

Maximum Potential Impacts of Tertiary Butyl Alcohol (TBA) on Groundwater from Small-Volume Releases of Ethanol-Blended Gasoline in the Vadose Zone

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

Transport modeling was applied to predict maximum potential tertiary butyl alcohol (TBA) impacts on groundwater from small-volume releases of ethanol (EtOH)-blended gasoline in the vadose zone. TBA may be present in EtOH-blended gasoline as a result of processes used to manufacture EtOH for use in motor fuel or be produced in the subsurface through biotransformation of methyl tert-butyl ether (MTBE), a potential impurity in EtOH-blended gasoline.

The upper-bound concentration of TBA in groundwater was predicted by applying particularly conservative source and transport assumptions. In particular, the small-volume release was defined assuming a maximum release of TBA into the vadose zone (based on a conservative small-volume release rate of 0.04 gal d⁻¹, a source containing 0.6 percent by volume MTBE, and complete and immediate biotransformation of MTBE to TBA), a source in close proximity (30 cm) to the water table, and no biodegradation of TBA in the vadose zone.

Concentrations of TBA at the water table in the source zone predicted by transport modeling ranged from approximately 10 to 1,000 ppb for reasonable approximations of groundwater flow. Actual concentrations of TBA observed in monitoring wells are likely to be substantially less than these values due to dilution attenuation in the saturated zone. Further, the assumptions used to define the amount of TBA produced from a small-volume release, were particularly conservative. TBA concentrations observed in domestic or public supply wells are expected to be below levels of detection (approximately 5 µg/L), unless the wells are located immediately adjacent to and directly downgradient from the source zone.

What is the background and purpose for the study?

With acceptance of ethanol (EtOH) as the replacement for methyl tert-butyl alcohol (MTBE) in reformulated gasoline, concern exists regarding whether small-volume releases of EtOH-blended gasoline pose risks to groundwater at underground storage tank (UST) sites. Recent modeling [Lahvis, 2003] and field studies [Dakhel et al., 2003] have shown that EtOH and benzene concentrations in groundwater will be insignificant (< 10 µg/L) unless the source is located in close proximity (< 0.5 m) to the water table, groundwater infiltration is significant (> 100 cm yr⁻¹) or biodegradation is limited. These results are in stark contrast to results of previous modeling [Lahvis and Rehmann, 2000] and field studies [Dakhel et al., 2003], showing groundwater could be impacted by small-volume releases of

oxygenated gasoline containing MTBE. EtOH and MTBE, however, may not be the only oxygenates of environmental concern in reformulated gasoline. For example, tert-butyl alcohol (TBA) could be present in EtOH-blended gasoline as a result of processes used to manufacture EtOH for use in motor fuel or TBA could be produced in the vadose zone by biotransformation of MTBE, a potential impurity of EtOH-blended gasoline.

The aim of this study was to predict the maximum concentration of TBA that could occur in groundwater associated with a small-volume release of EtOH-blended gasoline in the vadose zone. Conservative source and transport assumptions were applied. The approach used in this study is similar to that applied in previous modeling studies of Lahvis and Rehmann [2000] and Lahvis [2003].

How is TBA associated with EtOH-blended gasoline?

TBA may be present in EtOH-blended gasoline as a result of processes used to manufacture EtOH for use in motor fuel. For example, TBA may be used as a denaturant in pure-grade EtOH [Linder, 2000], or could be present in pure-grade EtOH as a byproduct of alcohol fermentation [Tibelius, 1996]. According to current regulations, EtOH-blended gasoline could also contain small amounts of MTBE [California Environmental Protection Agency, 2003], which could be potentially biodegraded to TBA in the vadose zone. EtOH-blended gasoline is currently allowed to contain up to 0.3 percent by volume MTBE. Prior to July 2004, the allowable fraction in reformulated gasoline (RFG) sold or distributed in California was 0.6 percent by volume MTBE. In December 2005, 0.15 percent by volume MTBE is the allowable fraction. These percentages are well below the 11 percent by volume MTBE that RFG contained before the 2003 phaseout.

What constitutes a small-volume release of gasoline?

Small-volume releases of gasoline may be liquid or vapor related, and can result from routine fueling operations, equipment repair, or leaky joints and connections in UST systems. The magnitude, type (liquid or vapor), and occurrence of small-volume releases are poorly understood. To date, the only investigation undertaken to address small-volume releases 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]. Nearly all of the small-volume 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 uncertainty in their mass-balance approach and the lack of field validation. In the case of small-volume liquid releases, the volume is not of sufficient magnitude for the liquid product to contact groundwater. Rather, individual constituents of the liquid product 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.

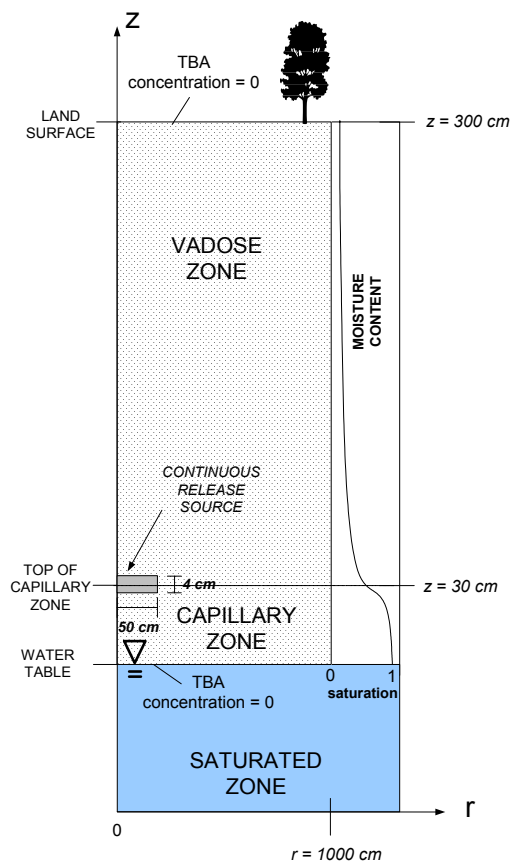


Figure 1. Model geometry and boundary conditions for simulation of a continuous small-volume release of EtOH-blended fuel in the vadose zone.

What approach was used in this study?

TBA 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. Gaseous-phase advection is not considered because this process is assumed to be negligible for compounds, such as TBA, which strongly partition to the aqueous phase.

The model was applied to simulate two-dimensional (axisymmetric) steady-state transport in a variably saturated vadose zone, assuming a variable (hydrostatic) moisture condition based on soil properties defined by van Genuchten [1980]. The model geometry and boundary conditions for this application are illustrated in Figure 1.

In order to determine an upper-bound concentration of TBA in groundwater, very conservative source and transport assumptions were applied. In particular, the model scenario involved:

- a small-volume release rate of 120 g d⁻¹ (0.04 gal d⁻¹ liquid gasoline equivalent) representative of the upper-bound rate for the vast majority of small-volume releases occurring at UST sites [Young and Golding, 2002];
- a source consisting of 10 percent EtOH and 0.6 percent MTBE;
- complete and instantaneous transformation of the MTBE to TBA by microbial degradation, resulting in a constant concentration of 0.6 percent TBA at the source;
- no biodegradation of TBA in the vadose zone;
- a sand vadose zone;
- a continuous release source located just above (30 cm) the water table, representative of the top of the capillary zone;
- a zero concentration boundary at the water boundary table; and
- a groundwater infiltration rate of 20 cm yr⁻¹.

Transport modeling provides estimates of the mass flux (or mass-loading rate) of TBA to groundwater. In the absence of biodegradation, the mass-loading rate to groundwater is proportional to the rate of groundwater infiltration and rate of diffusion across the water table (which, in turn, is proportional to the concentration gradient across the water table). The concentration at the water table is directly proportional to the rate at which TBA enters groundwater (i.e., the mass-loading rate) and the rate at which TBA migrates laterally (from the source area) in groundwater. The water-table concentration can be related to a groundwater concentration by assuming a dilution attenuation factor that accounts for mixing and dispersion in the saturated zone [Environmental Protection Agency, 1996].

What were the results?

Simulation of the small-volume release resulted in the steady-state distribution of TBA illustrated in Figure 2. Because there is no mass loss of TBA to the atmosphere or as a result of biodegradation in the vadose zone, the mass-loading rate of TBA to groundwater (0.71 g d⁻¹) is equivalent to the release rate from the source. TBA concentrations at the water table in the source zone corresponding to this mass-loading rate range from approximately 10 to 1,000 ppb depending on the groundwater flow rate (see Figure 3). Actual concentrations of TBA observed in monitoring wells are likely to be substantially less than these values depending on the extent of dilution attenuation in the saturated zone. For example, concentrations of TBA in groundwater would be more than an order of magnitude less than these

values assuming a dilution attenuation factor based on reasonable approximations of source size (50 ft), groundwater flow (0.1 ft d⁻¹), and dissolved plume thickness (10 ft). As noted previously, the assumptions used to define the amount of TBA produced from a small-volume release, were also particularly conservative.

Based on the mass-loading rate of TBA to groundwater predicted by transport modeling (0.71 g d⁻¹), dissolved-phase concentrations are expected to be below levels of detection (approximately 5 µg/L) in the vast majority of domestic or public supply wells if typical effects of mixing and dilution are assumed. For example, the maximum potential concentration of TBA achievable in a supply well would be approximately 5 µg/L assuming well discharge at a rate > 25 gal min⁻¹, complete plume capture by the well, constant and steady state flow (rate and direction), and no mass loss between the source and the well.

What key parameters affect transport of TBA to groundwater?

TBA partitions strongly to the aqueous phase as reflected by its extremely low Henry's constant (0.00048). Aqueous-phase transport processes (i.e., aqueous-phase diffusion and aqueous-phase advection caused by infiltrating recharge water) will thus govern TBA transport in the vadose zone. Because aqueous-phase transport processes (diffusion, in particular) are slow relative to vapor-phase transport processes, transport of TBA to groundwater will be slow relative to benzene, toluene, ethylbenzene, and xylenes (BTEX) and other more volatile gasoline constituents that favor transport in the vapor phase, especially when groundwater infiltration is limited. Further, because aqueous-phase diffusion is slow relative to aqueous-phase advection, small differences in the groundwater infiltration rate could cause significant differences in both concentrations of TBA in groundwater and travel times of TBA to groundwater (especially for sources located well above the water table). TBA transport to groundwater may also be sensitive to aerobic biodegradation in the vadose zone [Bradley *et al.*, 2002] although this pathway was not evaluated in this investigation. In summary, the key processes to consider in evaluating potential impacts of TBA on groundwater are depth to groundwater, groundwater infiltration, and biodegradation.

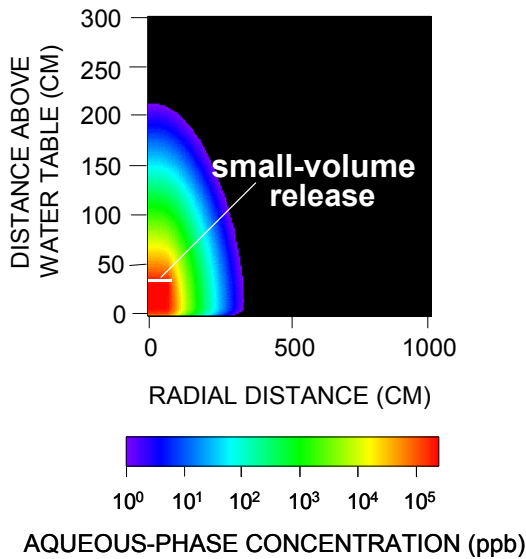


Figure 2. Steady-state distribution of TBA in sand assuming an infiltration rate of 20 cm yr^{-1} and no biodegradation.

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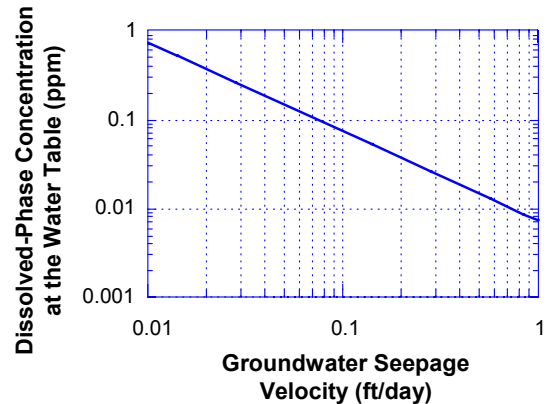


Figure 3. Dissolved phase concentrations of TBA in the source zone at the water table as a function of groundwater seepage velocity.

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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.

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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.

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NOTES

API Research Relevant to Characterizing Small Mass Releases of Petroleum Hydrocarbons

Simulation of Transport of Methyl Tert-Butyl Ether (MTBE) to Groundwater from Small-Volume Releases of Gasoline in the Vadose Zone

API Soil and Groundwater Research Bulletin No. 10

June 2000

<http://api-ep.api.org/filelibrary/bulletin10.pdf>

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

API Soil and Groundwater Research Bulletin No. 19

October 2003

http://api-ec.api.org/filelibrary/19_Bull.pdf

Evaluation Of Potential Vapor Transport To Indoor Air Associated With Small-Volume Releases Of Oxygenated Gasoline In The Vadose Zone

API Soil and Groundwater Research Bulletin No. 21

January 2005

http://api-ec.api.org/filelibrary/21_Bull.pdf

Groundwater Remediation Strategies Tool

API Publication 4730

December 2003

http://api-ec.api.org/filelibrary/4730_Final.pdf

Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE

API Publication 4699

February 2000

<http://api-ep.api.org/filelibrary/4699c.pdf>

Groundwater Sensitivity Toolkit

API Publication 4722

August 2002

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