

Evaluation of Potential Vapor Transport to Indoor Air Associated with Small-Volume Releases of Oxygenated Gasoline in the Vadose Zone

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

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

Potential human exposure from vapor transport to indoor air is evaluated for small-volume releases of oxygenated gasoline in the vadose zone at underground storage tank (UST) sites. For this analysis, potential human exposure is defined by model simulation as the distance at which benzene concentrations exceed $3.1 \mu\text{g m}^{-3}$, a proposed 10^{-6} risk-based screening level for shallow soil gas. Transport in the vadose zone was simulated assuming one- and two-dimensional model geometries, a range of biodegradation rates, and conservative (default) model parameters. Under anaerobic conditions, benzene is predicted to exceed the risk-based screening level in the vadose zone at distances ranging from approximately 55 ft. to 100 ft. from the source, depending primarily on model geometry. If benzene biodegradation is linked to oxygen availability, the distance over which there is a potential for risk reduces to less than 10 ft. Considering that the distances to nearest receptor will likely exceed model predicted estimates at most UST sites and that anaerobic conditions will be limited in extent in soils conducive to vapor transport, small-volume releases of oxygenated gasoline are not expected to pose a significant risk for vapor intrusion at UST sites.

What is the background and purpose for the study?

Data from field sites and a recent tracer investigation [Young and Golding, 2002] indicate that small-volume gasoline releases are currently more common than large-scale releases at underground storage tank (UST) sites. Potential risks to human health and the environment posed by these types of releases thus need to be fully examined. Previous modeling [Lahvis and Rehmann, 2000; Lahvis, 2003] and field [Dakhel et al., 2003] studies focused on potential impacts to groundwater posed by methyl tert-butyl ether, ethanol, and benzene. Potential risks associated with the vapor transport to indoor air pathway have never been evaluated.

The purpose of this study is to assess potential human exposure to vapor intrusion from a small-volume release of oxygenated gasoline in the vadose zone. The potential for exposure was defined by model calibration as the lateral offset distance at which benzene concentrations exceed a 10^{-6} risk-based screening level of $3.1 \mu\text{g m}^{-3}$ for shallow soil gas assuming a slab attenuation factor of 0.1 [Environmental Protection Agency, 2002]. This approach, therefore, does not consider mass flux in the exposure assessment.

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 groundwater. Rather, individual constituents of the gasoline migrate to groundwater by diffusion and advection. Resulting effects on groundwater are a function of the magnitude (volume and rate) of product released, its composition, the physiochemical properties of the constituents that compose the released gasoline, and the prevailing hydrogeologic conditions of the vadose zone into which the product is released.

The magnitude, type (liquid or vapor), and occurrence of small-volume releases are poorly understood. To date, the only investigation undertaken to address these issues was tracer study of recently upgraded UST systems in California. The study found detectable levels of tracer in 61% of 182 systems tested, all but one release was believed to be vapor related [Young and Golding, 2002]. Virtually all of the small-volume releases were estimated to occur at rates $< 0.04 \text{ gal d}^{-1}$ (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 uncertainty in mass-balance calculations and the lack of field validation.

What approach was used in this study?

Benzene transport in the vadose zone was simulated using the computer code R-UNSAT, developed and documented by the U.S. Geological Survey [Lahvis and Baehr, 1997]. The transport model accounts for diffusion, groundwater infiltration, adsorption, and biodegradation processes, variable soil-moisture content, and equilibrium partitioning among the solid, aqueous, and gaseous phases. As shown in Figure 1, the model was applied to simulate steady-state transport in one (Scenario 1) and two (Scenario 2) dimensions. Scenario 1 represents a case where vapor migration is confined between a capped surface cover (e.g., asphalt pavement) and the water table, both impervious to vapor transport. The source is vertically distributed across the entire thickness of the vadose zone, from land surface to the water table. Scenario 2 represents a case where the source is positioned at a finite depth (366 cm) below land surface, commensurate with the default basement mixing height defined in *Environmental Protection Agency* [2002]. The far-lateral and water table boundaries were established at distances defined from initial model simulations that were designed to minimize effects on vapor transport. For assessing risk, Scenario 1 represents the more conservative case; Scenario 2, represents the more realistic case. Model assumptions for both scenarios include:

- a small-volume release rate of 120 g d^{-1} (0.04 gal d^{-1} liquid gasoline equivalent) assumed to be representative of the upper-bound rate for the vast majority of small-volume releases occurring at UST sites [Young and Golding, 2002];
- a gasoline source containing 10 percent by volume ethanol and 1.4 percent by volume benzene, assumed to be consistent with the composition reported in *California Environmental Protection Agency* [1988];
- a homogeneous vadose zone consisting of sand at a residual moisture saturation of 0.053 (a default value recommended by the *Environmental Protection Agency* [2002]);
- variable biodegradation rates (half-lives) for benzene ranging from 0.69 - 69,000 days; and,
- no groundwater infiltration.

In Scenario 2, the lateral offset distance was defined as the minimum distance necessary to achieve a target concentration for benzene in soil gas of $3.1 \mu\text{g m}^{-3}$ at the depth of the basement foundation (366 cm).

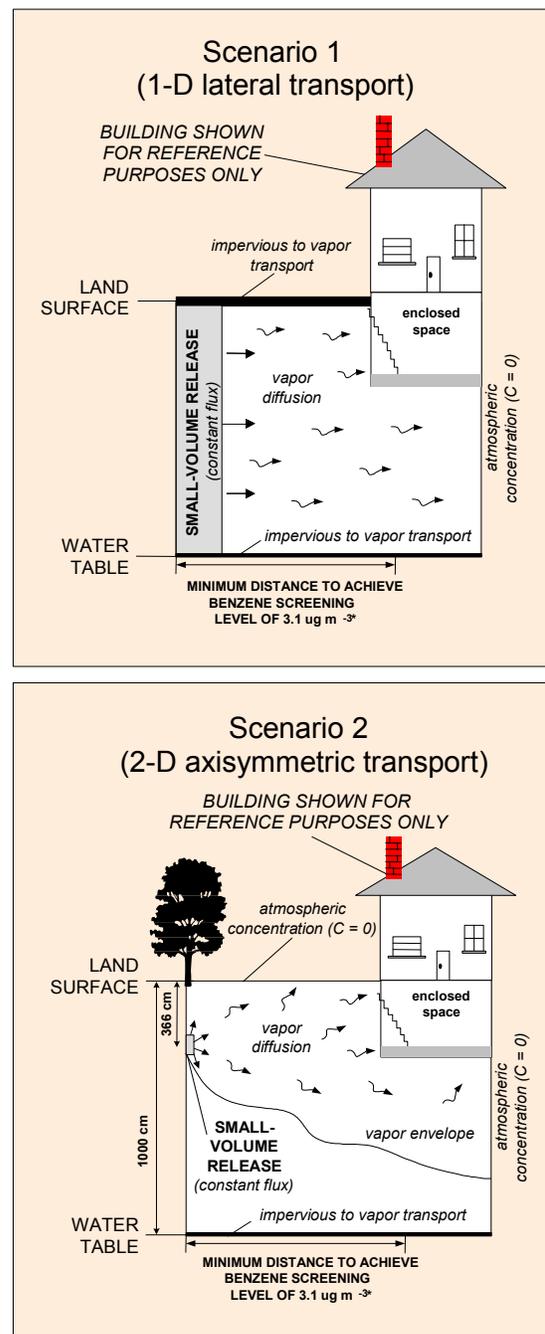


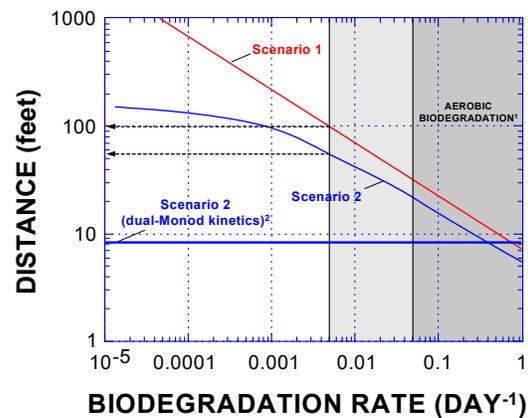
Figure 1. Model geometry and boundary conditions used in model simulations. The buildings shown in Figure 1 are used for reference only and were not part of the model simulation.

What were the results?

The potential for exposure to vapor intrusion varied depending on the model geometry (i.e. Scenario 1 or Scenario 2) and the biodegradation rate (see Figure 2). Assuming benzene biodegrades at rates greater than 0.05 d^{-1} (14 d half-life) consistent with aerobic biodegradation, the distance over which there is a potential for exposure to vapor intrusion ranges from approximately 20 (Scenario 2) to 30 ft. (Scenario 1). Assuming a conservative biodegradation rate of 0.005 d^{-1} (140 d half-life), consistent with anaerobic biodegradation, the distance increases to approximately 55 ft. (Scenario 2) to 100 ft. (Scenario 1). By comparison, if the benzene biodegradation rate is linked to oxygen (O_2) availability (e.g., dual-Monod kinetics), the lateral distance reduces to less than 10 ft. in sand (see Figure 2) [Lahvis, 2003]. Moreover, this result implies that anaerobic conditions should only occur within 10 ft. of a small volume release source. Given that residences would typically be located well beyond this distance at UST sites, small-volume releases of oxygenated gasoline (specifically) are not expected to pose a risk for vapor intrusion. Potential risk for vapor intrusion may, however, exist within a 100 ft. radius of the release, if O_2 is limited, say for example, by the presence of an additional petroleum source(s), unrelated to the small-volume release.

What key parameters affect transport of benzene transport in the vadose zone?

Benzene will tend to migrate in the vadose zone in the gaseous phase rather than the aqueous phase, unless vapor diffusion is severely limited, as can occur in fine-grained soils. Consequently, benzene transport is typically more sensitive to factors that affect vapor diffusion (e.g., soil type), than to factors that affect aqueous-phase transport (e.g., groundwater infiltration). Benzene transport can also be affected by biodegradation and, in turn, O_2 availability. Under conditions where O_2 is readily available, the vapor intrusion pathway will be limited. The potential for vapor transport to indoor air would increase, however, if O_2 is depleted by the presence of sinks unrelated to the small-volume release. In summary, the key factors to consider in evaluating the potential risk to vapor intrusion are distance between the source and receptor, and O_2 availability.



¹ from DeVaul et al. [1997]

² based on results from Lahvis [2003]

Figure 2. Lateral distances needed to meet a soil screening level for benzene in shallow soil gas of 3.1 ug m^{-3} .

References

- California Environmental Protection Agency, 1988, *Leaking underground fuel (LUFT) field manual*, California State Water Resources Control Board, State of California, Sacramento, California, May 1988.
- 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.
- DeVaul, G.E., Ettinger, R.A., Salanitro, J.P., and Gustafson, J.B., 1997, Benzene, toluene, ethylbenzene, and Xylenes (BTEX) degradation in vadose zone soils during vapor transport: First-order rate constants, in, *Proceedings of the 1999 Petroleum Hydrocarbons and Organic Chemicals in Ground Water – Prevention, Detection, and Remediation Conference, November 12-14, Houston, Texas*, Ground Water Publishing Company, Westerville, Ohio, 365-379.
- Environmental Protection Agency, 2002, *Draft guidance for evaluating the vapor intrusion to indoor air pathway from groundwater and soils: Subsurface vapor intrusion guidance*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response (OSWER), Washington D.C.
- Lahvis, M. A., 2003, *Evaluation of Small-Volume Releases of Ethanol-Blended Gasoline at UST Sites*, American Petroleum Institute Soil and Groundwater Research Bulletin, No. 19. American Petroleum Institute, Washington, D.C. 8 p. <http://www.api.org/bulletins>
- 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. <http://www.api.org/bulletins>
- 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/ust/leak_prevention/fbr/docs/FBR_Final_Report.pdf

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 and 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 issues. 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, Atlantic Richfield Company

Victor Kremesec, Atlantic Richfield Company

Norm Novick, Exxon Mobil Corporation

Adolfo Silva, Canadian Petroleum Products Institute

Xiaomin Yang, Atlantic Richfield Company

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