Ethanol and gasoline transport in the capillary fringe: unmonitored natural attenuation?

Juliana Freitas, James Barker
Department of Earth and Environmental Sciences – University of Waterloo, Waterloo, ON, Canada
John Molson
Dept. of Civil, Geological and Mining Engineering – Ecole Polytechnique Montreal, Montreal, QC, Canada

ABSTRACT
The use of ethanol-blended gasoline is increasing in North America. Ethanol denatured with up to 5% gasoline (E95) is typically delivered for blending, where spills of E95 into soil already contaminated by gasoline hydrocarbons will cause gasoline residuals to be remobilized and cosolubilized, with their migration mainly within the capillary fringe. Typical groundwater monitoring techniques result in highly diluted concentrations whereas more reliable methods for sampling the capillary fringe are reported here. Also, explosive levels of methane may be produced by fermentation of ethanol. A controlled field experiment at CFB Borden is quantifying these effects.

RÉSUMÉ
L'utilisation d’essence mélangée avec de l’éthanol augmente en Amérique du Nord. L'éthanol dénaturé avec jusqu’à 5% d'essence (E95) est typiquement transporté jusqu’aux sites de distribution. Des déversements d'E95 dans un sol déjà contaminé par des hydrocarbures d'essence pourraient mobiliser et co-solubiliser des sources résiduelles d'essence; leur migration sera effectuée principalement dans la frange capillaire. Dans cet article, des méthodes fiables pour échantillonner la frange capillaire sont rapportées. De plus, des concentrations explosives de méthane peuvent être produites par la fermentation de l'éthanol. Une expérience sur le terrain à BFC Borden montre ces effets de façon quantitative.

1 INTRODUCTION

Throughout the industrialized world, ethanol is increasingly being blended into gasoline, typically at 10-20% (E10 - E20), while E85 is being proposed in some North American jurisdictions. Ethanol is commonly denatured with gasoline (typically E95) before transport by rail and truck to refineries. The potential impacts of E95 and high proportions of ethanol in gasoline on the subsurface behaviour and remediation of impacted soil and groundwater need to be understood before high-ethanol fuels are widely distributed.

The release of gasoline high in ethanol (E85) or the release of denatured ethanol (E95) into residual gasoline contamination will change the gasoline distribution in the subsurface, with unknown consequences to the source dissolution rates and dissolved plume development.

Also, significant, even most, ethanol and cosolubilized gasoline hydrocarbons will accumulate in the capillary fringe. Although the capillary fringe represents only a very small fraction of regional volumetric flow, for shallow contaminant transport at local scales, it may play a very important role (Berkowitz et al. 2004). Several studies have indicated that significant horizontal flow and transport can occur within the capillary fringe (Ronen et al. 1997; Henry et al. 2002; Berkowitz et al. 2004).

However, there is a lack of field data supporting contaminant transport in the capillary fringe, which can be due to the difficulties associated with sampling under negative gauge pressure (Ronen et al. 1997; Berkowitz et al. 2004). Samples collected from typical monitoring wells screened across the water table are not expected to be representative of concentrations in the capillary fringe.

Monitored natural attenuation (MNA) is commonly applied at fuel station contaminated sites, since gasoline-derived hydrocarbon contaminants of concern, namely benzene and other monoaromatic hydrocarbons (BTEX as a group), are easily biodegraded in shallow aquifers.

However, the presence of ethanol at high concentrations may have direct impacts on MNA efficiency and may compromise commonly applied techniques for monitoring. First, ethanol in groundwater can decrease the biodegradation rate of the BTEX compounds, making them more persistent (Alvarez et al. 2002; Powers et al. 2001). Second, MNA implies that contaminant concentrations and mass in the subsurface can be reliably characterized over time. If a significant fraction of contaminants is being transported in the capillary fringe and monitoring techniques are not adequate to capture the total mass, the site may be misinterpreted as undergoing apparent attenuation.

2 IMPACTS ON GASOLINE SOURCE ZONE AND TRANSPORT IN THE CAPILLARY FRINGE

As ethanol is added to a system composed of gasoline and water, it partitions between the two phases, but preferentially to the aqueous phase. The increase in ethanol concentration results in an enhanced solubility of gasoline compounds in the aqueous phase and also of water in the gasoline. At high enough ethanol concentrations (around 70% by volume), the system is composed of a single phase (McDowell et al. 2003, Oliveira, 1997). Besides this cosolvent effect, another consequence of ethanol mixtures is a decrease in the interfacial tension between the NAPL and aqueous phases. Ultimately, this results in an increased mobility of the NAPL phase in a porous media.

The consequences of these changes in properties due to ethanol addition were investigated in lab experiments. A 2D plexiglass box was used to simulate an ethanol spill into a gasoline source zone. The box had interior dimensions of 0.48 m long × 0.025 m wide × 0.40 m high, and was packed with glass beads with a diameter of 390 μm, corresponding to a medium to coarse sand. The water table was established at a position of 5cm from the bottom of the box, and the capillary fringe was 9 cm thick. A constant hydraulic gradient was established to simulate groundwater flow.

After flow conditions had stabilized, 15mL of gasoline (API 91-01) with a red dye was injected in the unsaturated zone. The gasoline moved downwards in the unsaturated zone until it reached the top of the capillary fringe, where it accumulated. The gasoline accumulation resulted in a decrease in the capillary fringe thickness from 9 cm to around 6.5 cm, due to a decrease in the surface tension. Ethanol was injected on top of the gasoline-contaminated zone, and moved down in the unsaturated zone until it reached the top of the capillary fringe (Figure 1).

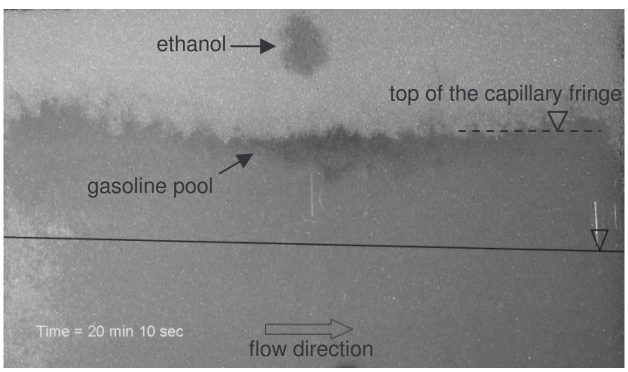

Figure 1. Ethanol injection

When ethanol reached the gasoline high saturation zone, it continued to migrate down, carrying the gasoline at its leading edge (Figure 2). This gasoline re-mobilization was a combined consequence of cosolvency and a decrease in interfacial tension.

The gasoline pool decreased in size and the saturation within the pool seems to have increased, as evidenced by a darker color. Similar results were reported by McDowell et al. (2003). The ethanol displaced the gasoline source zone vertically, but there was no evidence that the contaminants reached the groundwater below the water table.

Ethanol was transported horizontally in a very thin zone at the top of the capillary fringe (Figure 3), and most of the ethanol present in the saturated zone left the system, leaving gasoline behind. As ethanol moved downgradient, it decreased the aqueous phase surface tension and consequently caused further depression of the capillary fringe.

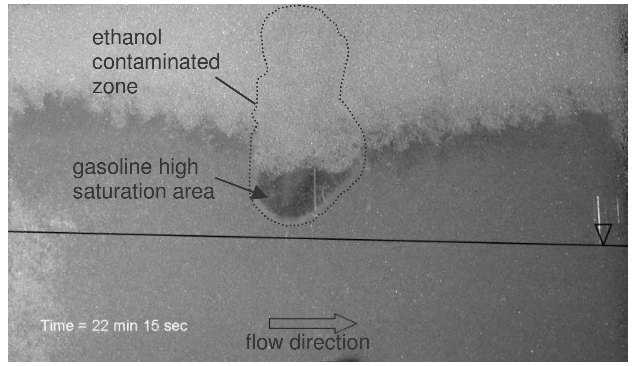

Figure 2. Gasoline redistribution caused by ethanol

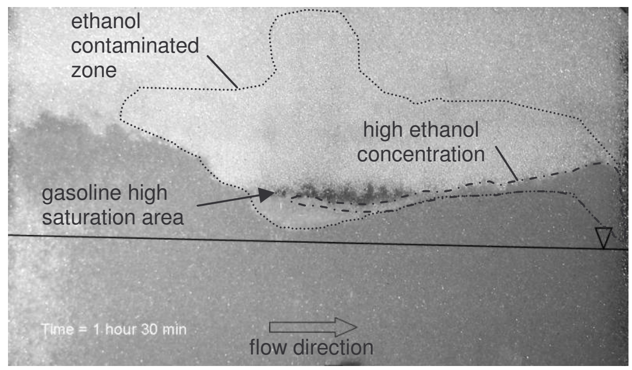

Figure 3. Ethanol transport in the capillary fringe

Although concentrations in the aqueous phase were not measured, we expect that cosolubilized hydrocarbons were transported together with the high-concentration ethanol layer at the top of the capillary fringe. It was also noticed that some of the ethanol was retained in the unsaturated zone, within the residual water phase. This ethanol would be able to reach the water table in a real aquifer system in the event of recharge or water table fluctuations.

3 CHALLENGES FOR SITE MONITORING

As discussed in the previous section, ethanol and cosolubilized gasoline hydrocarbons are expected to travel in a very thin layer at the top of the capillary fringe. However, typical groundwater monitoring wells installed at fuel contaminated sites are not intended to sample the capillary fringe.

The water present in the capillary fringe does not flow inside a well screened across the water table, therefore typical groundwater monitoring wells are unable to detect contamination in this zone. Under some conditions, such as long-term pumping or significant drawdown during sample collection, and also depending on well installation and soil properties, a typical monitoring well may draw some ethanol-contaminated water from the capillary fringe, providing an indication of contamination. However, significant dilution is expected, resulting in lower concentrations in the sample than the actual concentration in the capillary fringe. Therefore, it is important to apply techniques designed to obtain water from the capillary fringe to adequately characterize contaminant transport.

One typical device used for unsaturated zone monitoring is a porous suction sampler (Wilson et al. 1995). Sampling with these devices requires applying a negative pressure, which can result in significant losses due to volatilization.

In laboratory experiments (Freitas et al., in review) losses of up to 30% were measured for volatile organics. The losses were shown to be dependent on the compound properties and on the volume of ethanol in the sampling solution. Highest losses were observed for the most volatile (higher values of Henry's Law constant) compounds.

The losses were higher when intermediate volume fractions of ethanol (10% and 20%) were present. This happens because ethanol decreases the vapor pressure of the aqueous solution resulting in an increase of bubbles in the sampling tubing. At 50% ethanol volume fraction, the losses were significantly reduced, a consequence of the increased solubility of the organics in the presence of ethanol, which decreased the organic compound partitioning to the bubbles inside the tubing and consequently decreased the loss.

4 ETHANOL TRANSPORT AND FATE AT THE FIELD SCALE

A field test in the CFB-Borden sand aquifer is underway to study the effect of an E95 spill on top of gasoline residuals and to evaluate ethanol and gasoline transport in the capillary fringe. Gasoline will be spilled in the unsaturated zone, followed by an E95 spill. Groundwater concentrations are being monitored in three rows (A, B and C) located downgradient of the source zone (Figure 4); each row is composed of 11 multilevel wells.

To be able to monitor ethanol and hydrocarbon transport in the capillary fringe, each well has sampling points above and below the water table, with ceramic suction samplers in each sampling point. Ethanol is expected to flow relatively fast and in a thin zone at the top of the capillary fringe. To be able to detect the high ethanol concentration zone, the vertical spacing between sampling points ranges from 7 to only 3 cm.

Gasoline distribution in the source zone should change with the E95 spill, similarly to what was found in the 2D visualization experiments. The consequences to contaminant transport will be verified by downgradient monitoring.

Soil gas concentrations are also being monitored to follow the volatile gasoline hydrocarbons as well as methane. Methane production is a concern in aquifers contaminated with gasoline-ethanol mixtures, since the biochemical oxygen demand is usually higher than the available oxygen within the plume, and thus anaerobic conditions are likely to develop. Ethanol anaerobic biodegradation occurs in two stages: in the first stage acetate is produced (Eq. 1) and in the second stage mineralization is accomplished by methanogens (Eq. 2

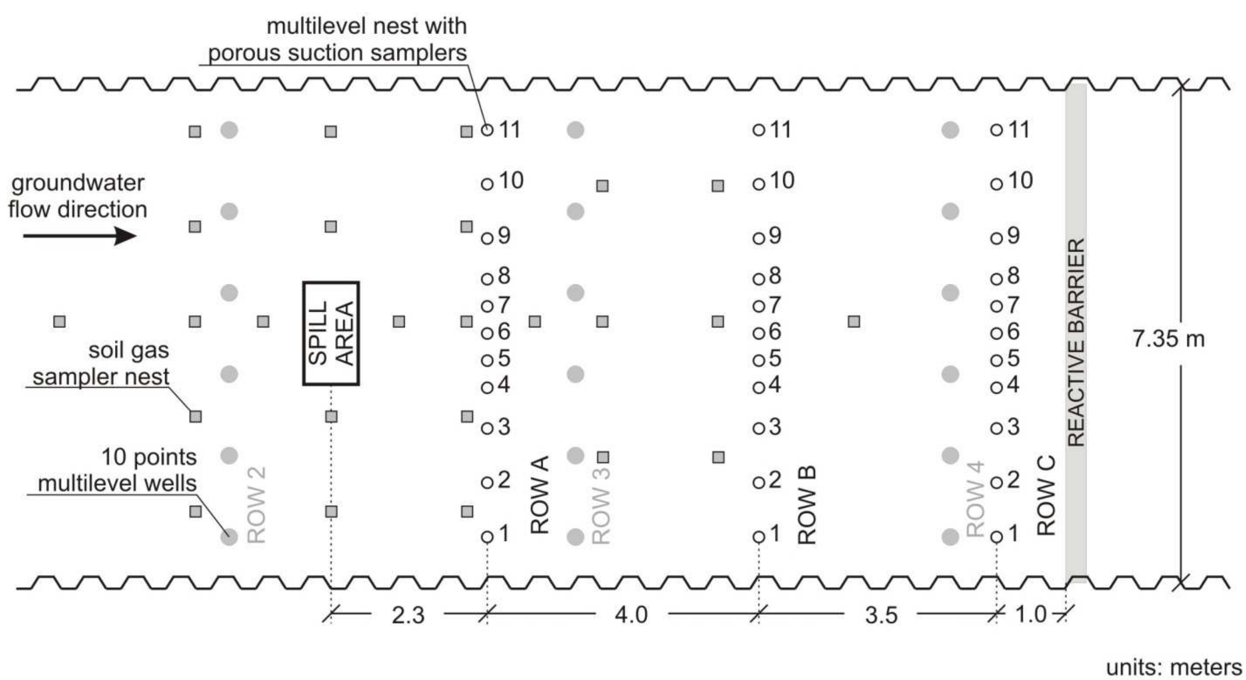

Figure 4. Site plan view

and 3).

$$CH_3CH_2OH + H_2O \rightarrow 2H_2 + CH_3COO^- + H^+ \quad [1]$$

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \quad [2]$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad [3]$$

Methane can migrate in the subsurface and reach indoor or confined spaces, such as basements and underground piping systems, leading to explosion risks. According to Gooddy et al. (2005), although the definition of a methane concentration in groundwater that will lead to explosive hazard is dependent on the confined space properties, a hazard potential exists if the partial pressure of methane is greater than 0.05 bars, which is equivalent to an aqueous concentration of 1600 µg/L.

Methane production from ethanol biodegradation is being monitored at one site in Ontario where 100m^3 of denatured ethanol (2 to 5% gasoline) was spilled in 2005, as a consequence of an accident with a train tanker car. At this site, methane concentrations up to 23 mg/L were measured in groundwater, which is clear evidence that the potential for methane generation from ethanol contaminated sites should be assessed.

5 SUMMARY

Three main issues related to E95 releases into gasoline contaminated groundwater and soils were investigated. First, E95 can mobilize the gasoline present in the source zone, changing the gasoline saturation and distribution in the subsurface, with potential consequences to source dissolution rates and to dissolved plumes. This behaviour was confirmed in a laboratory test and is being investigated in a field test.

Second, transport of ethanol and cosolubilized gasoline hydrocarbons in the capillary fringe were verified in laboratory experiments and are currently being assessed at the field scale. It was observed that transport occurs in a very thin layer at the top of the capillary fringe. A sampling technique using ceramic suction samplers was developed to monitor gasoline hydrocarbons and ethanol transport in the capillary fringe.

The third issue evaluated was the formation of hazardous concentrations of methane due to ethanol biodegradation. Methane was found in groundwater at high concentrations at one site where an E95 release occurred. These findings indicate that some of the current approaches to deal with gasoline-contaminated sites should be reviewed in the presence of high ethanol concentrations, such as methodologies for MNA.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the American Petroleum Institute, the NSERC CRD program, the Canadian Petroleum Products Institute, Water and Earth Science Associates Ltd. (WESA), Conestoga Rovers and Associates (CRA) and the Ontario Ministry of Environment. Juliana Freitas was supported by a scholarship from the Brazilian Government (CAPES - Brazil). Analyses were performed by Marianne Vandergriendt and Shirley Chatten at UW. The authors thank Vincent Martin for his help in translating the abstract.

REFERENCES

Alvarez, P.J.J. and Hunt, C.H. 2002. The Effect of Fuel Alcohol on Monoaromatic Hydrocarbon Biodegradation and Natural Attenuation. *Revista Latinoamericana de Microbiologia*, 44(2): 83-104.

Berkowitz, B., Silliman, S.E. and Dunn, A.M. 2004. Impact of Capillary Fringe on Local Flow, Chemical Migration, and Microbiology. *Vadose Zone Journal*, 3(2): 534-548.

Freitas, J.G. and Barker, J.F., in review. Sampling VOC's with Porous Suction Samplers: How much are we losing? Submitted to *Groundwater Monitoring and Remediation*.

Gooddy, D.C. and Darling, W.G., 2005. The potential for methane emissions from groundwaters of the UK. *Science of the Total Environment*, 339(1-3): 117– 126.

Henry, E.J. and Smith, J.E. 2002. The Effect of Surface-active Solutes on Water Flow and Contaminant Transport in Variably Saturated Porous Media with Capillary Fringe Effects. *Journal of Contaminant Hydrology,* 56(3-4): 247– 270.

McDowell, C.J., Buscheck, T. and Powers, S.E. 2003. Behaviour of Gasoline Pools Following a Denatured Ethanol Spill. *Groundwater*, 41(6): 746-757.

Oliveira, E. 1997. Ethanol flushing of Gasoline Residuals: Microscale and Field Experiments. Ph.D dissertation, University of Waterloo, Waterloo, ON, Canada.

Powers, S.E., Hunt, C.S., Heermann, S.E., Corseuil, H.X., Rice, D. and Alvarez, P.J.J. 2001. The Transport and Fate of Ethanol and BTEX in Groundwater Contaminated by Gasohol. *Critical Reviews in Environmental Science and Technology*, 31(1): 79–123.

Ronen, D., Scher, H. and Blunt, M. 1997. On the Structure and Flow Processes in the Capillary Fringe on Phreatic Aquifers. *Transport in Porous Media*, 28(2): 159-180.

Wilson, L.G., Everett, L.G. and Cullen, S.J. (ed).1995. *Handbook of Vadose Zone Characterization & Monitoring*. Lewis Publishers, Boca Raton, FL, USA.