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

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SUMMARY

Mathematical model simulations are used to predict the extent of groundwater contamination at gasoline-release sites where chronic and single small-volume releases of gasoline remain trapped in the unsaturated (vadose) zone. A vadose-zone transport model was used to predict mass fluxes (loading rates) and break-through times of methyl tert-butyl ether (MTBE) and benzene at the water table resulting from such releases. Mass transport to groundwater was quantified as a function of groundwater recharge rate, sediment (soil) type, depth to groundwater, biodegradation, and gasoline composition. Simulation results indicate that groundwater recharge had the greatest effect on mass-loading rates to groundwater because diffusive transport is limited in the capillary zone. Diffusion to the atmosphere and biodegradation also significantly affected the amount of contaminant mass available to enter groundwater. Mass loss to the atmosphere was determined largely by the proximity of the gasoline release to land surface and by soil type. This can be an important natural-attenuation pathway for MTBE, given that it is relatively slow to biodegrade. However, recharge can limit MTBE mass losses to the atmosphere, especially in fine-grained soils. For benzene, biodegradation in the vadose zone was a substantial limitation on mass loading to groundwater. Water that recharges an aquifer beneath a release site can therefore be enriched in MTBE relative to benzene compared to water that is in equilibrium with gasoline. Model-simulated breakthrough times for MTBE at the water table ranged from days to hundreds of years, depending primarily on depth to groundwater and soil type.

INTRODUCTION

The magnitude and rate of a petroleum-product release in the vadose zone determines whether the product migrates to the water table. Even in the case of a small-volume release, direct contact with groundwater is not necessary to cause groundwater contamination. For example, constituents of gasoline can reach the water table by groundwater recharge and vapor diffusion, as shown in Figure 1. Small-volume releases can be chronic or incidental, and can be associated with leaks from underground storage tank systems (including secondary vapor recovery) and the refueling of gasoline-powered equipment. At these release sites, groundwater contamination by MTBE, a gasoline oxygenate, is a potential concern. MTBE is more water-soluble, less well sorbed, and less likely to be biodegraded than other components of gasoline, such as benzene, toluene, ethylbenzene, and xylenes (BTEX). As a result, groundwater at these sites can exhibit high concentrations of MTBE relative to BTEX and other hydrocarbons (Rong, 1999). Simulations to compare the transport of MTBE and benzene in the vadose zone can be used to help explain these types of occurrences.

This report describes the results of a modeling study performed by the U.S. Geological Survey and API designed to simulate the effects on groundwater of small-volume releases of ether-oxygenated gasoline in the vadose zone. Mass fluxes (loading rates) and breakthrough times of MTBE and benzene to groundwater are predicted as a function of recharge, soil type, depth to groundwater, biodegradation, and gasoline composition. The effects on groundwater are determined for both chronic (constant) and incidental (time-dependent, finite) sources of gasoline that are immobile within the vadose zone.

MODEL DESCRIPTION AND MODEL SCENARIOS

The computer model R-UNSAT, developed and documented by the U.S. Geological Survey (Lahvis and Baehr, 1997; Lahvis and Baehr, 1998), was used to simulate the transport of chemicals of interest in the vadose zone. The model was designed to simulate multispecies transport in a vadose zone with variable moisture content. Diffusion, recharge, sorption, and biodegradation processes were simulated. Equilibrium partitioning among the immiscible, solid, aqueous, and gaseous phases was assumed.

Model scenarios involved simulation of MTBE, benzene, and oxygen transport. Simulation of oxygen transport was required in order to simulate benzene biodegradation. MTBE was
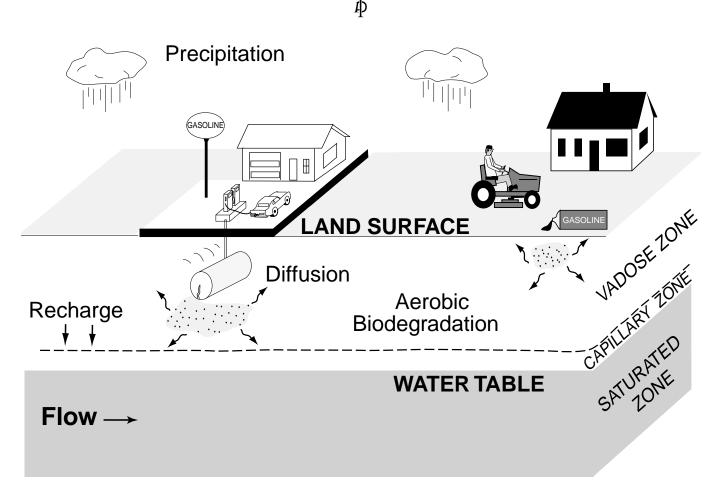
Figure 1. Conceptual diagram of contaminant transport in the vadose zone at small-volume gasoline-release sites where the released product is immobilized above the water table.

assumed to be non-degradable in order to predict maximum mass-loading rates of MTBE to groundwater. The gasoline source was assumed to be immobile and was simulated as a constant-concentration boundary for chronic releases and as a time-dependent-concentration boundary for incidental releases. Land surface was simulated as a constant- atmospheric-concentration boundary for all constituents. The water table was simulated as a zero-concentration boundary for MTBE and benzene, again, to maximize estimates of mass loading across the water table. The water table also was assumed to be impervious to oxygen diffusion. The initial condition was specified as a constant atmospheric concentration for all constituents.

Transport of MTBE and benzene from small-volume gasoline releases was simulated in representative sand and clay hydrogeologic systems. The soil and constituent properties used for model simulations are summarized in Table 1. The diffusive properties of the soils were determined by assuming a theoretical moisture distribution based on soil properties classified by van Genuchten (1980) and steady flow (constant recharge rate). The incorporation of depth-dependent moisture allowed for simulation of transport through the capillary zone, which was important given that diffusion diminishes by orders of magnitude near the water table. Vadose-zone transport was simulated for systems ranging from no recharge (0 cm yr^{-1}) to high recharge (100 cm yr^{-1}) in sand, and from 0 cm yr^{-1} to 20 cm yr^{-1} in clay, to bracket mass-loading rates to groundwater across a range of anticipated field conditions.

Gasolines containing 3 and 15 percent MTBE by volume were assumed in the simulations. Immiscible-phase concentrations of MTBE and benzene were calculated according to the ether-oxygenated-gasoline composition defined by Johnson et al. (1990). Release rates for chronic gasoline releases ranged from 1.1E-05 g/s (0.002 gal/d) to 1.8E-04 g/s (0.04 gal/d) in sand and from 5.5E-06 g/s (0.001 gal/d) to 3.8E-05 g/s (0.007 gal/d) in clay. Release rates varied depending on soil type and recharge rate. A representative volume of 1 gallon was chosen for single-release simulations. Gasoline releases were simulated occurring immediately below the land surface for 1 and 10 m-thick vadose zones and at 1 m below land surface for a 3 m-thick vadose zone.

MTBE AND BENZENE TRANSPORT IN THE VADOSE ZONE

The rate at which MTBE and benzene migrate through the vadose zone and enter groundwater is governed by diffusion, recharge, and biodegradation. The hydrogeologic parameters that affect these processes are recharge rate, depth to groundwater, soil type, biodegradation rate, and gasoline composition. For MTBE and benzene, differences in solubility and biodegradability govern their principal mechanisms of transport to groundwater. Diffusion and recharge are the principal mechanisms of MTBE transport, whereas diffusion and

Table 1. Summary of values of hydrogeologic, soil, and constituent properties used as input for transport simulations. [All porosity data are from van Genuchten (1980); -- indicates no data]

HYDROGEOLOGIC PROPERTIES

PROPERTY	VALUE	UNIT
Length of model domain	100 – 1,000	cm
Groundwater recharge rate	0 – 100	cm yr^{-1}

SOIL PROPERTIES

PROPERTY	SAND	CLAY	UNIT
Total porosity	0.437	0.475	dimensionless
Aqueous-filled porosity	variable	variable	dimensionless
Gaseous-filled porosity	variable	variable	dimensionless
Aqueous-filled tortuosity	variable	variable	dimensionless
Gaseous-filled tortuosity	variable	variable	dimensionless
Saturated hydraulic conductivity	21	0.06	cm hr^{-1}

CONSTITUENT PROPERTIES

PROPERTY	BENZENE	MTBE	OXYGEN	UNIT
Solubility[1]	1.78E-3	0.048	8.8E-6	g cm^{-3}
Mole fraction in immiscible phase for gasoline containing:				
15 percent MTBE by volume	0.009	0.150	0.0	dimensionless
3 percent MTBE by volume	0.010	0.030	0.0	dimensionless
Henry's Law constant[1]	0.17	0.024	32	dimensionless
Gaseous-phase diffusivity	0.08	0.079	0.19	cm^2 s^{-1}
Aqueous-phase diffusivity	1.0E-5	1.0E-5	1.0E-5	cm^2 s^{-1}
Maximum reaction rate	2.5E-10	0.0	--	g cm^{-3} s^{-1}
Monod half-saturation constant	0.2E-6	0.0	0.1E-6	g cm^{-3}

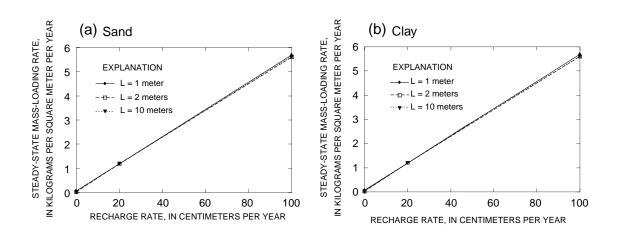[1]Property determined at 20 degrees Celsius

Figure 2. Steady-state mass-loading rate of MTBE to ground water as a function of recharge rate (q) and depth to ground water (L) for a chronic small-volume release of gasoline in (a) sand and (b) clay. (The relation of mass-loading rate to recharge rate is illustrated at recharge rates exceeding 20 centimeters per year for clay (Figure 2b) for comparative purposes only. Recharge rates as high as or exceeding 20 centimeters per year in clay are unlikely.) Plots for sand and clay are similar because the diffusion properties through the capillary fringe are similar in each soil type.

biodegradation are the principal mechanisms of benzene transport. Consequently, mass-loading rates of MTBE and benzene to groundwater can differ significantly under similar hydrogeologic conditions.

Differences in source concentration can also affect mass-loading rates of MTBE and benzene to groundwater. Substantially higher rates can be expected for MTBE than for benzene solely because source (pore-water) concentrations of MTBE in equilibrium with oxygenated gasoline can be as much as 400 times higher than those of benzene.

Simulated Mass-Loading Rates and Breakthrough Times

Chronic Small-Volume Releases of Gasoline in the Vadose Zone

Steady-state mass-loading rates of MTBE at the water table from chronic releases of gasoline containing 15 percent MTBE by volume (Figure 2) varied from approximately 0 to 5.7 kg m^{-2} yr^{-1}. Mass-loading rates for gasoline containing 3 percent MTBE by volume (not shown), are 20 percent of the values shown in Figure 2 because MTBE is assumed to be non-degradable. Mass-loading rates of benzene to groundwater, in contrast, were significantly lower as a result of biodegradation in the vadose zone and mass-transport limitations in the capillary zone. Mass-loading rates of benzene were, in general, more than two orders of magnitude lower than those of MTBE if no biodegradation was assumed, and were negligible if reasonable approximations of the benzene biodegradation rate were assumed (see Table 1 for rates used). Limited transport of benzene implies that water that recharges an aquifer can be enriched in MTBE relative to benzene and other hydrocarbons compared to water that is in equilibrium with the product source. In addition, mass-loading of benzene to groundwater may be significant only if the gasoline release occurs near the water table (< 1 m), biodegradation is limited, and the recharge rate is high (Lahvis and Rehmann, 1999.)

The steady-state distributions of MTBE, benzene, and oxygen resulting from a chronic release of gasoline 1 m below land surface in a 3 m-thick vadose zone are illustrated in Figure 3. As indicated, soil type can have a major effect on the constituent distribution in the vadose zone and, in turn, mass loss by diffusion to the atmosphere. For example, based on a ratio of the mass flux entering groundwater to the mass flux emanating from the source, diffusion to the atmosphere can reduce the total mass of MTBE available to affect groundwater by more than 49 percent for gasoline releases that occur in coarse-grained soils at a distance 2 m above the water table, regardless of the recharge rate. This percentage would be greater or smaller if the release occurred farther from, or closer to, the water table, respectively. This result implies that diffusion to the atmosphere can be a critical natural-attenuation pathway for MTBE, especially given that the compound is not easily degraded. Simulation results indicate, however, that minor rates of recharge can restrict diffusion to the atmosphere in fine-grained soils, even for releases that occur near land surface.

Breakthrough times for MTBE at the water table are summarized in Table 2 for the chronic-release scenarios. Breakthrough times were computed as the time required for the mass flux at the water table to reach 10, 50, and 90 percent of the steady-state mass flux. In sand, breakthrough times ranged from days to years depending on depth to groundwater and recharge rate. Breakthrough times in clay, however, can be as long as hundreds of years depending on these hydrogeologic conditions.

Single 1-Gallon Release of Gasoline in the Vadose Zone

Mass-loading rates of MTBE as a function of time and recharge rate for a 1 gallon (gal) release of gasoline at a depth of 1 m below land surface in a 3 m-thick vadose zone are illustrated in Figure 4. Mass-loading rates predicted for the 1 gal release (< 1 kg m^{-2} yr^{-1}) were less than 20 percent of the steady-state mass-loading rates obtained for chronic releases (< 5.7 kg m^{-2} yr^{-1}) and were, again, most sensitive to the recharge rate. The mass-loading rates decreased by more than an order of magnitude in systems ranging from high (100 cm yr^{-1}) to no (0 cm yr^{-1}) recharge. Total masses of MTBE entering groundwater at various recharge rates for a simulated 1 gal release are listed in Table 3. In some cases, only a small fraction of the initial source mass of MTBE (6.2 percent) was predicted to reach groundwater for releases occurring at a depth of 1 m below land surface in a 3 m-thick vadose zone. These results imply that some single small-volume releases of gasoline that occur at or near land surface may not pose a risk of groundwater contamination.

The time for the peak mass flux of MTBE to occur for a 1 gal release at a distance 2 m above the water table ranged from 61 to 121 days in sand and from 1,425 to greater than 8,000 days in clay, depending on the recharge rate (see Figure 4). (Although biodegradation of MTBE was not considered in these simulations, this process may affect the actual mass flux over the long time period of transport in clay.) The breakthrough time was highly sensitive to the recharge rate when vapor transport was a limitation (see Figure 4b).

SENSITIVITY ANALYSIS

Mass-loading rates of MTBE and benzene were most sensitive to changes in recharge rate. The sensitivity of the mass-loading rate of MTBE to recharge rate is illustrated in Figure 2. The mass-loading rate is sensitive to the recharge rate because transport near the water table is advection-dominated and mass loading to groundwater is limited by diffusion through the capillary zone. Furthermore, diffusion through the capillary zone is relatively independent of soil type. The parameters that affect diffusive transport (soil type and depth to groundwater), therefore, have little effect on the mass-loading rate. These parameters can, however, significantly affect breakthrough times to reach steady state mass flux to groundwater (see Table 2). For example, breakthrough times of MTBE at the water table varied by more than an order of magnitude depending on the values of these parameters. Soil type also can affect mass loss to the atmosphere, as previously stated. Mass losses to the atmosphere can significantly reduce mass loading to groundwater, as indicated in Table 3. Minor rates of recharge (20 cm yr^{-1}) may be sufficient, however, to restrict this natural-attenuation pathway for MTBE in fine-grained soils.

(a) Sand

MTBE

BENZENE

OXYGEN
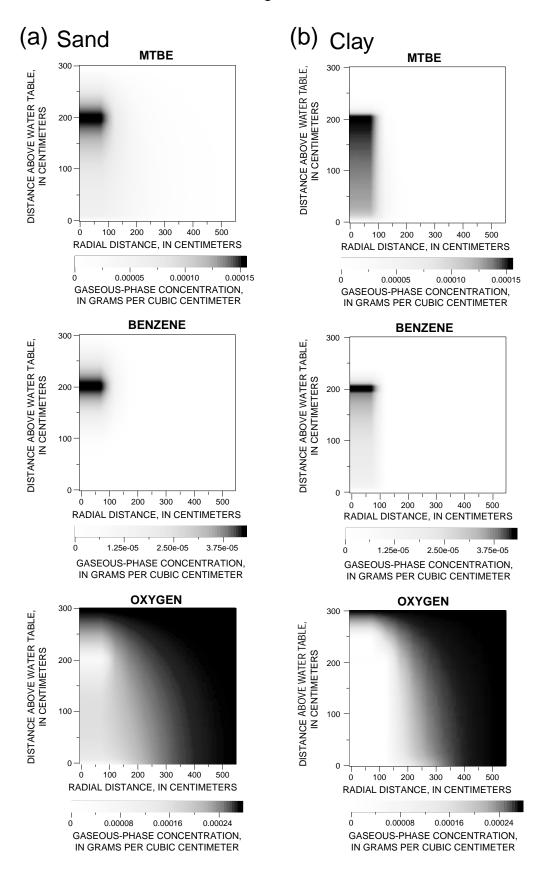

(b) Clay

MTBE

BENZENE

OXYGEN

Figure 3. Steady-state distributions of MTBE, benzene, and oxygen resulting from a chronic release of gasoline 1 meter below land surface in a 3 meter-thick vadose zone with a recharge rate of 20 centimeters per year in (a) sand and (b) clay.

Table 2. Summary of breakthrough times of MTBE at the water table obtained from model simulations of a chronic release of gasoline containing 15 percent MTBE by volume

Transport property	Simulated condition	Time (in years) required for mass-loading rate to reach indicated percentage of the steady-state mass flux		
		10	50	90
Sand				
Depth to groundwater (L)	$(0 \leq q \leq 100 \text{ cm yr}^{-1})$			
1 m		0.05 – 0.15	0.09 – 0.21	0.18 – 0.43
2 m		0.09 – 0.17	0.18 – 0.39	0.37 – 1.0
10 m		0.51 – 1.2	0.93 – 2.9	1.7 – 7.0
Clay				
Depth to groundwater (L)	$(0 \leq q \leq 100 \text{ cm yr}^{-1})$			
1 m		0.30 – 2.7	0.42 – 5.7	0.57 – 13
2 m		0.66 – 8.1	0.84 – 12	1.1 – 16
10 m		3.5 – 98	4.0 – >100	4.5 – >100

Table 3. Simulated mass of MTBE entering groundwater at various recharge rates for a 1 gallon release of gasoline at a depth of 1 meter below land surface in a 3 meter-thick vadose zone

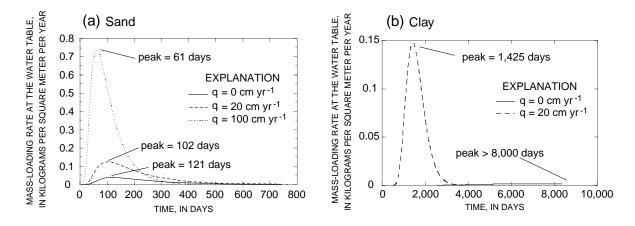| Groundwater recharge rate (q)	Cumulative mass entering groundwater (g)		Fraction of initial source mass (percent)	
	Sand	Clay	Sand	Clay
0 cm yr^{-1}	28	53	6.2	12
20 cm yr^{-1}	74	415	17	93
100 cm yr^{-1}	220	NA	49	NA

Figure 4. Mass-loading rate of MTBE at the water table as a function of time and recharge rate (q) for a 1 gallon release of gasoline in (a) sand and (b) clay at a distance 2 meters above the water table.

Relation of Mass-Loading Rates to Constituent Concentrations at the Water Table

Constituent concentrations at the water table can be computed from the mass-loading rate provided the regional groundwater flow rate is known. These concentrations can be determined by dividing the mass-loading rate to groundwater by the regional groundwater flow rate. No attempt was made to calculate constituent concentrations because groundwater flow rates are site-specific; however, mass-loading rates could be used in conjunction with solute-transport modeling to assess the extent of contaminant migration in groundwater and estimate the minimum release volumes necessary to affect sensitive receptors located downgradient from the source.

REFERENCES

Johnson, P.C., Kemblowski, M.W., and Colthart, J.D., 1990, *Quantitative analysis for the cleanup of hydrocarbon-contaminated soil by in-situ soil venting:* Ground Water, v. 28, p. 413-429.

Lahvis, M.A., and Baehr, A.L., 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 Baehr, A.L., 1998, *Simulating transport of volatile organic compounds in the unsaturated zone using the computer model R-UNSAT:* U.S. Geological Survey Fact Sheet FS-019-98, 4 p.

Lahvis, M.A., and Rehmann, L.C., 1999, *Simulation of methyl tert-butyl ether (MTBE) transport to groundwater from immobile sources of gasoline in the vadose zone,* in Proceedings of the NGWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation, Houston, Texas, November 17-19, 1999, National Ground Water Association, Westerville, Ohio, 247-259, 1999.

Rong, Yue, 1999, *Groundwater data analysis for methyl tertiary butyl ether:* Environmental Geosciences, v. 6, p. 76-81.

van Genuchten, M. Th., 1980, *A closed-form equation for predicting the hydraulic conductivity of unsaturated soils:* Soil Science Society of America Journal, v. 44, p. 892-898.

ACKNOWLEDGEMENTS

RELATED PUBLICATIONS

Publ 4592, Odor Threshold Studies Performed with Gasoline and Gasoline Combined with MTBE, ETBE and TAME, January 1994
This report examines the effects on odor detection and recognition of adding oxygenates such as MTBE, ETBE, and TAME to gasoline. Commercial grade MTBE is also evaluated for its taste threshold in water. The odor detection threshold is the minimum concentration at which 50% of a given population can differentiate between a sample containing the odorant and a sample of odor-free air. The recognition threshold is the minimum concentration at which 50% of a given population can recognize the odorant. The addition of 11% to 15% by volume MTBE or 15% by volume of TAME or ETBE reduce the odor detection and recognition thresholds of gasoline. Pages: 76.
Order Number: I45920   *Price: $42.00*

Publ 4699, Strategies for Characterizing Subsurface Releases of Gasoline Containing MTBE, March 2000
The document uses the principles of risk-informed decision making to guide the assessment of sites affected by MTBE and other oxygenates. Risk-informed decision making considers risk factors related to sources, exposure pathways and receptors. The centerpiece of this approach is the development of a conceptual site model (CSM). A new decision framework developed by API helps the environmental site assessor to determine an appropriate starting point or an initial level of assessment from which the CSM can be confirmed. Important risk factors are discussed in the report along with descriptions of characterization tasks suggested for various level of assessment. The report describes how current expedited site assessment techniques can be applied to the collection and field analysis of soil, soil gas and groundwater samples. A comprehensive guide to direct push assessment and monitoring tools, with emphasis on their proper use at MTBE-affected sites, is also provided. In addition to presenting state of the art strategies for MTBE site assessment, the report is an excellent reference on the chemical and physical properties of oxygenates, their use in gasoline and behavior in the subsurface environment. Analytical methods appropriate for MTBE detection are also discussed. This 116 page report is available for download now at: http://www.api.org/mtbe.

Publ 4668, Delineation and Characterization of the Borden MTBE Plume: An Evaluation of Eight Years of Natural Attenuation Processes, June 1998
In 1988, a natural gradient tracer test was performed in the shallow sand aquifer at Canada Forces Base (CFB) Borden to investigate the fate of a methyl-tertiary-butyl-ether (MTBE) plume introduced into the aquifer. Solutions of groundwater mixed with oxygenated gasoline were injected below the water table along with chloride (Cl-), a conservative tracer. The migration of benzene, toluene, ethylbenzene, the xylenes (BTEX); MTBE; and Cl- was monitored in detail for about 16 months. The mass of BTEX in the plume diminished significantly with time due to intrinsic biodegradation. MTBE, however, was not measurably attenuated. In 1995-96, a comprehensive groundwater sampling program was undertaken to define the mass of MTBE still present in the aquifer. Only about 3 percent of the initial MTBE mass was found, and it is hypothesized that biodegradation played an important role in its attenuation. Additional evidence is necessary to confirm this possibility. Pages: 88.
Order Number: I46680   *Price: $36.00*

Publ 4655, Field Evaluation of Biological and Non-Biological Treatment Technologies to Remove MTBE/Oxygenates From Petroleum Product Terminal Wastewaters, August 1997
A pilot/demonstration study was conducted on three treatment technologies—the fluidized bed biological reactor process, the activated sludge process incorporated with iron flocculation, and the ultraviolet light/hydrogen peroxide process—to evaluate their effectiveness in the treatment of petroleum marketing terminal wastewater contaminated with methyl tert-butyl ether (MTBE). Contaminated groundwater was the primary constituent of the wastewater, which also contained benzene, toluene, ethylbenzene, and xylenes (BTEX). All three technologies were able to remove at least 95% of the MTBE and BTEX in the feed waters. Pages: 194.
Order Number: I46550   *Price: $78.00*