

Evaluation of Small-Volume Releases of Ethanol-Blended Gasoline at UST Sites

MATTHEW A. LAHVIS
SHELL GLOBAL SOLUTIONS (US) INC.

A SUMMARY OF RESEARCH RESULTS FROM API'S SOIL & GROUNDWATER TECHNICAL TASK FORCE

In anticipation of widespread use of ethanol (EtOH) as a replacement for methyl tert-butyl ether (MTBE), transport modeling was applied to predict potential effects on ground water from small-volume releases of EtOH-blended gasoline (gasohol) in the vadose zone. In particular, mass loading rates (fluxes) and travel times of EtOH and benzene to ground water were evaluated as a function of soil type, biodegradation rate, ground-water infiltration rate, and depth to ground water. Model results indicate that migration of EtOH in the vadose zone is limited to less than 100 cm from the source for releases occurring in coarse-grained soil (sand) assuming highly conservative biodegradation- and infiltration-rate approximations. In fine-grained soil (sandy clay), EtOH transport is limited to less than 50 cm under equivalent biodegradation and infiltration conditions. In addition, the presence of EtOH in gasoline does not significantly affect benzene transport and mass loading to ground water. Travel times to ground water may be more than an order of magnitude greater for EtOH than for benzene depending primarily on the soil type, biodegradation rate, and depth to ground water. Collectively, the model results indicate that EtOH and benzene impacts on ground water from small-volume releases of EtOH-blended gasoline in the vadose zone are not expected to be significant unless the release occurs near the water table (< 100 cm) or, in the case of benzene, its biodegradation is limited.

What is the background and purpose for the study?

Recent modeling [Lahvis and Rehmann, 2000] and field studies [Dakhel et al., 2003] have shown that small-volume releases of oxygenated gasoline containing methyl tert-butyl ether (MTBE) have the potential to impact ground water at underground storage tank (UST) sites. These results are consistent with empirical ground-water data indicating enrichment of MTBE relative to benzene, toluene, ethylbenzene, and xylenes (BTEX) with respect to water in equilibrium with the gasoline source. With the acceptance of ethanol (EtOH) as the replacement for MTBE, concern exists regarding whether small-volume releases of EtOH-blended gasoline pose risks to ground water. The concern is not only over the potential for EtOH to impact ground water but also whether EtOH will enhance downward migration of the other gasoline constituents, such as BTEX, as a result of preferential EtOH biodegradation. The purpose of this study is therefore to evaluate potential effects on ground water from small-volume releases of EtOH-blended gasoline in the vadose zone. Conditions affecting transport of EtOH to ground water and potential effects of EtOH on BTEX migration are investigated. The approach used in this study is the same as that used in the previous modeling study of Lahvis and Rehmann [2000] on evaluation of small-volume releases of gasoline containing MTBE.

The magnitude, type (liquid or vapor), and occurrence of small-volume releases are currently not well understood. To date, the only investigation undertaken to address these issues was a tracer study of recently upgraded UST systems in California. The study found detectable levels of a tracer in 61% of 182 systems tested, all but one believed to be vapor related [Golding and Young, 2002]. Nearly all of the tracer releases were estimated to occur at rates < 0.04 gal d⁻¹ (liquid equivalent), with a maximum rate of 0.4 gal d⁻¹; rates well below the current liquid leak detection threshold of 2.4 gal d⁻¹ (0.1 gal hr⁻¹). The rate estimates, along with the actual type and frequency of occurrence remain in doubt, however, because of uncertainties in their mass-balance approach and the lack of field validation.

What constitutes a small-volume release of gasoline?

Small-volume releases of gasoline may be liquid or vapor and occur as a result of routine fueling operations, equipment repair, or leaky joints and connections in UST systems. In the case of a liquid release, the volume is not of sufficient magnitude for the released product to contact ground water. Rather, individual constituents of the gasoline migrate to ground water by diffusion and advection (see Figure 1). Resulting effects on ground water are a function of the magnitude (volume and rate) of product released, its composition, the physiochemical properties of the constituents that comprise the

released gasoline, and the prevailing hydrogeologic conditions of the vadose zone into which the product is released.

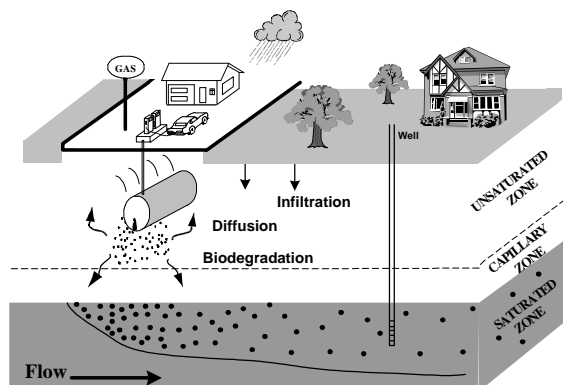


Figure 1. Conceptualization of a small-volume release at a UST site.

What approach was used in this study?

The effect on ground water from small-volume releases of EtOH-blended gasoline was achieved through model simulation using the computer model R-UNSAT, developed and documented by the U.S. Geological Survey [Lahvis and Baehr, 1997]. The model was applied to predict potential impacts of EtOH and benzene on ground water as a function of:

- distance between the source and ground water,
- soil type,
- biodegradation, and
- ground-water infiltration rate.

The computer model accounts for diffusion, ground-water infiltration, adsorption, and biodegradation processes, variable soil-moisture content, and equilibrium partitioning among the solid, aqueous, and gaseous phases. Other potential processes related to EtOH transport, such as co-solvency [Barker *et al.*, 1991; Molson *et al.*, 2002], capillarity reduction [Kowles and Powers, 1997; Powers and McDowell, 2001], and EtOH toxicity [Alvarez, 2001], are not considered because of the absence of an immiscible phase.

What scenarios were modeled?

The model was applied to simulate two-dimensional (axisymmetric) multispecies transport of EtOH, in the vadose zone. The gasoline source was assumed to contain 10 percent by volume EtOH and occur at a release rate of 120 g d^{-1} (0.04 gal d^{-1} liquid gasoline equivalent); a rate assumed to be conservative with respect to the vast majority of small-volume releases occurring at UST sites [Young and Golding, 2002]. To bracket a range of anticipated field conditions, model scenarios involved simulation of:

- 4 constituents: EtOH, benzene, a composite hydrocarbon with properties consisting of virtually all remaining gasoline constituents less EtOH and benzene, and O_2 ;
- a 3-m thick vadose zone with variable depths from the release point to ground water of 30, 100, and 200 cm;
- coarse-grained (sand) and fine-grained (sandy clay) soil types;
- depth-dependent soil moisture;
- variable biodegradation rates (half-lives) for EtOH of 0, 7, 14, and 69 days; and
- ground-water infiltration rates of 0, 10, and 20 cm yr^{-1} .

EtOH and benzene biodegradation were simulated using alternative reaction models. EtOH biodegradation was simulated according to a first-order decay model on the basis of laboratory results from Corseuil *et al.* [1998] that showed relatively little functional dependence on O_2 availability. Benzene biodegradation, which is highly sensitive to O_2 availability, was simulated according to a dual-Monod kinetics model. The capillary zone, which can have significant effects on vapor diffusion [Lahvis and Rehmann, 2000] was simulated assuming a moisture distribution based on steady infiltration in the vadose zone and soil properties classified according to van Genuchten [1980].

What were the results?

The model results are illustrated in Figures 2-5. In summary, EtOH and benzene effects on ground water are not expected to be significant for most small-volume releases of EtOH-blended gasoline unless the source is located near the water table ($z_1 < 100 \text{ cm}$), or, as in the case for benzene, its biodegradation is limited. These results contrast those for MTBE [Lahvis and Rehmann, 2000], which showed that under similar transport conditions, MTBE impacts on ground water from small-volume releases of MTBE-blended gasoline in the vadose zone could be significant.

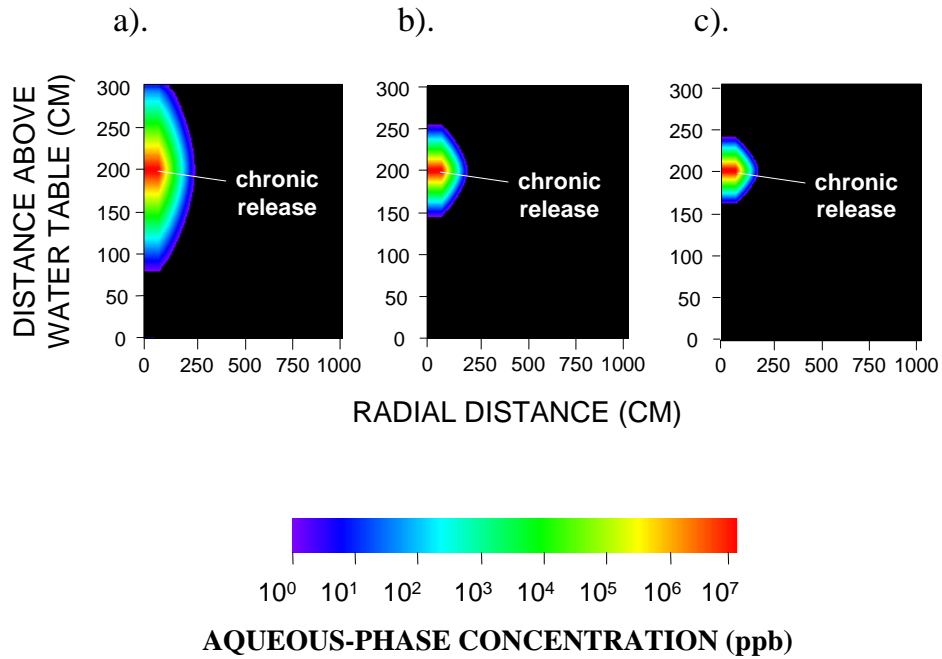


Figure 2. Steady-state distributions of EtOH in sand for a) half-life of 69 days, b) half-life of 14 days, and c) half-life of 7 days, assuming no infiltration.

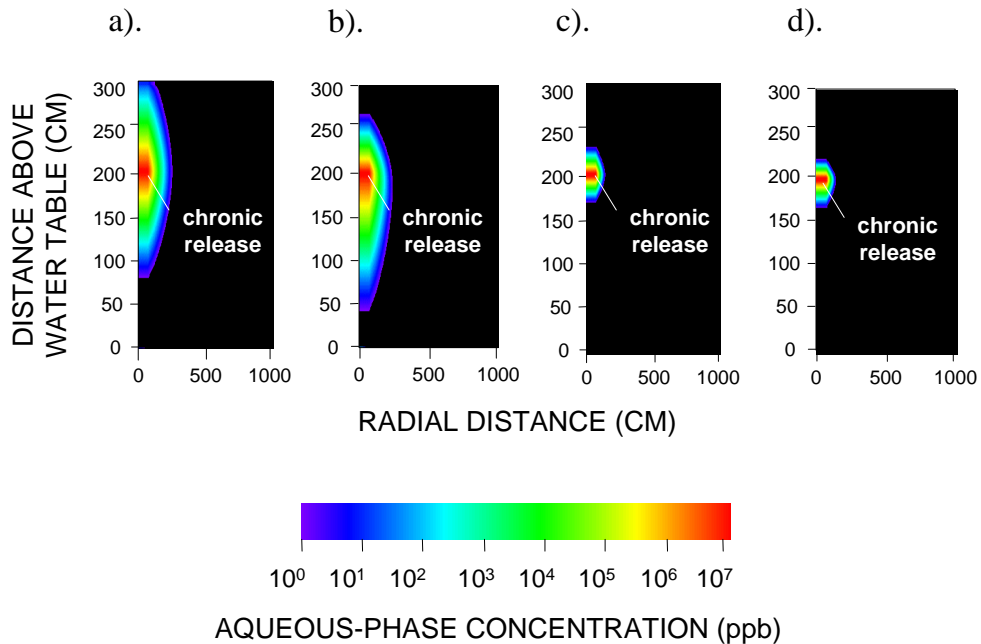


Figure 3. Steady-state distributions of EtOH for a) no infiltration and a half-life of 69 days, and b) infiltration = 20 cm yr⁻¹ and a half-life of 69 days, c) no infiltration and a half-life of 7 days, and d) infiltration = 20 cm yr⁻¹ and a half-life of 7 days.

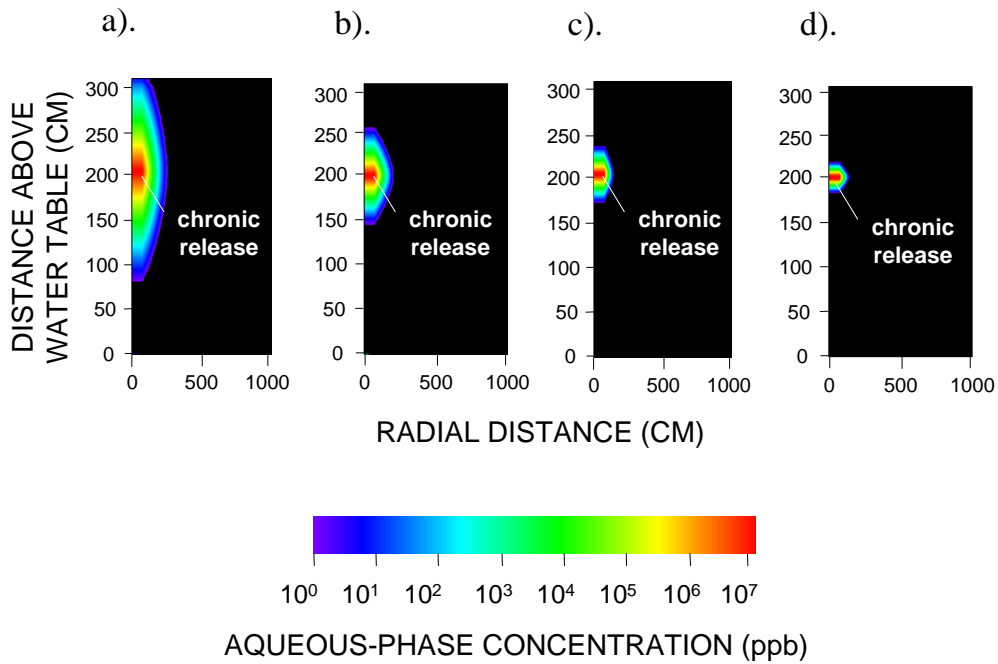


Figure 4. Steady-state distributions of EtOH in a) sand (half-life = 69 days), and b) sandy-clay (half-life = 69 days), c) sand (half-life = 7 days), and d) sandy clay (half-life = 7 days), assuming no infiltration.

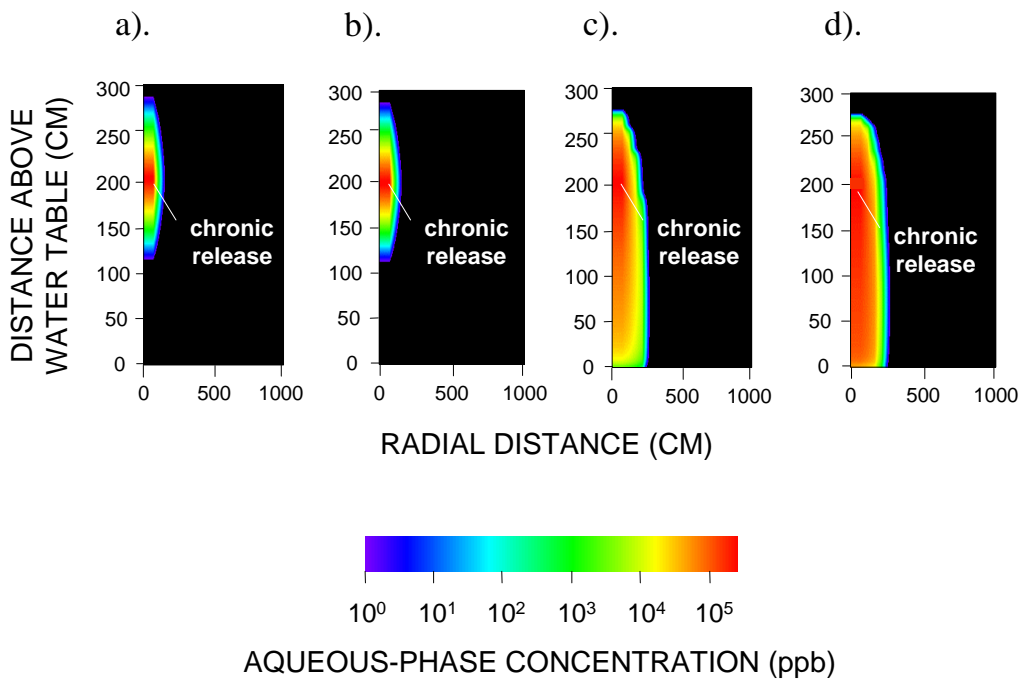


Figure 5. Steady-state distributions of benzene in a) sand (no infiltration), b) sand (infiltration rate = 20 cm yr⁻¹), c) sandy-clay soil (no infiltration), and d) sandy-clay (infiltration rate = 20 cm yr⁻¹), assuming biodegradation according to dual-Monod kinetics (half saturation constant = 0.2 g cm⁻³, maximum reaction rate = 2.5E-10 g cm⁻³ s⁻¹).

The following results relate specifically to EtOH and benzene:

EtOH

- Biodegradation limits the downward migration of EtOH to approximately 100 cm from the source assuming a highly conservative biodegradation rate (half-life of 69 days) that is more than an order of magnitude less than biodegradation rates reported in the literature (half-lives < 7 days) [Corseuil *et al.*, 1998; Howard, 1991] (see Figure 2). At anticipated biodegradation rates (half-lives < 7 days), downward migration is limited to less than 50 cm (see Figure 2c).
- Ground-water infiltration occurring at a rate of 20 cm yr⁻¹ can enhance the vertical migration of EtOH to ground water, but only when biodegradation is extremely limited (see Figure 3b). At anticipated rates of biodegradation (half-lives < 7 days), the effect of infiltration on EtOH migration is negligible (see Figures 3c and 3d).
- EtOH migration is sensitive to the soil type as illustrated in Figure 4, but only at low rates of biodegradation. The dependence is related to the effective diffusion coefficient, which is approximately 5 times less for EtOH in sandy clay than in sand. In addition, the effect of soil type on EtOH migration is considerably less than on other gasoline-range compounds (e.g., benzene) which favor migration by vapor diffusion.
- Soil moisture significantly retards EtOH transport and thus the travel time to ground water. Travel times to ground water can be more than an order of magnitude greater for EtOH than for benzene depending primarily on the soil type, biodegradation rate, and depth to ground water. Naturally, the travel time for EtOH to ground water is only a consideration for sources located in close proximity (< 50 cm) to the water table if anticipated rates of biodegradation are assumed.

These model results are consistent with those of *Dakhel et al.* [2003] that show no impacts of EtOH on ground water for small-volume sources located more than 1 m above the water table unless considerable (0.5 cm d⁻¹) ground-water infiltration is applied.

Benzene

- Transport of benzene in the vadose zone, like EtOH, is highly affected by biodegradation. In coarse-grained soils (e.g. sand), biodegradation limits transport to less than 100 cm from the source for reasonable approximations of the biodegradation rate (see Figures 5a and 5b). If, however, benzene biodegradation is limited by O₂ availability due to diffusion-limited mass

KEY VADOSE- ZONE TRANSPORT PROCESSES TO CONSIDER

| <u>Process</u> | <u>Ethanol</u> | <u>Benzene</u> |
|--|----------------|----------------|
| Vapor Diffusion | NO | YES |
| Aqueous-Phase Diffusion | YES | NO |
| Aqueous-Phase Advection (ground-water infiltration) | | |
| -- coarse-grained soil (e.g., sands, gravels) | YES | NO |
| -- fine-grained soil (e.g., silts, clays) | YES | YES |
| Aerobic Biodegradation | YES | YES |
| Anaerobic Biodegradation | YES | NO |

transport or competing reactive sources, mass loading of benzene to ground water could be at ppb levels or higher (see Figures 5c and 5d).

- The effect of ground-water infiltration on benzene transport is also related to soil type. In sand, infiltration occurring at 20 cm yr⁻¹ has a negligible effect on benzene transport because of the compound's relatively low aqueous solubility (see Figures 5a and 5b). Benzene migration can, however, be affected by infiltration under conditions where vapor diffusion is limited (see Figures 5c and 5d).
- The effect of soil type on benzene transport is also illustrated in Figure 5. Migration of benzene to ground water is enhanced in fine-grained soils (e.g. sandy clay) because aerobic biodegradation is limited below the source [Lahvis and Rehmann, 2000].
- Preferential biodegradation of EtOH has only a minor effect on benzene transport. In coarse-grained soils (e.g. sand), benzene migrates far ahead of EtOH, precluding any limitations caused by EtOH degradation near the source. In fine-grained soil (e.g. sandy clay), the effects of preferential EtOH biodegradation are eclipsed by limitations on O₂ availability associated with biodegradation of benzene and other reactive gasoline constituents.
- Travel time for benzene to ground water is primarily a function of the depth to ground water and soil type.

What key parameters affect transport of EtOH and benzene to ground water?

EtOH and benzene migrate in the vadose zone via contrasting mechanisms because of differences in aqueous/vapor-phase partitioning (Henry's Law) and biodegradation behavior.

EtOH

- EtOH partitions strongly to the aqueous phase as reflected by its extremely low Henry's constant ($H_k = 0.00024$). The primary processes affecting EtOH transport are thus aqueous-phase diffusion, aqueous-phase advection (caused by infiltrating recharge water) and biodegradation.
- Biodegradation is the most critical factor affecting the transport of EtOH because of the compound's susceptibility to microbial metabolism, affinity for the aqueous phase, and slow rate of transport in the vadose zone relative to other less soluble gasoline compounds. The sensitivity to biodegradation increases in coarse-grained soil at half-lives > 14 days (see Figures 2a and 2b).
- Over the range of simulated rates ($0 - 20 \text{ cm yr}^{-1}$), the effects of infiltration on EtOH transport are relatively insignificant; in particular, if biodegradation is occurring at anticipated rates (half lives < 7 days). It is important to note, however, that these results are based on assuming a constant infiltration rate. Actual rates associated with individual precipitation events could be much greater, affecting EtOH transport more than was demonstrated in this study.
- Key factors to consider in evaluating potential impacts of EtOH on ground water are the depth to ground water and the soil moisture content.

Benzene

- Benzene, by contrast, has a much higher Henry's constant than EtOH ($H_k = 0.18$) and tends to migrate in the vadose zone by vapor diffusion. Benzene transport is therefore highly sensitive to soil type (i.e., air-filled porosity) and is relatively unaffected by the aqueous-phase processes (diffusion and advection) that affect EtOH migration, unless vapor diffusion is severely limited as occurs in fine-grained soils.
- Like EtOH, benzene transport to ground water can be significantly affected by biodegradation; however, its significance is critically dependent on O_2 availability. Under conditions where O_2 is readily available, benzene transport is limited and the potential for ground water impacts is small. If O_2 concentrations are depleted (i.e., anaerobic conditions exist), either by the presence of competing sources or by restrictions on O_2 diffusion, then the potential for benzene to impact ground water is greatly increased.

- Key factors to consider in evaluating potential impacts of benzene on ground water are the depth to ground water and whether biodegradation is limited in the vadose zone.

References

- Alvarez, P. J. J., 2001, *Effect of ethanol on BTEX natural attenuation: Biodegradation, kinetics, geochemistry, and microbial community implications*, in Proceedings of the Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California, April 10-11, Oakland, California, Lawrence Livermore National Laboratory.
- Barker, J. F., Gilham, R. W., Lemon, L., Mayfield, C. I., Poulson, M., and E. A. Sudicky, 1991, *Chemical fate and impact of oxygenates in groundwater: Solubility of BTEX from gasoline-oxygenate compounds*, Report prepared for the American Petroleum Institute Publication Number 4531, American Petroleum Institute, Washington, D.C., 90 p.
- Corseuil, H. X., Hunt, C. S., dos Santos Ferreira, R., and P. J. J. Alvarez, 1998, *The influence of the gasoline oxygenate ethanol on aerobic and anaerobic BTEX biodegradation*, *Wat. Resour. Res.*, 32, 2065-2072.
- Dakhel, N., Pasteris, G., Werner, D., and P. Hohener, 2003, *Small-volume releases of gasoline in the vadose zone: Impact of the additives MTBE and ethanol on groundwater quality*, *Env. Sci. Technol.*, 10, 2127-2133.
- Howard, P. H., 1991, *Handbook of Environmental Degradation Rates*, Lewis Publishers, Chelsea, Michigan, 725 p.
- Kowles, J., and S. E. Powers, 1997, *Reformulated gasolines: Effects on ethanol on the interfacial tension between gasoline and water*, Undergraduate Research Thesis, Clarkson University, Potsdam, New York.
- Lahvis, M. A., and A. L. Baehr, 1997, *Documentation of R-UNSAT, a computer model for the simulation of reactive, multispecies transport in the unsaturated zone*, U.S. Geological Survey Open-File Report 97-630, 104 p.
- Lahvis, M. A. and L. C. Rehmann, 2000, *Simulation of transport of methyl tert-butyl ether (MTBE) to groundwater from small volume releases of gasoline in the vadose zone*, American Petroleum Institute Soil and Groundwater Research Bulletin, No. 10. American Petroleum Institute, Washington, D.C. 8 p.
- Lahvis, M. A., 2003, *Simulation of the Effects on Ground Water From Small-Volume Releases of Ethanol-Blended Gasoline in the Vadose Zone*, in Proceedings of the 2003 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation, Houston, Texas, August 19-22, 2003, National Ground Water Association, Westerville, Ohio.
- Molson, J. W., Barker, J.F., and Frind, E.O., and M. Schirmer, 2002, *Modeling the impact of ethanol on the persistence of benzene in gasoline-contaminated groundwater*, *Wat. Resour. Res.*, 38, 1-12.
- Powers, S. E., and C. J. McDowell, 2001, *Mechanisms affecting the infiltration and redistribution of ethanol-blended gasoline in the vadose zone*, in Proceedings of the 2001 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation, Houston, Texas, November 14-16, 2001, National Ground Water Association, Westerville, Ohio, 32-40.
- van Genuchten, T. T., 1980, *A closed form equation for predicting hydraulic conductivity of unsaturated soils*, *Soil Sci. Soc. Amer. J.*, 44, 892-898.
- Young, T. M., and R. D. Golding, 2002, *Underground storage tank system field-based research project report*, Paper submitted to the California State Water Resources Control Board, Sacramento, California, 22 p.
<http://www.swrcb.ca.gov/cwphome/ust/docs/fbr/index.htm>

About The Author

Matthew A. Lahvis holds a Bachelor's Degree in Geology from Bucknell University, a Master's Degree in Engineering Geology from Drexel University, and a Ph. D. in Civil Engineering from Drexel University. His research focuses on quantifying fate and transport of petroleum compounds in the unsaturated zone at gasoline-spill sites. He developed several mathematical models, most notably, R-UNSAT, a model for the simulation of reactive transport in the unsaturated zone. Matt joined the New Jersey District office of the U.S. Geological Survey in 1989 and was involved in the assessment of vapor transport at three prominent research sites in Galloway Township, New Jersey, Laurel Bay, South Carolina, and Bemidji, Minnesota. Research activities included installation of large soil-gas monitoring networks, field experiments to quantify physical properties of unsaturated-zone sediments and the performance of bioventing remediation, and the development of analytical techniques for soil-gas sampling. Matt also served as an adjunct professor in the Civil Engineering Department at Drexel University from 1995-1999. In March 2000, Matt joined Shell Global Solutions in Houston, Texas, as a senior consultant. He directs hydrogeology support for Shell and the Shell Alliance, provides technical training pertaining to vapor intrusion and oxygenate assessment and remediation, and develops corporate guidance on remediation strategies and site investigations.

About The API Soil and Groundwater Technical Task Force

The API Soil and Groundwater Technical Task force provides an expert, multidisciplinary focal point within API to address soil and groundwater issues. The Task Force identifies and defines emerging technical issues develops research programs to address these issues. API-sponsored research yields practical tools and basic science for risk-based, cost-effective solutions to the oil and natural gas industries' soil and groundwater protection problems. The Task Force disseminates information and research results through publications, presentations and interaction with industry clients and regulatory agencies.

Acknowledgements

API wishes to acknowledge the API Soil and Groundwater Technical Task Force (S/GTTF), particularly the following individuals who contributed to this document:

Curtis Stanley, Shell Global Solutions (US) Inc. (Chairman, S/GTTF)

Tim Buscheck, ChevronTexaco

Sanjay Garg, Shell Global Solutions (US) Inc.

Harley Hopkins, American Petroleum Institute

Ravi Kolhatkar, BP p.l.c.

Victor Kremesec, BP p.l.c.

Norm Novick, Exxon Mobil Corporation

Xiaomin Yang, BP p.l.c.

Notice

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability of responsibility for loss or damage resulting from its use or for the violation of any federal, state, or municipal regulation with which this publication might conflict.

This publication may be downloaded from API's Groundwater Protection Website at <http://www.api.org/bulletins>

Information about API Publications, Programs and Services is available on the World Wide Web at <http://www.api.org>



**American
Petroleum
Institute**

1220 L Street, Northwest
Washington, D.C. 20005-4070
202-682-8000