Potential Impacts on Groundwater of Pure-Phase Methanol Releases

Leslie Smith               University of British Columbia
John Molson               École Polytechnique
Kevin Maloney           Methanex Corporation

Abstract

A model study is presented which examines the transport and persistence of methanol in a shallow aquifer. Site conditions are patterned after those found in the Borden aquifer in Ontario. Two scenarios are considered; one involving a release of pure phase methanol into a pristine aquifer, and the other a release of pure-phase methanol into an aquifer containing a gasoline residual and a 5 year old BTEX plume. Processes that are considered include multi-component dissolution of gasoline, enhanced solubility of BTEX due to co-solvency, inhibition of methanol and BTEX degradation at high methanol concentrations, 3D advective dispersive transport, and electron acceptor limited competitive biodegradation with microbial growth. In the situation where a methanol spill on the ground surface leads to concentrations of methanol at the water table that are at or below the inhibition threshold, the simulations suggest a methanol plume may persist in groundwater for a period of 1 to 2 years. If site conditions and the spill volume result in high concentrations of methanol at the water table, methanol will persist in groundwater until dispersive processes lead to concentrations in the core of the plume that fall below the inhibition threshold. For the site conditions considered here, this initial phase is 5 to 10 years in duration. If methanol escapes containment at a site where an existing gasoline pool or residual is present, the simulations suggest that relatively high concentrations in the core of the benzene plume will extend significantly greater distances beyond the source zone, and the total length of the benzene plume may increase by 30 – 35%.

Introduction

Methanol is considered a fuel of choice to provide a source of hydrogen for fuel cell applications. A greater likelihood of accidental releases of pure-phase methanol from transport or storage tanks can be anticipated if methanol becomes widely used in fuel cell vehicles or local stationary power units. There is little published information, however, that documents the behavior of methanol releases to groundwater. Where accidental spills have been described, data are not readily available to provide either insight to representative methanol concentrations in groundwater shortly after a spill, or to quantify the rates at which a methanol plume may dissipate. Malcolm Pirnie (1999) provides an overview of the factors influencing the fate and transport of methanol and its potential environmental impacts.

The US EPA has not set a maximum concentration for methanol in drinking water, although it has set a reference dose (RfD) of 0.5 mg/kg/day. An estimate of a maximum concentration value can be derived from this RfD using a formula that accounts for the typical weight of an adult, and a typical daily amount of water consumption. If this formula is applied using the RfD for methanol, a maximum concentration of 3.5 mg/l is obtained. Several states have published drinking water guidelines for methanol. Florida and Wisconsin have a guideline of 5 mg/l while Minnesota uses a value of 3 mg/l.

The objective of this paper is to evaluate the transport and persistence of methanol in a shallow aquifer using a numerical modeling approach. The first scenario we consider involves a pure phase methanol release into a pristine aquifer. A second scenario is examined that considers a pure-phase methanol release at a site with an existing BTEX plume. Methanol in high concentrations has a significant co-solvency effect on the effective solubilities of BTEX. Furthermore, methanol appears to be a preferential substrate (carbon source) when it co-exists with benzene. The degradation of methanol will deplete dissolved oxygen in the groundwater, creating anaerobic conditions, which will significantly reduce the benzene biotransformation rate. As a consequence, a benzene plume emanating from the site of a gasoline spill is likely to migrate a greater distance from the source if methanol co-mingles with the BTEX plume. This plume extension is similar in concept to that noted for gasoline / ethanol releases (Malcolm Pirnie, 1998; McNab, 1999; Molson et al., 2002).
Environmental Characteristics of Methanol

Methanol (CH₃OH) is completely miscible in water, with pure methanol yielding a saturation concentration of 792,000 mg/l. Following a spill at the ground surface, methanol will infiltrate through the soil profile and dissociate into the available soil moisture. Methanol has a relatively high vapor pressure (0.16 atm @ 25 °C); in the pure phase there can be a significant transfer of mass to the atmosphere or soil gas. Once methanol dissociates into water, however, it is not readily transferred to the vapor phase (Henry’s Law constant of 1.09 x 10⁻⁴ @ 25 °C). The area on the ground surface across which methanol flows as it infiltrates is a key factor in determining the total volume of soil moisture that will be contacted and available for dilutive mixing above the water table. If the volume of a methanol release is small in comparison to the volume of soil moisture present in the soil beneath the surface footprint of a spill, then significant dilution should occur as methanol infiltrates toward the water table. Conversely, a large release confined to a small footprint, in a region with a shallow water table, is likely to result in high concentrations of methanol in the fluid reaching the water table. In the case of a continuous leak from an underground tank or pipe, it is expected that after a relatively short initial period where dilution dominates the composition of the fluid reaching the water table, a pathway will be established where the pore spaces are occupied with essentially pure-phase methanol. From that time onwards, pure phase methanol is likely to mix across the water table into the underlying saturated groundwater flow system.

Methanol does not readily partition from the aqueous phase onto mineral surfaces or organic carbon present in an aquifer (log Kow = -0.77). As a result, the average velocity at which methanol is transported in groundwater is the same as the average velocity of the water itself.

Methanol is metabolized by a wide range of aerobic and anaerobic bacteria. Under aerobic conditions, methanol degradation occurs as:

\[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

Under anaerobic conditions degradation can occur as:

\[ \text{CH}_3\text{OH} + \text{NO}_3^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \frac{1}{2} \text{N}_2 \]

\[ \text{CH}_3\text{OH} + 0.75 \text{SO}_4^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 0.75 \text{S}_2^- \]

Quantitative evidence to estimate degradation rates comes primarily from laboratory microcosm studies using sediment samples collected from various geologic settings (Novak et al., 1985; White et al., 1986; Bulter et al., 1992; Hubbard et al., 1994a; Aronson and Howard, 1997). Laboratory microcosm experiments have yielded half lives between 1 and 135 days, with the majority of values less than 40 days. Rate constants do not seem to depend upon which electron acceptor is being consumed. The best field evidence characterizing methanol degradation is from a methanol fuel oxygenate experiment carried out in the Borden aquifer in Ontario (Hubbard et al., 1994b). The Borden field test clearly established that it is possible for a methanol plume with initial concentrations as high as 7000 mg/l to dissipate within 300 to 400 days. Hubbard et al. (1994b) concluded that much of the methanol degradation proceeded by anaerobic biotransformation, after depletion of background oxygen in the aquifer.

The main conclusions relevant to degradation that can be drawn from these studies are:

1. At concentrations less than about 3000 mg/l, methanol can be expected to biodegrade at a relatively fast rate, in a wide range of groundwater environments. It is degradable under both aerobic and anaerobic conditions. The majority of the studies support the inference that if the maximum concentration of methanol is less than about 100 mg/l, then it can be expected that a methanol plume will be largely dissipated by natural attenuation within a period of 3 to 6 months.
2. If the methanol concentration exceeds 8000 to 10,000 mg/l, there is likely to be a significant inhibitory effect on the microbial population, which is expressed as either an extension of the acclimation period before biotransformation of methanol proceeds, and/or by a reduction in the rate of methanol degradation.

3. If concentrations of methanol exceed 50,000 to 100,000 mg/l, it is likely that microbial degradation of methanol will not occur at any significant rate. High methanol concentrations can sterilize a soil.

These observations suggest the presence of an inhibition threshold, on the order of 10,000 mg/l, above which methanol tends to persist in groundwater. Below this threshold, we assume methanol degradation follows a first order rate model. In the simulations presented below, the decay constant is derived from data obtained in the Borden fuel oxygenate experiment (Hubbard et al., 1994b).

The amount of dilutive mixing that occurs above the water table is likely to be a key issue in determining the persistence of methanol in groundwater. Even high-volume spills of methanol (e.g. 25,000 gals) may lead to methanol concentrations below the inhibition threshold on degradation if the surface infiltration area is large. Degradation would then be expected to begin soon after the release. In the alternate case, where high concentrations of methanol reach the water table, much slower dispersive processes must act to reduce concentrations below the inhibition threshold before degradation begins.

**A Model Study of Methanol Releases to Groundwater**

*Model Domain, Aquifer Properties, and Source Characteristics*

The model design is based on conditions found in the Borden aquifer, a well-characterized groundwater system in southern Ontario. This aquifer is composed of clean, well-sorted, fine- to medium grained sand. The depth to the water table varies with local relief, but it is typically between 1 and 3 m. The aquifer is 10 m thick and is located above a thick, silty-clay deposit. The Borden aquifer has been adopted as an example in several model studies of the mobility and persistence of BTEX / ethanol mixtures (Ulrich, 1999; Schirmer et al., 1999; Molson et al., 2002) and pure-phase ethanol releases (Molson, 2000).

Figure 1 is a schematic of the model domain. The full 3D system is 400 m long, 30 m wide, and 10 m deep. Assuming no transverse horizontal flow gradients, we take advantage of vertical symmetry about the central vertical plane and only simulate a 15 m wide domain. The computational effort is therefore reduced by one-half. The upper boundary of the domain is the water table; the lower boundary is impermeable. As shown by the flow lines, groundwater enters the domain both from the left-hand side of the model domain and as local recharge across the water table. The average groundwater velocity is 36 m/yr. Oxygen enters the domain across the left boundary and across the water table at a background concentration of 3.8 mg/l. Methanol is released into the saturated zone just below the water table, in a source zone that starts 13 m from the left-side boundary. A gasoline residual is represented by a set of mixing cells located above the water table, outside of the flow domain. The footprint of the zone containing residual gasoline coincides with that of the methanol spill (note: all references to source area, volume and mass refer to the full source, not adjusted for model symmetry). Table 1 lists the values of the key parameters in the model study.
Table 1: Parameter Values Used in Model Study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity</td>
<td>$1 \times 10^{-4}$ m/s</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.35</td>
</tr>
<tr>
<td>Background $O_2$ (aerobic)</td>
<td>3.8 mg/l</td>
</tr>
<tr>
<td>Groundwater velocity on left-side boundary</td>
<td>7.3 m/yr</td>
</tr>
<tr>
<td>Recharge rate at water table</td>
<td>0.2 m/yr</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>1 m</td>
</tr>
<tr>
<td>Transverse horizontal dispersivity</td>
<td>0.02 m</td>
</tr>
<tr>
<td>Transverse vertical dispersivity</td>
<td>0.01 m</td>
</tr>
<tr>
<td>Diffusion coefficient – methanol</td>
<td>$11.5 \times 10^{-10}$ m$^2$/s</td>
</tr>
<tr>
<td>Diffusion coefficient – benzene</td>
<td>$7.7 \times 10^{-10}$ m$^2$/s</td>
</tr>
<tr>
<td>Footprint of spill at water table</td>
<td>10 m in direction of flow</td>
</tr>
<tr>
<td></td>
<td>3 m transverse to flow</td>
</tr>
<tr>
<td>Gasoline composition$^1$</td>
<td>PS-6 gasoline standard</td>
</tr>
<tr>
<td>Degradation rate – methanol</td>
<td>First order decay with 36 day half life</td>
</tr>
<tr>
<td>Degradation rate – benzene</td>
<td>Dual Monod kinetics</td>
</tr>
<tr>
<td>Inhibition threshold on degradation</td>
<td>8000 mg/l methanol</td>
</tr>
<tr>
<td>Retardation factor – benzene</td>
<td>1.1</td>
</tr>
</tbody>
</table>

To simulate a large volume spill of methanol (9500 l) occurring in the 10 m by 3 m footprint of the source, a methanol concentration of 400,000 mg/l is applied in a zone that extends 1.8 m below the water table. To simulate a small volume spill (205 l), a methanol concentration of 20,000 mg/l is applied in a zone that extends 0.77 m below the water table. These concentrations are derived under the assumption that the volume of methanol that is spilled dissociates completely into the available soil moisture above the water table (for a water table depth of 2 m and an average moisture content prior to the spill of 0.15). This volume of liquid is transferred into an equivalent volume just below the water table, and it is assigned a methanol concentration determined by mixing in the vadose zone. This plume immediately detaches from the site of the spill.

To consider the potential impact of a methanol leak from a storage tank, two scenarios are examined. The first scenario assumes a leak of 3 gal per day, the second a leak of 0.3 gal per day. Leak detection systems on tanks are currently designed to detect leaks as small as 3 gal/day. The footprint of the methanol leak at the water table
is 2 m by 1 m. In both cases, the volume of pure phase methanol is added in a mixing zone immediately below the water table (0.25 m), and concentrations approaching 100% methanol can develop beneath this source. The precise value that develops is dependent upon the methanol leak rate, the flux of groundwater immediately beneath the spill site, and the specified mixing volume.

The simulations we present are based on the code BioNAPL/3D, a three-dimensional finite element model developed at the University of Waterloo (Molson, 2002). This model simulates groundwater flow, multi-component dissolution of gasoline, advective-dispersive transport, and electron acceptor-limited competitive biodegradation with microbial growth. For the scenario of a methanol release at a site containing a BTEX source, the calculations are based on the simultaneous transport of methanol, three gasoline components (benzene, TEX, and a lumped component reflecting the remaining compounds), and dissolved oxygen. Only the methanol and benzene plumes are illustrated in this paper. Methanol degradation is simulated using a first order rate law, while accounting for the concurrent depletion of dissolved oxygen. Degradation of BTEX is simulated using a dual Monod formulation. Dissolution of the gasoline source located above the water table is simulated as an equilibrium process, using a simple mixing cell algorithm based on Raoult’s Law (Paulson et al., 1992). Properties of this residual gasoline source are given in Table 2.

Table 2 Assumed Residual Gasoline Source Characteristics

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g/mole)</th>
<th>Pure phase Solubility (mg/l)</th>
<th>Density (g/l)</th>
<th>Source mass (kg)</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>78</td>
<td>1780</td>
<td>878.6</td>
<td>117</td>
<td>0.018</td>
</tr>
<tr>
<td>TEX</td>
<td>104</td>
<td>288</td>
<td>870.0</td>
<td>1338</td>
<td>0.158</td>
</tr>
<tr>
<td>Other compounds</td>
<td>100</td>
<td>20</td>
<td>900.0</td>
<td>6914</td>
<td>0.824</td>
</tr>
</tbody>
</table>

BioNAPL/3D accounts for the enhanced transfer of benzene to the aqueous phase due to the co-solvency effect of methanol. Cosolvency is expressed as a dissolution enhancement factor (Ji and Brusseau, 1998), with a cosolvency factor that provides a match to Donaldson’s (1992) data on the increase in benzene solubility in the presence of methanol. In the simulations presented below, cosolvency effects increase the benzene concentration immediately beneath the spill site from ~ 32 mg/l in the absence of methanol to ~ 60 mg/l when methanol is spilled within the source zone, to ~ 400 mg/l when a continuous leak of methanol passes through the BTEX source.

The dual Monod degradation parameters for the gasoline components are given in Table 3. For all simulations, the initial microbial concentration is 3 mgcell/l, and it is assumed uniform throughout the domain.

Table 3 Assumed Biodegradation Parameters For Residual Gasoline Source

<table>
<thead>
<tr>
<th>Component</th>
<th>Maximum rate (mgorganic/mgmicrobe/day)</th>
<th>Organic half Constant (mg/l)</th>
<th>O2 half constant (mg/l)</th>
<th>O2:substrate mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>3.08</td>
</tr>
<tr>
<td>TEX</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>3.13</td>
</tr>
<tr>
<td>Other gasoline</td>
<td>0.2</td>
<td>2.0</td>
<td>2.0</td>
<td>3.46</td>
</tr>
<tr>
<td>Compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Principal Assumptions

The following assumptions underpin the calculations presented here.

1. The groundwater flow system is at steady state. The aquifer has a uniform porosity and isotropic hydraulic conductivity.
2. The density contrast between the methanol plume and native groundwater is neglected. In reality, the methanol plume will be less dense than the native groundwater, which would tend to counteract the downward motion of the plume caused by groundwater recharge across the water table.
3. The total mass of methanol that is released is transferred across the water table to enter the groundwater system. Mass loss due to volatilization, vapor phase transport, or biodegradation in the vadose zone is neglected.

4. Methanol does not sorb to the aquifer material, nor does methanol modify the retardation factors for BTEX, even at the high concentrations near the source zone.

5. At methanol concentrations exceeding the inhibition threshold, no biodegradation of methanol, benzene, or other gasoline components will occur.

6. Once the methanol concentration falls below the inhibition threshold, the microbial population recovers on a time scale that is short in comparison to the characteristic advective groundwater travel time. This recovery occurs even within the core of the methanol plume, where concentrations may have been high enough to sterilize the soil. No account is made of changes in the biomass of methanol degraders when using a first order rate law.

7. Reaction stochiometries assume complete degradation of methanol and benzene to carbon dioxide and water.

8. The BTEX source is immobile and coincident with the footprint of the methanol release. Potential changes in the interfacial tension of BTEX due to methanol are neglected.

Case Study 1: Instantaneous Methanol Release into a Pristine Aquifer

On the left side of Figure 2 we illustrate the fate of a 9500 l methanol spill in a pristine aquifer, for the condition where the methanol concentration reaching the water table is 400,000 mg/l. Unless otherwise noted, the inhibition threshold on degradation is a methanol concentration of 8000 mg/l. Simulations are presented as vertical plume profiles along the symmetric centerline of the plume. The plume migrates from the site of the spill at the average groundwater velocity, and disperses to the extent that after 5 years, the methanol plume is approximately 50 m long in the direction of flow. During this initial 5 year period, concentrations exceed the inhibition threshold and biodegradation is restricted to the outermost edges of the plume. After year 5, due to dispersive mixing, concentrations in the core of the plume fall below the inhibition threshold. Degradation then proceeds rapidly, and by 7.1 years, the entire plume, when mapped to a concentration of 1 mg/l, is eliminated. For the assumed hydrogeologic conditions, the methanol plume does not advance beyond 60 m from the spill site.
Figure 2. Left side - Plume evolution for an instantaneous methanol release into a pristine aquifer. Right side – Benzene plume generated by the release of an equivalent volume of gasoline into the same aquifer.

On the right side of Figure 2, we illustrate the fate of a benzene plume resulting from the instantaneous release of an equivalent volume of gasoline (9500 l) into the same pristine aquifer. The gasoline forms a residual phase that continually releases benzene to the aquifer for the entire 20 year simulation period illustrated here, unlike the methanol spill which dissociates completely into the groundwater and forms a plume that immediately detaches from the source zone. In addition, the benzene plume extends considerably farther from the site of the spill than does the methanol plume. The difference in the downstream extent of the two plumes will be even greater in an aquifer with a lower dissolved oxygen concentration than applied in this simulation (3.5 mg/l).

The persistence of the methanol plume is dependent upon the inhibition threshold. If the inhibition threshold is 4000 mg/l, methanol is transported further from the source zone (85 m), and peak concentrations remain above 1 mg/l for about 9.6 years. If the inhibition threshold is 12,000 mg/l, the methanol plume migrates about 50 m beyond the footprint of the source, and peak concentrations are reduced below 1 mg/l in 6 years.

In the case of a small methanol spill (205 l) that reaches the water table at a concentration of 20,000 mg/l, the plume dissipates rapidly. It is removed from the aquifer within about 1.5 years, and the plume does not advance beyond a region 15 m from the spill site.

Case Study 2: Continuous Methanol Release into a Pristine Aquifer

The concentration plots on the left side of Figure 3 illustrate the fate of a plume created by a methanol leak of 3 gal/day entering a pristine aquifer. The methanol plume advances for about 10 years, extending a distance of about 65 m from the source, before it stabilizes. Plume stability occurs when the mass influx from the release point is balanced by the mass lost due to microbial degradation and the dispersive mass flux across the outer fringes of the plume. Very high methanol concentrations develop within 50 m of the source. A smaller plume is created if the leak rate is 0.3 gal/day. In this case, the methanol plume stabilizes after 5 years, and it extends about 25 m from the source.
For purposes of comparison, the concentration plots on the right side of Figure 3 illustrate the fate of a benzene plume resulting from the instantaneous release of 9500 l of gasoline into the same pristine aquifer. Because this gasoline forms a residual phase that acts as a continuous source of benzene over the 20 year time frame of the simulation, a case is established where neither the methanol or benzene plumes detach from the source zone. At 20 years, the leading edge of the benzene plume is approximately 100 m farther from the source zone than is the leading edge of the stable methanol plume.

Figure 3. Left side - Plume evolution for a continuous methanol release of 3 gal./day into a pristine aquifer. Right side - Benzene plume generated by the release of 9500 l of gasoline into the same aquifer.

The time at which the plume stabilizes, and the distance it migrates from the source, is dependent on the groundwater velocity in the aquifer. Figure 4 shows the evolution of a methanol plume if the groundwater velocity on the left side boundary is increased to 73 m/yr, for the case of a 3 gal/day leak. The plume stabilizes after 3 years, but the 1.0 mg/l concentration contour extends about 140 m beyond the source zone. With the higher flux of clean groundwater passing beneath the leak point, plume concentrations near the source are lower because of increased mixing and dilution. In addition, the plume does not extend as deeply into the aquifer.
Figure 4. Plume evolution for a continuous methanol release of 3 gal/day into a pristine aquifer, groundwater velocity at left-side boundary increased to 73 m/yr.

Case Study 3: Instantaneous Methanol Release into a 5-Year Old BTEX Plume

It is conceivable that a truck transporting methanol could accidentally release its contents at a refueling station into an area previously contaminated by gasoline. To examine a case of greater concern, a model is developed for a site where a release of gasoline occurred 5 years earlier, and no remedial scheme had been implemented to remove residual gasoline located below the ground surface. BTEX does not appear to inhibit methanol biotransformation at the BTEX concentrations typically found downgradient from a gasoline release. Therefore, the methanol plumes illustrated earlier are transferable to this case study. Figure 5 compares the benzene plume that develops in the presence of a methanol spill, with a benzene plume not contacted by methanol. The methanol and gasoline releases are both 9500 l, and the methanol concentration at the water table is 400,000 mg/l. The preferential degradation of methanol, once concentrations fall below the inhibition threshold, reduces the dissolved oxygen concentration in groundwater, creating conditions that markedly decrease the rate at which microbial degradation of benzene will occur. Because methanol degrades both aerobically and anaerobically, methanol biotransformation is not limited to the outer edges of the plume, as it is in the case with benzene. Beyond the point where the methanol plume has dissipated (eg. see Figure 2), the benzene degradation rate is unaffected. The net effect of the methanol release is elongation of both the higher-concentration core of the benzene plume, and a 20% extension of its leading edge in this 20 year simulation.
Figure 5. Comparison of a benzene plume originating from a gasoline residual (left) with a benzene plume impacted by a 9500 l methanol spill into the source zone, occurring 5 years after BTEX release (right).

**Case Study 4: Continuous Methanol Release into a 5-Year Old BTEX Plume**

To examine an improbable but potentially higher-impact scenario, a model is developed for a site with an undetected gasoline pool (9500 l spill), at which a methanol tank is placed, which then begins to leak at a rate of 3 gal/day. The methanol leak occurs 5 years after the gasoline release. As noted for the case with an instantaneous methanol release, the benzene plume is elongated in the direction of groundwater flow. In this instance the benzene plume at 20 years is approximately 30 – 35 % longer. Because the continuous leak leads to methanol concentrations above 700,000 mg/l in the source zone, much higher concentrations of benzene are released into the aquifer due to co-solvency effects. As a consequence, the benzene plume is more extensive in the vertical direction, and high benzene concentrations in the core of the plume extend substantially greater distances away from the source zone.
Summary of Potential Groundwater Impacts

The transport and persistence of methanol plumes in the subsurface is strongly linked to the local geology at the site of the release and to the extent of dilutive mixing with soil moisture in the vadose zone. Even high-volume spills of methanol may lead to methanol concentrations close to or below the inhibition threshold on degradation if the area of infiltration is large. In these cases, it seems likely a methanol plume could persist in groundwater at concentrations above 1 mg/l for a period of one to two years. The distance the plume will move beyond the spill point during this time frame will be determined by the groundwater velocity at the site.

At sites where the water table is shallow and the release volume is relatively large, or where there is a continuous leak of methanol from a storage tank, methanol concentrations far above the inhibition threshold can be anticipated. Methanol will persist in the groundwater until concentrations in the central core of the plume fall below the inhibition threshold due to dispersive processes. For the shallow, unconfined aquifer considered here, this initial phase was five to ten years in duration. Once concentrations throughout the plume fall below the inhibition threshold, the plume is likely to be dissipated in an additional one or two years. Methanol originating from a continuous leak will eventually form a stable plume in groundwater, with high concentrations that may extend many tens of meters from the release point. In the case study, the outer boundary of these stable plumes moved 60 to 150 m beyond the source zone.

A benzene plume generated from a gasoline spill persists in groundwater at greater distances beyond the spill site than is the case with methanol. When viewed from this perspective, a methanol release to a pristine aquifer seems likely to present a significantly lower risk to the environment than does a gasoline release. If however, methanol were released at a site where there were gasoline pools or residuals in the subsurface, it is expected that benzene concentrations in the core of the BTEX plume may rise dramatically, and the total length of the benzene plume may extend by 30 – 35%. Therefore, protective measures will need to be exercised if methanol...
tanks are installed at sites where gasoline was used in the past, or where methanol and gasoline tanks may be located at the same facility.

References


Donaldson, C.R., 1992, Oxygenated fuel behaviour in the subsurface - a quantitative and qualitative laboratory scale investigation, MSc. Thesis, Department of Earth Sciences, University of Waterloo.


McNab, W., S.E. Heermann, and B. Doohoer, 1999, Screening model evaluation of the effects of ethanol on benzene plume lengths, Vol. 4, Ch. 4 in Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate, U.S. Department of Energy by Lawrence Livermore National Laboratory.


**Biosketches**

Leslie Smith is a Professor in the Department of Earth and Ocean Sciences at the University of British Columbia, where he holds the Cominco Chair in Minerals and the Environment. John Molson is a Research Associate at the École Polytechnique in Montreal and an Adjunct Professor in the Department of Earth Sciences at the University of Waterloo. Kevin Maloney is an engineer with the Emerging Energy Applications group of the Methanex Corporation.

Leslie Smith, Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, V6T 1Z4
John Molson, Department of Civil, Geological, and Mining Engineering, École Polytechnique, 2500 Chemin de Polytechnique, Montreal, Quebec, H3T 1J4
Kevin Maloney, Methanex Corporation, 1800 Waterfront Centre, 200 Burrard Street, Vancouver, British Columbia, V6C 3M1