive field study at the CFB Borden site in Canada, the fate and persistence of an M85 fuel was investigated in an aerobic shallow sandy aquifer (Barker et al., 1990). The average concentration of methanol introduced into the aquifer was 7030 ppm. By day 476 of the experiment, about 99% of the methanol was degraded (see Table 3-2 for the effective first order degradation rate). Insufficient oxygen was present in the plume to account for the removal of all the methanol; the researchers therefore concluded that the methanol degraded first aerobically then anaerobically (Hubbard et al., 1994).

In a laboratory study, methanol biodegradation was investigated in soils from three different subsurface sites under various redox conditions (Novak et al., 1985). The first site was aerobic and also had high nitrate levels; the second site was anoxic and had low nitrate but high sulfate concentrations; and the third site was anoxic and had low nitrate and sulfate levels. Rapid biodegradation took place in the microcosms at the first site from both the saturated (4.19 to 4.55 ppm/day) and unsaturated zones (4.44 to 5.15 ppm/day) although the amount of methanol added was sufficient to create anaerobic conditions. Rapid methanol biodegradation was also observed in the microcosms from the saturated zone of the second site (1.33 to 3.18 ppm/day) and the third sites (1.0 to 2 ppm/day). This study concluded that methanol concentrations up to 1,000 ppm were removed in less than a year at temperatures of 10 to 11°C and at pH range of 4.5 to 7.8. Methanol was found to be readily biodegradable in all subsurface soils examined, with biodegradation proceeding more rapidly in the saturated region. This research suggests that methanol contamination in groundwater is unlikely to persist for lengthy periods of time because of its susceptibility to biodegradation under both aerobic and anaerobic conditions.

In another laboratory study, Suflita and Mormile (1993) measured acclimation periods (periods before degradation proceeded) and biodegradation rates of methanol and various other alcohols and fuel oxygenates in anaerobic aquifer slurries at organic concentrations of 50 ppm. These researchers reported a methanol acclimation period of 5 days, the shortest among the alcohols tested (the other alcohols being ethanol, 2-propanol and tert-butanol), as well as an anaerobic methanol biodegradation rate of 7.4 ± 0.7 ppm/day. In a later study, these researchers investigated methanol biodegradation under a range of redox conditions (Mormile et al., 1994). Under nitrate reducing conditions, methanol was degraded with stoichiometric amounts of nitrate consumed. However, under sulfate reducing conditions the researchers concluded that the sulfate reducing bacteria were not utilizing the methanol. Generally speaking, high concentrations of methanol are not used by sulfate-reducing bacteria to an ecologically significant extent. However, sulfate reducers have been found to contribute to methanol depletion in other studies, and at least four species of sulfate-reducing bacteria have been isolated that can utilize methanol (Nanninga and Gottschal, 1986; Esnault et al., 1988).

Other laboratory studies have reported the biodegradation of methanol under various redox conditions and by microorganisms from diverse environments. For example, the methanogenic degradation of methanol was demonstrated for an enrichment culture derived from an anaerobic digester as well as for a pure culture. The rates of methanol degradation by the enrichment and pure cultures without acclimation periods were reported to be 1.92 and 1.37 ppm/minute (extrapolated from Figures 2 and 6B, respectively) (Bagley and Gossett, 1995). Fitch et al. (1996) also grew methanol-utilizing cultures in a chemostat culture at methanol concentrations of 1500 to 2700 ppm and found the cell yield of methanol-grown cells to be consistent with what has previously been reported for methanotrophs. Florencio et al. (1993) investigated the anaerobic biodegradation of methanol at a range of pH values by a culture derived from an anaerobic granular sludge reactor used to treat alcohol distillery wastewater. Florencio et al. (1995) monitored the anaerobic removal of methanol by methanogens and acetogens in upflow anaerobic sludge blanket reactors. Results from these studies showed that methylotrophic methanogens dominated in a broad pH range (4.2 to 7.2) while significant acetogenesis occurred in the presence of high methanol concentrations. Finally, Beeman and Suflita (1987) measured methanol biodegradation in microcosms from a shallow anoxic aquifer underlying a municipal landfill in Oklahoma. By recovering 70 to 100% of the methane produced during methanogenesis, they were able to demonstrate that methanogenesis of methanol was occurring.

3.1.2.2 Adsorption

Another methanol loss mechanism from the groundwater is adsorption to soil materials. However, adsorption will not contribute significantly to the loss of methanol from the environment due to the rapid rates of biodegradation in soil and groundwater and vaporization from dry soils. Little adsorption is expected for compounds such as methanol because of its polarity, low K_D values, and miscibility as discussed previously.

3.1.2.3 Volatilization from Groundwater and Vaporization from Soil

Methanol's high solubility and low Henry's constant are expected to result in minimal methanol losses from groundwater due to volatilization or off-gassing. However, in the soil, methanol will vaporize from the residual phase or source area under low soil moisture conditions (ENVIRON, 1996). Vaporization will occur much quicker for M100 fuels than conventional gasoline due to the high vapor pressure of methanol. This may result in migration of methanol away from the source area due to vapor phase, diffusion driven transport. Despite the potential for lateral distribution of methanol in the subsurface, analytical soil samples often do not contain detectable levels of methanol near an M85 spill. This is likely due to the mass loss from vapor phase microbial degradation of methanol (Beck, 1991).

3.2 Surface Water

3.2.1 Sources of Methanol in Surface Water

The potential dominant source of methanol in surface water is the direct release of neat methanol into a surface water body following accidental release or catastrophic failure during transport, such as is outlined in Scenario 2. Nonpoint sources of methanol include precipitation from the atmosphere, which is not expected to be significant, as noted earlier.

3.2.2 Losses of Methanol in Surface Water

The processes that contribute to methanol losses from surface water bodies include biodegradation, abiotic degradation, volatilization and bioaccumulation. As with groundwater, the dominant loss mechanism in surface waters is expected to be biodegradation. Methanol concentrations in the vicinity of a surface water release will rapidly decrease due to advection, dispersion, and diffusion. Due to methanol's infinite solubility in water, an M100 release in open water, as discussed in Scenario 2, will disperse to non-toxic levels (< 1%) at a rate much faster than a parallel gasoline release. The rate of dispersion is directly proportional to the amount of mixing in the aquatic environment. Tidal flows combined with wind-induced wave action will cause a large methanol spill to rapidly disperse to levels below toxic thresholds. The effect of wave action on the speed of contaminant mixing in surface waters has been measured extensively for gasoline components following release from recreational vehicles (Malcolm Pirnie, 1998). In all cases measured, gasoline components quickly mixed throughout the upper layer of the surface water bodies; methanol is even more soluble in water than most gasoline components and will, consequently, mix even more rapidly.

To verify these predictions, several computer simulations were done to model the advective dispersion of methanol away from a source area (Machiele, 1989). The first hypothetical simulation revealed that a 10,000 ton methanol release in the open sea would reach a concentration of 0.36% within an hour of the spill. The second hypothetical simulation of a spill at a rate of 10,000 liters/hr from a coastal pier exhibited a concentration of less than 1 percent at the spill site within 2 hours and to 0.13 percent within 3 hours after the spill ceased.

3.2.2.1 Biodegradation

The dominant process responsible for removal of methanol in surface water bodies is biodegradation. The reported half-life of methanol in surface waters under aerobic conditions is short and has been reported to be as low as 24 hours (see Table 3-2) (Howard et al., 1991).

In flowing water bodies, wind- or current-enhanced mixing maintains dissolved oxygen concentrations at a level sufficient to support aerobic microbial processes. 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 methanol biodegradation under anaerobic conditions ranges from 1 to 5 days (Howard et al., 1991). Additionally, the nutrient supply in rivers and lakes is generally not expected to restrict the rate of methanol metabolism because the required nutrient supplies are constantly recharged by runoff (Alexander, 1994). However, high concentrations of methanol resulting from a large spill in an enclosed area will deplete the surface water of oxygen required to sustain aquatic life.

3.2.2.2 Abiotic Degradation

Abiotic degradation (i.e., non-biological or chemical) reactions are not likely to contribute significantly to methanol removal from surface water bodies. Hydrolysis reactions usually transform compounds into more polar products; methanol is a very polar molecule and is stable in water. Photolysis involves the transformation of a compound as a consequence of its direct absorption of light. Methanol does not adsorb light in the visible spectrum and long wavelength UV. It does adsorb very short wavelength UV, which is present in negligible amounts in solar radiation. In addition, methanol can be naturally oxidized by hydroxyl radicals formed in the water by the photolysis of nitrate, nitrite, and hydrogen peroxide resulting from reactions with excited humic materials or from the reaction of H_2O_2 with Fe(II) (Schwarzenbach et al., 1993). Thus, naturally occurring photooxidation of methanol via direct or indirect oxidation is possible; however, these reactions are slow and, thus, not expected to be significant in surface waters.

3.2.2.3 Bioaccumulation

The bioaccumulation of fuel hydrocarbons and certain additives has been studied extensively (e.g. Brault et al., 1994). As shown by various studies, uptake and elimination of organic pollutants in freshwater fish and invertebrates may occur through gill membranes, the efficiency of which depends on blood proteins and the hydrophobicity of the compounds. Bioaccumulation in aquatic organisms is expressed by bioconcentration factors, BCF (Streit, 1994). To our knowledge, no studies have been reported for methanol bioaccumulation. However, octanol-water coefficients (K_{ow}) and bioconcentration factors for methanol and other oxygenates have been reported (see Table 3-3). Octanol-water coefficients may be used as an indicator for bioaccumulation potential and are widely used as a descriptor of hydrophobicity (Mackay et al., 1992). In conclusion, methanol is expected to bioaccumulate slightly less than ethanol, and significantly less than benzene and most other more hydrophobic constituents in gasoline. Regardless, small quantities of methanol introduced into mammals as a result of bioaccumulation from methanol fuel releases can be rapidly metabolized, negating any long term effect.

Table 3-3
Comparative values of octanol-water coefficients and bioconcentration factors

Compound	Log K_{ow}	Log BCF
Methanol	-0.82 (1)	-2.09 (1)
	-0.77 (1)	
	-0.16 (2)	
	-0.31 (2)	
Ethanol	-0.32 (1)	-1.63 (1)
	-0.31 (1)	
	-0.75 (2)	
Benzene	2.13 (2)	6.8 (3)
	1.56 - 2.15 (2)	

(1) Mackay et al., 1992; (2) Zogorski et al., 1997; (3) RSP, 1994

3.2.2.4 Volatilization

Volatilization is not a primary source of loss for methanol since methanol has a low air/water partition coefficient and the rate of biodegradation most likely exceeds the rate of volatilization. In the environment, methanol has similar properties to ethanol and, therefore, the volatilization rate of ethanol from surface waters can be used to describe the relative volatilization rate of methanol. In a recent study, the volatilization rates for several oxygenates and gasoline constituents were calculated based on their chemical properties for various lake conditions (Malcolm Pirnie, 1998). 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 BTEX compounds. Under these conditions and ignoring biotic reactions, benzene has a half-life of approximately 9 days; whereas, ethanol has a half-life of approximately 40 days. Using the model and the conditions discussed above, methanol has a predicted half-life of approximately 60 days. In another evaluation, the half-life of methanol in a river and a pond were modeled to be approximately 4.8 days and 51.7 days, respectively; however, this model included other transport mechanisms besides volatilization (USEPA OPPT, 1994). In conclusion, despite the slow volatilization and minimal adsorption, methanol will not persist in surface waters due to its intrinsic tendency to be degraded quickly.

3.3 Methanol / BTEX Commingled Plumes

BTEX compounds are the most toxic group of hydrocarbons in gasoline. Naturally occurring biodegradation controls the persistence of these compounds in the subsurface environment. High concentrations of alcohols and ether oxygenates can potentially impede the biodegradation of BTEX (Salanitro, 1993). Alcohols will be biodegraded in preference to BTEX and can therefore consume the oxygen required for BTEX biodegradation. Alcohols can also be toxic or inhibitory to subsurface populations of BTEX-degraders at elevated concentrations (Barker et al, 1990).

Information on the effect of methanol on the biodegradation of BTEX in the field is available from the Borden site study in Canada. Three gasolines (M85, 15% MTBE, and base gasoline) were allowed to migrate in an aquifer (Barker et al., 1990). By day 476 most of the methanol was degraded, but BTEX compounds in the methanol plume were at higher relative concentrations than in the MTBE and non-oxygenated plumes. These data suggest that methanol may have slowed BTEX biodegradation rates compared to BTEX biodegradation in MTBE-containing and oxygenate-free groundwater. Laboratory experiments found no significant biodegradation of BTEX in the presence of 7000 ppm methanol but some BTEX biodegradation was noted when the methanol concentration was only 1000 ppm. It was concluded that the mechanism for greater BTEX persistence in the presence of methanol is the initial inhibition of BTEX biodegradation by toxic methanol concentrations followed by inhibition due to the removal of oxygen by preferred methanol biodegradation. Such results are particularly important in assessing the fate of benzene, a known carcinogen (Dean, 1985) and the most recalcitrant monoaromatic under anaerobic conditions.

In another laboratory microcosm study, the biodegradation of BTEX was reportedly impaired at 1.4% (14,000 ppm) methanol and was completely inhibited at higher methanol levels (Novak et al., 1985). In conclusion, the biodegradation rate of BTEX compounds in a gasoline plume that has become commingled with a methanol plume (Scenario 3) could be significantly retarded in the presence of high methanol concentrations. This reduction in BTEX biodegradation could effectively increase the length of BTEX plumes. A complete evaluation of this effective plume elongation has not been completed for this evaluation, but is likely to be a function of the distance between the methanol leaking UST (LUST) and the petroleum LUST and the placement of the two USTs relative to groundwater movement.

3.4 Conclusions

Applying the hazard assessment guidelines from USEPA's Office of Pollution Prevention and Toxics, a recent study concluded that methanol is not persistent in the environment because it readily degrades in air, soil and water, and has no persistent degradation intermediates (ENVIRON, 1996). In the event of a catastrophic methanol spill, methanol will rapidly dilute to low concentrations (< 1%) and subsequently quickly biodegrade. If clean-up measures are implemented, they must be instituted at a much faster pace compared to petroleum spills in order to capture the methanol plume prior to significant dilution. However, the relative speed of methanol's biodegradation is expected to result in natural cleanup times that are faster than the active cleanup times for methanol or gasoline releases.

4.1 Purpose and Background of Additives

Methanol is a demonstrated alternative to gasoline and other fossil-based fuels; however, most evaluations of potential environmental impacts due to releases of methanol have focused primarily on fate of methanol and circumvented any potential ancillary impacts. Similar to other fuels, methanol may require the use of additives to address performance, pollution, or health issues.

Although it is currently unknown whether additives will be required for wide-spread use of methanol fuel, several potential safety concerns regarding methanol use as a fuel source have been identified based on its chemical and physical properties. Several investigations, conducted in the eighties and early nineties, identified the known safety, health, and environmental issues associated with methanol and developed a list of potential additives to address these concerns (Machiele, 1989, 1990). Manufacturers are currently focusing their additive investigation and testing efforts on luminosity (the ability to see a burning flame), taste (to prevent ingestion), and color. Investigation efforts focus on evaluating the need for these additives, identifying the most suitable compound, determining their impact on fuel cell efficiency, if any, and documenting their effectiveness at addressing certain human health and safety issues. Therefore, it is useful to evaluate the physical characteristics of the additives themselves and how these additives could impact soil, air, or groundwater following a methanol fuel release.

4.2 Fate and Transport of Three Known Additives

This section provides a brief summary of the fate and transport of the leading candidate compounds for additives and the potential environmental impacts of these compounds if released into the environment.

4.2.1 Luminosity

Several types of compounds have been identified to increase the luminosity of methanol, including: hydrocarbon mixtures, aromatics, aliphatics, olefins, other alcohols, ethers, metal organic salts, and alcohol soluble organic dyes. In tests conducted by Southwest Research Institute and California Air Resources Board (Fanick, 1990), toluene (>4% volume) and two proprietary alcohol-soluble solids (MO and AO) provided the most promising results. For example, by varying the toluene content from 4% to 10%, the luminosity increases 10 to 100 times. Select chemical and physical properties of these potential luminosity additives are presented in Table 4-1.

In general, the fate and transport of toluene and hexane is well understood based on their physiochemical properties. They have a relatively high vapor pressure, are readily biodegraded under aerobic conditions, and exhibit more retardation than methanol due to their lower solubility and higher soil partition coefficient. Given the proprietary nature of MO and AO, the potential fate and transport characteristics of these compounds could not be evaluated.

Table 4-1
Select Chemical and Physical and Properties of Potential Luminosity Additives

Parameter	AO/ MO	Toluene	Hexane
Chemical Name	PROP	phenyl methane	n-Hexane, dipropyl
Molecular Formula	PROP	C_7H_8	C_6H_{14}
Molecular Weight (g/mol)	PROP	92.14	86.18
Specific Gravity	PROP	0.867	0.6548
Boiling Point (^oC)	PROP	110.6	-95
log Kow (-)	PROP	2.73	4.11
Henry's Constant (-)	PROP	0.272	0.130
Solubility (water) (mg/L @ 20 ^oC)	PROP	526	9.47
Vapor Pressure (atm)	PROP	26.31	4.89
Appearance	PROP	colorless, liquid w/ aromatic odor	

Note: UNK - Unknown or not available information
PROP - Proprietary materials, chemical data not available.

4.2.2 Taste

Studies conducted by Lawless and Hammer (Lawless, 1983) demonstrated that addition of a bitterant reduces accidental ingestion of a product. Another study, conducted by C. Bering, J. Griffiths and J. Wild in the early 1980s (Bering et al., 1982), concluded that the average volume of liquids containing a bitterant, that would be ingested is less than one teaspoon. The potential health concerns at elevated levels of methanol has prompted the consideration of bitterants to prevent ingestion of methanol containing fuels.

A possible bitterant candidate is Denatonium Benzoate, or Bitrex, which has become a widely used defensive measure to prevent ingestion of products from several industries, including:

Alcohol: Denatured alcohols

Medical Products: Medical wipes, nail-biting deterrents, rubbing alcohol

Agricultural Products: pesticides, plant nutrients

Automotive Products: Anti-Freeze, brake fluid, polishes

Household Products: Cleaners, disinfectants

Bitrex can be detected at 10 ppb and is noticeably bitter at concentrations greater than 50 ppb. Common applications of Bitrex range from 6 ppm up to 100 ppm. Anonymous research disclosures indicate that concentrations as low as 1 ppm Bitrex reduced ingestion of detergent by children by over 75%. The appropriate quantity of Bitrex is case-specific and is dependent upon the viscosity and existing taste of each product. Preliminary estimates indicate that 10 ppm of Bitrex by volume in M100 would be sufficient to prevent ingestion of methanol. Select chemical and physical properties for Bitrex are listed in Table 4-2 below.

Table 4-2
Select Chemical and Physical and Properties of Bitterant Additives

Parameter	**Bitrex/ Denatonium Benzoate**
Molecular Formula	$C_{28}H_{34}N_2O_3$
Molecular Weight (g/mol)	446.5
Specific Gravity	1.12
Boiling Point	UNK
log Kow (-)	0.9
Henry's Constant	UNK
Solubility (water) (mg/L @ 20 °C)	45,000
Solubility (methanol) (mg/L @ 20 °C)	690,000
Vapor Pressure (atm)	UNK
Appearance	white granules

Note: UNK - Unknown or not available information
Source: MSDS, Macfarlan Smith Data Sheet

According to Material Safety Data Sheets and Bitrex Information Sheets provided by the Macfarlan Smith distributor, Bitrex is generally stable at neutral pH values for up to two years (Bitrex, 1998). Although no transformation of Bitrex has been observed in acidic conditions, under alkaline conditions it is converted to an hydroxide salt. Chemical or physical variations will not affect the performance of Bitrex since the bitter quality is imparted by the denatonium cation which remains in solution.

The solubility of Bitrex in solvents such as methanol and water can be attributed to its polarity; conversely Bitrex is relatively insoluble in petroleum based solvents. The solubility and octanol-water partition coefficient of Bitrex indicate that it would be less soluble in water than methanol. The fate and transport of Bitrex in the environment, specifically, the biodegradability, retardation, and bioaccumulation is not well understood. However, the manufacturers of Bitrex report a biodegradation half life, derived under laboratory conditions and temperature of about 20°C, of approximately 45 days (Bitrex, 1998).

4.2.3 Colorant

Methanol is a relatively colorless liquid compared with gasoline which has an orange hue. To visually distinguish methanol from gasoline and other liquids, colorant additives may be required for its wide-spread use.

Studies conducted in 1994 by Japanese researchers have identified a food additive, Acid Blue 9 that would apparently provide an adequate, identifiable color to methanol at a concentration of 1 ppm (Yutaka and Kasamatsu, 1998). The studies evaluated twenty-three (23) dyes to distinguish neat methanol from other liquids and to minimize the potential performance impacts of adding dyes to methanol. Dyes were evaluated based on tests for health impacts, quality deterioration, performance impacts and economic factors including cost and availability (Yutaka and Kasamatsu, 1998).

Table 4-3
Select Chemical and Physical and Properties of Colorant Additives

Parameter	Acid Blue 9
Chemical Class	Triphenyl-methane (Non-halogenated)
Molecular Formula	$C_{37}H_{43}N_4O_9 S_3Na_2$
Molecular Weight (g/mol)	829.72
Specific Gravity	UNK
Boiling Point	UNK
log Kow (-)	0.9
Henry's Constant	UNK
Solubility (water) (mg/L @ 20 °C)	miscible in water
Solubility (methanol) (mg/L @ 20 °C)	UNK
Vapor Pressure (atm)	UNK
Appearance	Bright greenish blue

Note: UNK - Unknown or not available information

Acid Blue 9 is typically used as a non-toxic food dye. It is also relatively inert and does not cause chemical reactions with other materials. However, the reactivity of Acid Blue 9 within a fuel cell vehicle has not been tested. Specific chemical and physical parameters for Acid Blue 9 are not available. However, some general characteristics were drawn from the evaluation report (see Table 4-3).

Based on the limited chemical and physical compound information available, the actual fate and transport of Acid Blue 9 could not be evaluated.

4.3 Conclusion

There are several potential additives that may be used in methanol fuel, however, the fate and transport of these additives in the environment is not well understood. This is primarily a result of the proprietary nature of these additives and their complex chemical structure. Based on the projected widespread usage of methanol in the future and the possible widespread usage of these or other additives, a detailed evaluation of the fate and transport of potential additives is warranted.

5.1 Remediation of Methanol

Following a release of methanol to the subsurface as a result of the release scenarios discussed in Section 1, remediation may be required if the spill is in a high-risk area (i.e., potential receptors are nearby). Methanol will quickly biodegrade as discussed in Section 3 and, therefore, natural attenuation is likely to be an effective and inexpensive remediation strategy in most soil, groundwater, and surface water scenarios. However, if a methanol plume becomes commingled with a gasoline plume, rapid biodegradation of methanol may deplete the surrounding soil and groundwater of electron acceptors and nutrients required for the biodegradation of gasoline. Therefore, a successful natural attenuation strategy for all contaminating constituents may require that the natural environment be enhanced with the addition of oxygen, nutrients, or other amendments to facilitate biodegradation of other gasoline constituents.

If methanol is released to a subsurface environment with low microbial activity and/or deep groundwater, there may not be sufficient microbial activity to completely degrade the released methanol. Consequently, an alternative remediation strategy is required. Under such circumstances, the high vapor pressure of methanol suggests that soil vapor extraction will effectively remove residual methanol from the soil. Once extracted from the subsurface, the methanol vapors can be biodegraded using vapor phase biofilters. In summary, the remediation of methanol from soil and groundwater is not expected to pose insurmountable technical challenges due to it tendency to quickly biodegrade.

5.2 Impetus for Drinking Water Treatment

While it is unlikely that elevated levels of methanol will persist in groundwater due to the rapid rate of biodegradation, neat methanol releases near drinking water supply wells could impact a water supply source. Unlike certain gasoline additives, the taste and odor threshold concentration for methanol is high, ranging from 10 ppm to 20,000 ppm in air (USEPA, 1994a). Alternatively, in order for any toxic symptoms to occur, drinking water concentrations would have to exceed roughly 9,200 ppm (Machiele, 1989). Based on the groundwater measurements that have been obtained, and an estimated ‘worst-case scenario’ model for methanol release into groundwater, it is highly unlikely that methanol concentrations will exceed the toxicity level in drinking water supply wells, assuming the methanol source is a sufficient distance from the supply well. Similarly, the U.S. Department of Energy released a report which refers to the unlikely possibility of toxic contamination (defined as concentrations greater than 1,000 ppm) in drinking water. (USDOE, 1991).

Regardless, it is likely that drinking water sources containing elevated levels of methanol 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 filters. Each of these treatment technologies is discussed briefly below.

5.3 Air Stripping

The effectiveness of air stripping for removing a contaminant from water is a direct function of that contaminants 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 ($20^{o}C$) are not amenable to removal by air stripping (Roberts, 1995). Consequently, conventional air stripping can not be used to remove methanol (H[-] <0.00011) from drinking water. However, increases in the water temperature will increase the Henry's constant, which will allow use of stripping for removing methanol. This process, known as steam stripping has been used to remove alcohols from industrial waste waters, and could conceivable be used to remove methanol from drinking water. However, high costs (>$5.00/1,000 gallons) are required to raise the temperature of water from $10^{o}C$ to $40^{o}C$ which will likely limit the acceptability and feasibility of this technology for removal of methanol from drinking water.

5.4 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, methanol has a very low soil/water partition coefficient due to its high polarity and, hence, solubility. Therefore, methanol will not adsorb strongly to granular activated carbon (GAC) or other adsorbents when present in water. The ineffectiveness of adsorption is also demonstrated by noting the magnitude of the Freundlich isotherm constants for methanol. While it was not possible to locate any isotherms for methanol, isotherms for ethanol and acetone are likely surrogates for methanol's adsorptivity. The Freundlich isotherm constants for ethanol and acetone range from 0.0 to 14 [mg/g(L/mg)^1/n] (Crittenden et al., 1997). Compared to benzene which adsorbs relatively well (isotherm constant range from ~20 to 117 [mg/g(L/mg)^1/n]), ethanol and acetone have a very small equilibrium adsorption coefficient (Crittenden et al., 1997). Thus, adsorption processes, such as GAC have limited application for methanol removal from water.

5.5 Advanced Oxidation

The factors that control the effectiveness of advanced oxidation for removing contaminants from water include type of oxidation process, the water quality, contact time, and contaminant oxidation potential. Advanced oxidation treatment becomes most competitive for chemicals, such as methanol, that neither readily volatilize from water ($H < 0.005$ [-]) nor are easily adsorbed onto carbon. Calgon, a major vendor of advanced oxidation processes (AOP) verified that methanol treatment in drinking water is achievable, but electrical energy consumption per order of magnitude methanol reduction (EE/O) values and, thus, feasibility will vary according to influent concentrations and water quality (Reko, 1998). This vendor stated that if influent concentrations of methanol are 100 ppm, 1,000 ppm, and 10,000 ppm, the corresponding EE/Os will be 20, 100, and 500, respectively. These EE/O values imply that 20 kilowatt hours are required to lower methanol from 100 ppm to 10 ppm for every 1000 gallons of treated water, or an energy cost of approximately $2/1000 gallons. Actual costs are potentially lower than this because methanol levels in water supply sources will likely not exceed 10 ppm.

Compared to MTBE treatment, methanol treatment will require twice as much electricity, which results in higher treatment costs. Unit costs also rise with a decrease in system size. In a recent study by Malcolm Pirnie on treatment costs associated with removal of MTBE from drinking water, the cost to remove MTBE from drinking water may be as low as $0.50/1,000 gallons for a large scale treatment system (6,000 gpm) and as high as $1.50/1,000 gallon for a smaller scale treatment system (60 gpm). It is also possible, and in some cases more feasible, to combine UV/oxidation technology with other treatment technologies (particularly biological treatment), as a finishing process to treat the last 5-10% of methanol contamination. Finally, AOP technologies can cause oxidation by-product formation which must be considered on a site specific basis. Thus, the suitability of AOP for removal of methanol requires site specific pilot studies to resolve treatment cost and by-product formation issues.

5.6 Membranes

Reverse osmosis or nanofiltration membranes can be used to remove some organic compounds from water. These processes remove organic molecules by size exclusion. However, because methanol is similar to water in its small size and low molecular weight, membranes will not typically be effective. A major vendor of reverse osmosis membranes reports that methanol removal using this technology will likely be less then 20%. Comparatively, they stated that larger alcohols such as isopropyl alcohol (with five carbon atoms) can be removed by membranes up to levels of 98%.

5.7 Biological Treatment (Biologically Activated Filters)

Methanol in drinking water supplies can be treated effectively through biological treatment. The type of technology used depends on the anticipated influent concentrations. For influent methanol levels of 1 ppm, a slow sand filter should provide the required microbial activity for successful treatment for drinking water. Higher influent levels (on the order of 100 - 1000 ppm) would require treatment in a biologically activated filter (BAF) with counter air flow. Design of a BAF for methanol treatment would require pilot studies to determine the optimum design capacity and appropriate operating conditions for the desired methanol removal efficiency.

In 1997, the University of Colorado at Boulder completed a pilot project for removal of nitrate in a biological process that utilizes indigenous bacteria (Scott, 1997). The pilot plant consists of towers containing layers of bacteria that reduce the nitrates to nitrogen. The simple, low maintenance system produced an effluent which met the federal and state drinking water standards for nitrate. Methanol could also be removed in a similar process.

Upton et al. (1993) evaluated a wastewater treatment process which combines a tertiary solids removal sand filter with denitrification. Methanol was used as the carbon source required for growth and cell metabolism of the heterotrophic bacteria. Theoretically, reduction of one gram of nitrate (NO_3^-) to nitrogen gas requires 1.9 grams of methanol; however, pilot studies with a 1,000 m^3/d filter showed methanol consumption on the order of 4.4 g methanol / g nitrate.

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. Disinfection with chlorine or ozone following the BAF may reduce the purveyors' concerns over microbial levels in the treated water. Although this treatment option is conceptually feasible with moderate costs, there will be resistance on the part of water utilities because of inherent limitations of biological processes in drinking water treatment. Consequently, the use of BAFs to remove methanol from drinking water will likely be limited.

5.8 Conclusion

In conclusion, conventional drinking water treatment technologies used for removal of organic compounds (air stripping and activated carbon) are not effective for removal of methanol. Advanced oxidation processes have been proven for methanol treatment, but may be cost prohibitive, and must be analyzed on a site by site basis. Alternatively, biologically activated filters represent a cost-effective proven technology to remove methanol from drinking water, though this technology may be limited by treated water quality concerns of water purveyors. Very little field site documentation is available due to the fact that methanol has not been reported as a contaminant in drinking water sources. The most promising technologies for methanol removal in drinking water applications are some form of biological treatment and advanced oxidation either separately or in combination.

6.0 METHANOL TOXICOLOGY

6.1 Health Effects of Methanol

Methanol's properties and toxicity are well understood. Human exposure to methanol can occur via the inhalation, ingestion, or dermal contact pathways. Identified human illnesses associated with methanol exposure include organic solvent poisoning, systemic acidosis, optic nerve damage and central nervous system (CNS) effects.

TABLE 6-1
HAZARD SUMMARY[a]

	M100	Gasoline
Flammability		
Ease of Occurrence		
Open & Restricted Areas	4	9
Enclosed Spaces	8 (2-4) [b]	2
Relative Hazard if Fire		
Fire Severity	3	10
Ease of Extinguishing	7	10
Flame Visibility	8	1
Toxicity		
Inhalation-Low Conc.		
Toxicity	3	10
Ease of Occurrence	10	10
Inhalation - High Conc.		
Toxicity	10	10
Ease of Occurrence	3	4
Skin Contact.		
Toxicity	9	8
Ease of Occurrence	3	3
Ingestion		
Toxicity	10	10
Ease of Occurrence	8(2) [c]	3

Table adapted from Machiele, 1998; [a] 1-No concern. 2 to 3 = Low Level concern. 4 to 6 = moderate concern. 7 to 8 = high-level concern. 9 to 10 = extreme hazard. [b] Numbers in parenthesis reflect hazard reductions resulting from design changes. [C] Number in parenthesis incorporates the lowered likelihood of ingestion due to the presence of additives.

Though often considered to be more toxic than gasoline, methanol's occupational Threshold Limit Value (TLV) is only slightly lower than that of gasoline (a TLV of 200 ppm versus gasoline's 300 ppm). Table 6-1 contrasts the hazards associated with M100 (100 percent methanol used in fuel cells) versus gasoline fuels. In 1991, the U.S. Department of Energy reported that overall, gasoline is considered to be more hazardous to human health than neat methanol (USDOE, 1991).

6.1.1 Inhalation

Inhalation of methanol vapors is the most frequent type of exposure. Exposure to fuel vapor sources can be attributed to exhaust emissions, vehicle refueling emissions, and emissions from spills and uncovered fuel. Acute methanol inhalation toxicity does not appear to be a problem for drivers or service station attendants exposed to methanol vapors during refueling and under a wide range of traffic conditions (HEI, 1987). Measured exposure levels were well less than methanol's 8-hour TLV (200 ppm) and the highest exposure duration was determined to be approximately 15 minutes.

The calculated dosage based on worst-case methanol inhalation exposures of 150 ppm for 15 minutes results in a maximum dose of 0.6 mg/kg body weight. This analysis assumes a 70 kg person breathing at twice the resting rate where 60 percent of the inhaled vapor is absorbed into the body. A body burden of 0.6 mg/kg is similar to the amount created through normal fruit, vegetable and alcoholic beverage intake (0.3-1.1 mg/kg/day) (Machiele, 1988) and is 500 times less than methanol's minimum lethal dose. Most methanol related activities result in much lower inhalation exposures and related body burden.

Chronic inhalation exposure to methanol of greater than 200 parts per million has resulted in irritation to the mucus membranes, dizziness, nausea, headaches and blurred vision. Generally, there are no overt health problems associated with low-level exposures (USDOE, 1991). EPA's Office of Air Quality Planning and Standards has evaluated methanol for chronic toxicity and has given it a composite score of 7 (where scores range from 1 to 100, with 100 being the most toxic).

The American Conference of Governmental Industrial Hygienist (ACGIH) has established an 8-hour time weighted average threshold limit value (TLV) of 200 ppm for worker exposure to methanol. Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed daily, for a working lifetime, without adverse health effects. Exposure to airborne methanol concentrations greater than the National Institute for Occupational Safety and Health (NIOSH) Immediately Dangerous to Life or Health (IDLH) value of 6,000 ppm represents a condition under which workers may not be able to escape without loss of life or irreversible health effects. A summary of relevant airborne methanol occupational exposure limits is presented in Table 6-2.

TABLE 6-2
Methanol Toxicity Exposure Limits (1)

Occupational Work Standard -TWA [a]	8 hr workday	200 ppm (OSHA, ACGIH)
TLV-STEL [b]	15 minute exposure	250 ppm
IDLH [c]	immediate	6,000 ppm

1) Festa, 1996. a) Time Weighted Average. b) Short Term Exposure Limit. c) Immediately Dangerous to Life or Health.

6.1.2 Ingestion

Inhalation exposure is the most common route of entrance into the body; however, ingestion represents the most serious route of exposure. Methanol ingestion exposure typically could occur as a result of intentional drinking, unintentional drinking during siphoning, or unintentional drinking due to ignorance of the potential consequences. The toxicity effects of ingestion follow the same pattern described above for inhalation. The ingestion threshold for toxic effects can be as little as 6 to 18 ml (USDOE, 1991; Machiele, 1989). There is a wide disparity in these toxic levels based on the natural variability in the recipients ability to metabolize methanol.

Observed human lethal dosages via ingestion range from 15 to 250 grams (Wimer, et al., 1983). However, only a few documented cases are found in the literature and almost all of the cases predate 1920. In a review of the actual case evidence in medical literature for methanol toxicity at low ingested doses (30 ml or less) Kopinski (1993) concludes that the published literature on actual methanol ingestion cases does not support a minimum lethal adult dose of less than 30 ml (approximately 24 grams). Areas of uncertainty in analyzing these cases included the potential for synergistic effects due to other constituents in ingested drinks and the difficulty in obtaining reliable dose estimates. LD50 (i.e., the lethal dose affecting 50 percent of a test population) data points for methanol ingestion in animals are presented in Table 6-3.

Table 6-3
Lethal Doses of Methanol and Benzene in Animal Studies

LD_{50}	**Methanol**	**Benzene**
Oral-rat—mg/kg	5,600-13,000[a], 12,800[b]	4,894[c]
Oral-mouse—mg/kg	9,000[b]	4,700[c]
Oral-monkey—mg/kg	7,000[b]	
Dermal-rabbit—ml/kg	20[a,b]	
Inhalation-rat—ppm	64,000[a]	9,980[c]

a MSDS, 1996. b Exxon, 1991. c MSDS, 1987

6.1.3 Dermal Exposure

There are many possible instances in which people come in contact with vehicle fuels. Generally, exposure through spillage or use of a solvent will cause only mild effects on the skin (defatting or a mild dermatitis). Methanol readily adsorbs into the dermal layer at a rate of 0.2 mg/cm^2 per minute (Machiele, 1988). Repeated exposure may cause eczema, redness, and scaling. Methanol's more serious toxic effects described previously are only a threat in the event of excessive absorption. Thus, momentary contact is not a large concern (USEPA, 1994a).

6.2 Aquatic Toxicity

High concentrations of methanol are toxic to most plants and animals. In the event of a large, concentrated spill from a tanker ship, the acute effects of methanol exposure would result in damage to biota in the immediate spill area.

The USEPA Office of Pollution Prevention and Toxics (1994a) reported on the sensitivity to methanol for several aquatic species. This study reported values of median lethal concentrations, LC_{50}, and median effective concentrations, EC_{50}, for methanol (Table 6-4). LC_{50} is the estimated concentration that is expected to be lethal to 50% of the test animals or plants, and EC_{50} 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).

Table 6-4
Reported Median Lethal and Median
Effective Concentrations for Methanol and Benzene

Test animal or plant	Methanol LC_{50} (mg/L)	Methanol EC_{50} (mg/L)	Benzene LC_{50} / EC_{50} (mg/L) (3)
Pimephales promelas (Fathead Minnow)	28,100 (96 hrs) (1)	NA	15 (96 hrs)
Oncorhynchus mykiss (Rainbow trout)	20,100 (96 hrs) (1)	13,000-13,200 (EQU) (216 hrs) (2)	5
Alburnus alburnus (Bleak)	>28,000 (96 hrs) (1)	NA	NA
Lepomis macrochirus (Bluegil)	15,400 (48 hrs) (1)	16,000-16,100 (EQU) (216 hrs) (2)	22
Cyprinus carpio (Common carp)	28,000 (48 hrs) (1)	NA	NA
Carassius auratus (goldfish)	1,700 (48 hrs) (1)	NA	34
Anabaena (blue green algae)	NA	2.57-3.13% (10-14 days) (1) growth inhibition	NA

(1) USEPA, 1994a; (2) Zogorski et al., 1997; (3) USEPA, 1980; NA = Not Available.

The results of this study indicated that methanol is essentially non-toxic to the species tested. Based on an in-depth review of the toxicity and environmental distinctions between methanol and conventional fuels, Machiele concludes that in general, methanol is significantly less toxic to marine life than petroleum fuels, and that many of the effects of short term exposure are temporary and reversible (Machiele, 1989). Water quality criteria for methanol to protect aquatic life have not yet been established by the EPA.

6.2.1 Toxicity of Methanol to Microbial Populations

In general, high concentrations of alcohol (10 to 15%) are considered to be toxic to most microorganisms (Brusseau, 1993; Ingram and Buttke, 1984). A number of studies have been conducted to evaluate the effect of methanol on subsurface microbial populations. In a laboratory study, methanol up to a concentration of 1,000 mg/L was found to biodegrade in soil microcosms from three different sites with no apparent toxicity to the microorganisms (Novak et al., 1985). In another laboratory study, the presence of 19% methanol caused a 10,000 fold decrease in the microbial population of aquifer material (Butler et al., 1992). These researchers suggested that methanol from an M85 plume may adversely affect the indigenous microbiota's ability to contribute to attenuation of petroleum hydrocarbon contaminants in situ.

Verschueren (1983) reviewed the biological effect of methanol and reported that methanol has been reported to impact sludge digestion at a concentration of 800 mg/L and NH_3 oxidation (50% inhibition) in *Nitrosomonas* at a concentration of 160 mg/L. Toxicity thresholds for other microorganisms are reported in Table 6-5.

Table 6-5
Biological effects of methanol on various microorganisms as measured by the toxicity threshold from a cell multiplication inhibition test

Microorganism	Toxicity threshold (cell multiplication inhibition test)
Bacteria (*Pseudomonas putida*)	6600 mg/L
Algae (*Microcystis aeruginosa*)	530 mg/L
Green algae (*Scenedesmus quadricauda*)	8000 mg/L
Protozoa (*Entosiphon sulcatum*)	>10,000 mg/L
Protozoa (*Uronema parduczi Chatton Lwoff*)	>10,000 mg/L

from a cell multiplication inhibition test.; Adapted from Verschueren (1983).

7.0 FUTURE RESEARCH NEEDS

This report contains a comprehensive evaluation of the fate and transport of methanol in the environment. As noted, there are several areas where the available literature is not sufficient to address all fate and transport issues associated with unintentional releases of methanol to the soil, groundwater, or surface water. Based on the review provided in this report, the following research suggestions are recommended:

1) As discussed in Section 5, the selection of methanol additives, if needed, may significantly alter the risk posed by methanol releases into the environment. As the need for additives and their possible choices are evaluated, the fate and transport of the additives will need to be addressed as part of the evaluation process.

2) The literature reviewed for this report suggests that methanol will rapidly degrade once introduced to the subsurface. However, high concentrations of methanol near the source may be toxic to microorganisms resulting in limited or no source area biodegradation. Consequently, an analysis of methanol releases that have occurred at methanol fueling areas, storage areas, production locations, or during transportation would serve to verify that methanol does not significantly accumulate in the environment, nor does it pose a threat to drinking water resources.

3) The fate and transport of a methanol plume that may become commingled with a gasoline plume is briefly discussed in section 3 of this report; however, there remain several uncertainties. The effect of methanol on the fate and transport of BTEX plumes needs to be better understood. In addition, if the BTEX biodegradation rate is reduced, the effect of this reduced rate on increases in BTEX plume lengths should be further evaluated.

4) If any of the above studies indicate that methanol or methanol additives may persist in the subsurface, an evaluation should be completed to determine the best technology for remediation and treatment of these compounds. The chosen technology should address removal of these compounds in the source area, plume area, or at the drinking water source

well. For drinking water applications, it should be determined whether the selected technology, or a combination of technologies, meets the requirements posed by the drinking water community with respect to process reliability and regulatory approval.

8.1 Fate and Transport

The fate and transport of methanol released into the environment has been evaluated in the context of three conceptual release scenarios: 1) a rail car or tank truck spill during transport; 2) an ocean or river spill during transport; and 3) an underground storage tank release at a methanol dispensing location. In each of these scenarios, methanol is unlikely to persistent in any of the environmental compartments due to its rapid biodegradation. Methanol is miscible in water, and will consequently dissolve and dilute to very low concentrations in the event of a surface water spill (Scenario 2). Similarly, groundwater methanol concentrations are highly dependent on the nature and magnitude of the release, but will likely fall to low concentrations once complete dissolution has occurred. In both of these scenarios, the low concentrations of methanol will likely be easily biodegraded under a wide range of geochemical conditions.

Biodegradation is the primary process for methanol removal from the environment. Relative to gasoline, methanol is safer and more environmentally benign. Hazards incurred by gasoline releases are greater than those of methanol releases, and will persist much longer in the environment (USDOE, 1991).

8.2 Methanol Additives

It is currently unknown whether additives will be required for wide-spread use in methanol fuel. Because of several potential safety concerns over the use of methanol as a fuel source the need for additives must be evaluated. Manufacturers are currently focusing their additive investigation and testing efforts on three chemical or physical characteristics of methanol: luminosity, taste, and color.

For each category, there may exist a set of candidate chemicals which addresses the stated problem. However, often these chemicals are proprietary in nature, such that the chemical properties are not published. Consequently, a detailed analysis of the fate and transport of these additives was not possible.

8.3 Remediation and Treatment

Most treatment technologies that are commonly used to remove gasoline components from water (e.g., air stripping, granular activated carbon) are not effective for removing methanol from water due to the high solubility and low Henry's constant relative to other gasoline components. In the majority of remediation cases, the inability of these technologies to remove methanol from water is inconsequential because biodegradation of methanol in the soil, groundwater, and surface water will readily occur. If methanol were to impact drinking water sources, advanced oxidation processes have been proven, though the feasibility and costs of the treatment are very site specific. Biological treatment processes are effective at removing methanol from water, and are increasingly being used to polish the effluent from advanced oxidation processes. However, biological treatment in drinking water applications is still not extensively used and, therefore, would require regulatory acceptance. In conclusion, methanol can be removed in both a remediation and drinking water treatment context using biological degradation; however, the effectiveness, cost and public acceptability will be site specific.

8.4 Human and Aquatic Toxicity

Methanol's properties and toxicity are well understood, and the *ocular toxicity* and metabolic acidosis that are effects of acute high doses of methanol are well-known. Methanol is neither mutagenic, nor carcinogenic. While methanol produces toxic effects on humans and animals, the current evidence suggests that these effects only occur at high doses (Festa, 1996). While methanol is often considered to be more toxic than gasoline, the threshold limit value (TLV) for methanol vapor is only slightly lower than that for gasoline; and the U.S. Department of Energy considers gasoline to be 'overall' more hazardous to health than neat methanol.

Methanol is significantly less toxic to marine life than petroleum fuels, and many of the effects of short term exposure are temporary and reversible. Based on the reported values of median lethal and effective concentrations for methanol, the Office of Pollution Prevention and Toxics indicated that methanol is essentially non-toxic to the four aquatic fish species that were tested. However, a surface water spill of methanol could result in the depletion of oxygen which would prove to be toxic to local fish species. Methanol has a negligible bioaccumulation potential and is relatively non-toxic to ecological receptors. While the aquatic toxicity of methanol is high, toxic concentrations could be observed near a LUST source area or after a pure product methanol spill; this concentrations will likely quickly dissipate. Thus, in most cases, methanol concentrations will be benign to surrounding organisms, but in extreme circumstances, methanol could prove toxic to indigenous microbes or aquatic life.

In conclusion, the fate and transport of methanol in the environment is well understood. Methanol spills to the soil, groundwater, and surface water will quickly biodegrade under both aerobic and anaerobic conditions and, consequently, methanol is not expected to persist. Methanol exhibits a lower toxicity to both humans and indigenous microbes then conventional gasoline. Therefore, based on this analysis, methanol appears to be a more environmentally benign fuel compared to conventional gasoline.

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