

Role of Volatilization in Changing TBA and MTBE Concentrations at MTBE-Contaminated Sites

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Tertiary butyl alcohol (TBA) is commonly found as an impurity in methyl tertiary butyl ether (MTBE) added to gasoline. Frequent observations of high TBA, and especially rising TBA/MTBE concentration ratios, in groundwater at gasoline spill sites are generally attributed to microbial conversion of MTBE to TBA. Typically overlooked is the role of volatilization in the attenuation of these chemicals especially in the vadose zone, which is a source of contamination to groundwater. Here we show that volatilization, particularly through remediation by vapor extraction, can substantially affect the trends in TBA and MTBE concentrations and the respective mass available to impact groundwater aquifers, through the preferential removal of more volatile compounds, including MTBE, and the apparent enrichment of less volatile compounds like TBA. We demonstrate this phenomenon through numerical simulations of remedial-enhanced volatilization. Results show increases in TBA/MTBE concentration ratios consistent with ratios observed in groundwater at gasoline spill sites. Volatilization is an important, and potentially dominant, process that can result in concentration trends similar to those typically attributed to biodegradation.

Introduction

Methyl tertiary butyl ether (MTBE) was first added to gasoline in 1979 as an octane enhancer to replace lead in gasoline (1). It was later used extensively as a fuel oxygenate in part to meet the requirements of the 1990 Clean Air Act Amendments, accounting for up to 15% of gasoline by volume. Within a short period of time, releases of MTBE to the subsurface, primarily through leaking underground fuel tanks (LUFTs) resulted in widespread contamination to groundwater systems. In a nationwide study, MTBE was found to be the second most frequently detected volatile organic compound (VOC) in samples collected from domestic and public supply wells (2).

The presence of MTBE in groundwater is often associated with the presence of tertiary butyl alcohol (TBA) (3, 4). The source of TBA at MTBE-contaminated sites is difficult to identify. TBA has been shown in laboratory studies to be a product of MTBE biodegradation under both aerobic and

anaerobic conditions (5). A more recent study (6) showed MTBE can be transformed abiotically to TBA under methanogenic conditions. TBA is a fuel oxygenate, and is also used in the manufacturing of MTBE (7). It is therefore commonly present as an impurity in commercial MTBE (5, 8, 9). The TBA content of MTBE varies widely, accounting for up to 10% of the MTBE added to gasoline (10). TBA can also be present in ethanol as a denaturant (7, 11), or as a result of manufacturing processes (11). This is important, since ethanol is replacing MTBE as the oxygenate of choice in states where the use of MTBE has been banned or restricted.

While MTBE is highly soluble in water, TBA is completely miscible and has a low affinity for gasoline (low K_{fw} , Table 1). Therefore, minute amounts of TBA in the MTBE blended in gasoline can result in high aqueous TBA concentrations when MTBE oxygenated gasoline comes in contact with water. For example, Zwank et al. (12) found TBA concentrations of up to 340 mg/L (ppm) in the aqueous extracts of 7 different gasoline samples containing MTBE, even though the technical specification for all gasoline samples indicated no TBA (content below the detection limit of 0.1 vol %). Kramer and Douthit (10) found that the aqueous TBA concentrations from 5 different gasoline samples averaged 1356 mg/L, with TBA concentrations in water at approximately 83% of the concentration of MTBE. At the same time, a study by Shell Global Solutions (13) indicates that TBA was present in many of the shipments of MTBE that were added to gasoline in California. Of the samples analyzed, 95% had TBA at levels of 370 mg TBA/kg MTBE or more, and 50% had TBA at levels of 1300 mg TBA/kg MTBE or more, corresponding to aqueous-phase TBA concentrations of 330 mg/L and 1158 mg/L, respectively (based on equilibrium partitioning computations for gasoline with 11 wt % MTBE in contact with water (13); note that resulting aqueous concentrations in the field would be lower due to dilution).

Data from monitoring wells at contaminated sites show that the frequency of occurrence of TBA and the range of concentrations observed are similar to those of MTBE (3, 4, 14). For example, out of 868 randomly selected LUFT sites in the greater Los Angeles area, MTBE was detected at 82.7% of sites, while TBA was detected at 61.1% of sites (4). TBA was found to have the greatest site maximum concentrations, compared to MTBE and benzene, with concentrations up to 4400 mg/L. Wilson et al. (9) compared field-measured MTBE and TBA concentrations at contaminated sites in Orange County, California, to those predicted from dissolution of MTBE-oxygenated gasoline into water. Predicted concentrations were based on the assumption that gasoline contained 11 vol % MTBE, and 0.22 vol % TBA (based on 2% TBA by weight in MTBE). Wilson et al. (9) noted that measured TBA concentrations at these sites were in agreement with those predicted from dissolution, whereas the measured MTBE concentrations were commonly one or more orders of magnitude less than predicted from dissolution of MTBE-oxygenated gasoline into water. The researchers theorized that "some process or processes" are acting to lower MTBE and increase TBA concentrations (9). Using carbon isotope fractionation in a focused study of 13 sites, with TBA/MTBE ratios greater than those expected from the dissolution of fresh MTBE oxygenated gasoline, Wilson et al. (9) concluded that MTBE biodegradation could explain the majority of TBA concentrations at a fraction of the sites (4 out of 13), but could not explain the majority of TBA concentrations at a majority of the sites (9 out of 13).

Here we consider volatilization as a process that can explain observed trends in TBA and MTBE concentrations.

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TABLE 1. Properties of TBA, MTBE, Benzene, and *p*-Xylene

compound	solubility (mg/L)	vapor pressure (kPa)	Henry's law (dimensionless)	fuel-water partitioning K_{fw}
TBA	miscible ^a	5.3–5.6 ^a	0.00048–0.00059 ^a	0.15–0.33 ^b
MTBE	43,000–54,000 ^a	32.7–34.1 ^a	0.023–0.123 ^a	15.5 ^c
benzene	1,780 ^a	10.1–12.7 ^a	0.22 ^a	350 ^c
<i>p</i> -xylene	589 ^d	1.2 ^d	0.283 ^d	4350 ^c

^a Adapted from reference 8. ^b Adapted from ref 12. ^c Adapted from ref 30. ^d Adapted from ref 39. Solubility and vapor pressure measured at 25 °C, except for *p*-xylene, which was measured at 20 °C. Henry's Law measured at 25 °C.

We simulate the effects of volatilization, by soil vapor extraction (SVE), on MTBE-oxygenated gasoline constituents in the unsaturated zone. We show that because of the significant differences in the physical/chemical properties of MTBE and TBA, SVE preferentially removes MTBE through volatilization while TBA tends to persist. The loss of the more volatile VOC mass, including MTBE, results in redistribution of the remaining mass between phases in the unsaturated zone, including an increased TBA mole fraction in the nonaqueous phase gasoline, an apparent enrichment of TBA mass due to increased aqueous TBA concentrations, and aqueous TBA/MTBE concentration ratios that increase with time. Thus, volatilization may play a role in, or dominate, TBA and MTBE concentration trends observed at MTBE-oxygenated gasoline spill sites.

Background

Since most gasoline releases occur above the water table (3), a significant mass of contaminants can be held in the unsaturated zone as residual gasoline. Residual gasoline acts as a continuous source of contamination to the groundwater through vapor migration and leaching following precipitation events. Similarly, fluctuations in groundwater levels result in water coming in contact with residual gasoline in the vadose zone, which can be reflected in the concentrations of contaminants measured in monitoring wells (15, 16). Volatilization, through natural weathering or active remediation such as SVE and dual phase (liquid and vapor) extraction (DPE), preferentially removes the more volatile constituents, thus reducing the mass that can impact groundwater.

Volatilization using SVE is the most commonly used technology for treating soil contaminated with MTBE (16). In the USEPA's database on MTBE remediation case studies (17), SVE is the most highly cited technology used at the field scale, followed by air sparging. Out of 358 MTBE remediation case studies listed, 177 (49%) used SVE. At the same time, the results of a survey of state experiences (the 50 states, the District of Columbia, and the U.S. territories) with MTBE and other oxygenates at LUFT sites showed SVE was the most widely cited technology for treating contaminated soil (18).

SVE, alone or in combination with other technologies, can be very effective at reducing MTBE concentrations in groundwater, achieving more than 99% reduction in concentrations (16). Similarly, volatilization and vapor migration through diffusion to the land surface can be an effective natural attenuation pathway for MTBE (19), accounting for significant mass loss, depending on soil type and depth of contamination (20, 21). In contrast, TBA is much less volatile, and much more water soluble than MTBE (Table 1), and so is less likely to be lost to volatilization. As a result, SVE and other processes that involve volatilization, while very effective

at removing MTBE, are expected to be much less effective at removing TBA.

TBA is of concern because it is potentially more toxic than MTBE (5). Though an unregulated chemical at this time, the notification level for TBA in California is 12 $\mu\text{g/L}$ based on evidence of potential carcinogenicity (22). In contrast, the primary maximum contaminant level (MCL) and secondary MCL for MTBE in California are 5 $\mu\text{g/L}$ and 13 $\mu\text{g/L}$, respectively. Unlike MTBE, TBA has a high taste and odor threshold, which means that some segments of the population, especially those relying on private wells, where periodic sampling and analysis for water contamination is not mandated by regulatory agencies, may become exposed to high concentrations of TBA without knowing it (23). At the same time, the presence of TBA in MTBE-contaminated drinking water is expected to add to the cost of treatment (24).

Materials and Methods

A representative gasoline spill and remediation effort using SVE was simulated using the code VENT3D (25, 26). The code simulates chemical partitioning in the vadose zone under the influence of volatilization. The model has no groundwater component as it focuses on the fate of chemicals in the unsaturated zone. The code was chosen because it is fully three-dimensional and has the ability to simulate a broad range of conditions and numerous chemical components (27). VENT3D simulates the vapor migration of each specified gasoline compound under the influence of a vapor extraction system, while computing and maintaining equilibrium partitioning in four phases: vapor (air), liquid (pore water), nonaqueous phase liquid (NAPL; i.e., gasoline), and solid (soil grains). The model continuously recalculates whether a NAPL phase is present at all points in the model domain, and adjusts the distribution of contaminants among the phases accordingly. The code accounts for the infinite solubility of TBA by calculating its activity from its fuel-water partition coefficient, K_{fw} (Table 1), rather than the infinitely dilute approximation for relatively insoluble hydrocarbon compounds. Details regarding the phase equilibrium calculations and the VENT3D algorithm are provided in the Supporting Information (SI).

A gasoline mixture containing 39 compounds, including MTBE and TBA, was used in the simulations. The mass contributions of 37 of the compounds (the dominant species in a representative gasoline sample) were based on measurements by Johnson et al. (28), adjusted to account for a 10 wt % MTBE and different mass fractions for TBA: 1.0, 0.1, and 0.01 wt % in gasoline. The properties and mass contribution of all 39 compounds in the gasoline mix are given in SI Table S1. For TBA partitioning calculations, two values for K_{fw} were applied: 0.24 and 2.22. The lower value for K_{fw} falls in the middle of the range of laboratory measured values (0.15–0.33) reported by Zwank et al. (12) and falls near the upper end of the range of measured values (0.05–0.26, with a geometric mean of 0.11) reported by DeVaul et al. (13). The range in measured values of K_{fw} is partly attributed to differences in gasoline (fuel) composition and content of oxygenates in the gasoline samples tested (13). The higher K_{fw} (2.22) was computed to yield an initial vapor/ aqueous phase concentration ratio consistent with a dimensionless Henry's Law constant of 4.8×10^{-4} (Table 1). Smaller values of K_{fw} increase aqueous-phase TBA concentrations dissolved from NAPL, and therefore result in greater persistence because TBA has a relatively low volatility from water. When three or four phases are present, obtaining agreement with published Henry's Law coefficients measured for vapor–aqueous systems requires that K_{fw} be increased above laboratory-measured values in a fuel–water system.

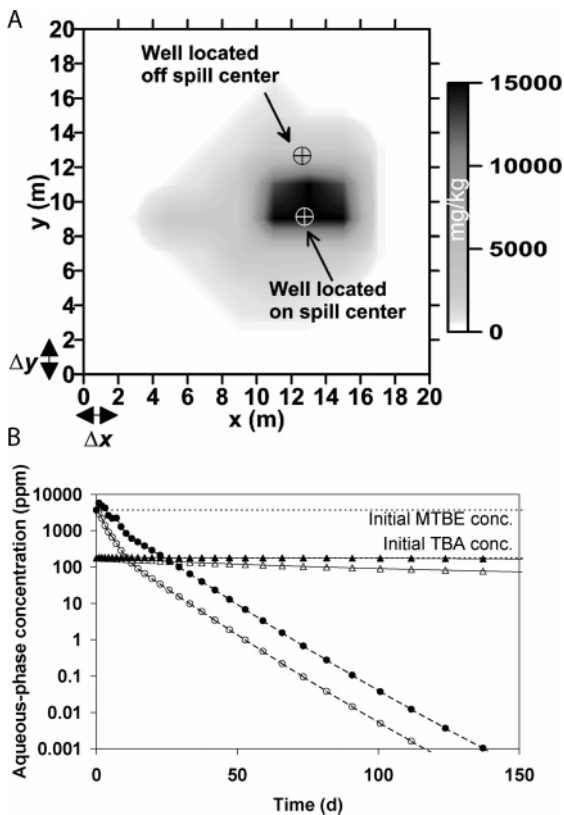


FIGURE 1. (A) Plan view of the model domain and initial concentration of gasoline contaminants in soil (mg/kg) in the lower two layers. (B) Simulation results for dissolved-phase TBA (triangles) and MTBE (circles) concentrations at the extraction well located on the spill center (open symbols), and at the location of maximum concentrations in the domain (solid symbols), versus time, during SVE at 566 L/min for $K_{fw} = 0.24$, and a 0.1% mass fraction of TBA in gasoline. For comparison, initial dissolved-phase concentrations of TBA and MTBE are given by the dashed lines as labeled.

Thus the higher value for K_{fw} likely represents an unrealistically high upper bound, useful for sensitivity analysis.

The model domain was specified with a 4.0 m depth and an area of 400 m² (20 m by 20 m; Figure 1A). The domain was discretized into 2.0 m by 2.0 m by 1.0 m finite difference cells in the *x*-, *y*-, and *z*-directions, respectively. A spill of 1542 kg of gasoline was placed uniformly over the vertical within the lower two layers of soil (Figure 1A). Initial concentrations ranged from 500 to 15 000 mg of gasoline per kg of soil. Fifteen percent (approximately 24 m²) of the area of the initial spill was present at high enough concentrations (above ~8000 mg/kg) for a NAPL phase to be present. The soil porosity was set at 0.4 with a volumetric water content of 0.1. To investigate the effects of enhanced volatilization through SVE, simulations were performed for an extraction rate of 566 L/min for 250 days from a single well screened in the lower two layers and with the top of the upper layer pneumatically sealed. The effects of inducing vapor-phase transport from zones of high to low concentration were also investigated by moving the well to a location off the spill center (Figure 1A). The concentrations of TBA and MTBE in the aqueous phase at the vapor extraction well were recorded. The maximum dissolved concentrations in the model domain were also recorded. The maximum value may not coincide with the extraction well(s), since the depletion of lighter compounds in the NAPL at any location depends on the flow field and the nearby distribution of NAPL present. Specified model parameter values are given in Table S2 in the Supporting Information.

Results and Discussion

Persistence and Enrichment of TBA. Results from the simulation with the extraction well located in the center of the spill (Figure 1A), using a 0.1% mass fraction for TBA, and a value of $K_{fw} = 0.24$ are presented in Figure 1B. Because of its high volatility, MTBE is quickly depleted from the system, reducing its concentration in the NAPL and pore water. In contrast, TBA is removed very slowly, and therefore persists in the pore water. The persistence of TBA relative to MTBE is consistent with studies of volatilization from surface waters (29). Results also exhibit a 5% “enrichment” of dissolved-phase TBA concentrations, in agreement with Raoult’s Law that dictates that if at least one organic compound is present at high enough concentrations, then a NAPL phase is present and each compound will partition into the NAPL.

Furthermore, the dissolved concentration of each compound will be proportional to the mole fraction of that compound in the NAPL phase (30, 31). Enrichment therefore ensues when a NAPL is present and there is depletion of the more volatile compounds resulting in a relative increase in the mole fraction of less volatile chemicals.

This phenomenon of enrichment has been noted in simulations of SVE of non-oxygenated gasoline compounds (28), as well as in laboratory studies of the effects of volatilization on binary NAPL mixtures in unsaturated porous media (32). The response of benzene and *p*-xylene (representative of the BTEX group) to SVE show similar behavior and are discussed in the Supporting Information.

Note that the simulations presented in Figure 1B are for fresh gasoline, a pneumatically sealed top, and removal via the vapor phase as the dominant mechanism for depletion from the vadose zone. This is to demonstrate, and bound from above, the potential for increased TBA/MTBE concentration ratios and TBA enrichment, resulting from volatilization from vapor extraction. In the field, weathering through volatilization and diffusion to the surface, as well as water washing through infiltration and fluctuations in groundwater table, can locally alter the composition of gasoline before the onset of SVE.

Figure 2 further illustrates the disparity in the distribution of MTBE and TBA in liquid and vapor phases. At the start of SVE (Figure 2A), MTBE and TBA dominate the mass of contaminants in the pore water (93.2% and 4.5%, respectively, of total mass in the aqueous phase), because both are highly soluble from gasoline, and because MTBE makes up a significant fraction of gasoline. The most volatile compounds dominate the mass in the vapor phase, including 6.6% accounted for by MTBE. Even accounting for its small fraction of the total mass of contaminants in the domain, TBA concentrations in the vapor phase are disproportionately small due to its high solubility in, and low volatility from, water. By the end of SVE operations (250 days) the relative mass fraction of TBA in pore water increases to 92.7% as the more volatile compounds, including MTBE, are preferentially removed from the domain (Figure 2B). As a result, the dissolved-phase TBA/MTBE concentration ratio increases with time and essentially without bound.

Sensitivity. The effects on dissolved-phase TBA and MTBE concentrations from changes in (a) extraction well position relative to the center of mass of the spill; (b) changing the mass fraction of TBA in the fresh gasoline; and (c) adjusting the fuel-water partitioning coefficient K_{fw} for TBA, were investigated. In all simulations of SVE remediation, the NAPL-containing soil was reduced to a volume of 4 m³. All cases exhibited rapid depletion of MTBE and “enrichment” and persistence of dissolved-phase TBA concentrations (details are provided in the discussion of sensitivity and in Figure S2 in the SI).

Natural Weathering. The weathering of gasoline, through slow volatilization and vapor-phase diffusion to the atmo-

in 2002 (9). This correspondence is consistent with the theoretical behavior where, for contaminants entering groundwater through infiltration to the water table or water level rise, processes such as dissolution, dilution, and mixing through dispersion in groundwater with different concentrations of MTBE and TBA could moderate trends in TBA and MTBE concentrations resulting from volatilization.

Pure dilution of contaminant concentrations previously altered by volatilization, for example, would move a point downward along a line with a 1:1 slope, so that the resulting dissolved-phase concentrations in a monitoring well would correspond more closely to detections at field sites (Figure 3A). On the other hand, for a NAPL in equilibrium with water, most of the TBA resides in the aqueous phase (see Figure 2A) where it is highly susceptible to water washing and groundwater transport. As a result, for contamination relatively unaffected by volatilization but highly affected by water washing, groundwater transport away from the source zone could reduce TBA to MTBE concentration ratios locally near the source. This process might explain those detections plotted in Figure 3A that fall below the range expected from pure dissolution. Those detections could also be explained by lower concentrations of TBA in the gasoline spill than were assumed for the equilibrium calculations. It is noteworthy that reductions in TBA concentrations at the source due to dissolution and downgradient transport would be balanced by higher TBA concentrations in the downgradient plume. Overall, this process could lead to trends of declining MTBE and increasing TBA downgradient along the plume centerline, similar to trends expected if MTBE were being transformed to TBA during transport *in situ*.

In the study conducted by Wilson et al. (9), 13 out of the 354 sites in Orange County, California (Figure 3A) were chosen for measurements of $^{13}\text{C}/^{12}\text{C}$ MTBE isotopic fractionation to determine if MTBE biodegradation could explain the TBA/MTBE concentration ratios present in groundwater. USEPA (34) used the results of that study in assessing the potential for monitored natural attenuation (MNA) as a remediation option at MTBE-contaminated sites. USEPA selected concentration trends measured in groundwater from wells at two of these sites (00UT038 well MW8 and 87UT211 well MW5) as exemplary of those resulting from natural attenuation through anaerobic MTBE biodegradation (see page 27 in ref 34). Our review of these sites has found that DPE was performed in, and adjacent to, both of these wells (site remediation histories are given in SI Tables S5 and S6). Figure 3B shows data for TBA and MTBE concentrations and groundwater levels from well MW8 (00UT038) (see ref 34). Note that TBA concentrations remained high whereas the decline in MTBE concentrations coincided with the DPE events as well as the rise in groundwater level. Similar trends are evident for well MW5 (87UT211), although there is a delay following the initial water level rise and the eventual decline in MTBE concentrations (SI Figure S4). Isotope samples were collected in October 2002 (9).

Concentration trends in both wells are consistent with a theoretical response to DPE, and subsequent rise of the water table into the vadose zone, enriched with residual TBA and depleted in MTBE (see SI Figure S5 comparing results from the VENT3D model with observations from well MW8). Our results appear to contradict previous conclusions (9, 34) that $^{13}\text{C}/^{12}\text{C}$ MTBE isotope ratios indicate that anaerobic "biodegradation of MTBE makes an important contribution to the high concentrations of TBA in groundwater" (9). It is possible, however, that concentration ratios were affected by both volatilization and anaerobic biodegradation at these sites. While biodegradation can contribute to rising TBA concentrations, substantiation of the process is necessary. Isotopic fractionation by itself is a proxy indicator that can also be affected by physical processes (35), a factor not

considered in the aforementioned research (9, 34). Detections of isotopically enriched $^{13}\text{C}/^{12}\text{C}$ MTBE in the field, although consistent with laboratory microcosm studies of MTBE biodegradation, do not necessarily result exclusively from MTBE biodegradation. For example, although isotopic fractionation due to volatilization has been previously assumed to be negligible, recent research indicates that volatilization can result in enrichment of $^{13}\text{C}/^{12}\text{C}$ ratios (36). These recent results are consistent with earlier research indicating that SVE could be particularly effective at isotopically fractionating volatile compounds (37). Similarly, under certain hydrogeologic conditions, and for a difference in the aqueous diffusion coefficients between an isotopically light and heavy solute, research has shown that diffusion can lead to the enrichment of the isotopically heavy solute (38). To our knowledge, the extent to which MTBE isotopically fractionates from these, and other, physical processes has not been assessed at field sites undergoing DPE and/or SVE remediation. Moreover, the potential for isotopic fractionation resulting from abiotic transformation of MTBE to TBA (6) has not been investigated.

Implications for Site Characterization and Future Research Directions. Our findings have significant implications for site characterization and the application of monitored natural attenuation at MTBE-contaminated sites. Until now, MTBE biodegradation was the only process investigated as a potential source for TBA/MTBE concentration ratios greater than those expected through the dissolution of fresh gasoline. Yet, while studies have shown that TBA can be produced as an intermediate of MTBE biodegradation, biodegradation does not necessarily result in TBA accumulation. In contrast, volatilization through natural weathering is ubiquitous, and remediation processes that use volatilization, such as SVE, air sparging, and DPE, are commonly employed at contaminated sites (16, 31).

Volatilization, particularly through remediation, is an important mechanism that greatly influences the fate of contaminants in the vadose zone, leading to a reduction in the mass of MTBE, and relative persistence of TBA, that together can result in TBA/MTBE concentration ratios in groundwater similar to those expected from biodegradation. Consequently, the relative importance of each mechanism, volatilization versus biodegradation, needs to be considered on a site-specific basis when evaluating the role of natural attenuation for long-term fate and transport of these contaminants. For example, our findings indicate that TBA/MTBE concentration ratios at the sites selected by the USEPA (34) to assess the potential for MNA as a remediation option at MTBE-contaminated sites were likely affected by volatilization through engineered remediation. The extent to which concentration ratios were significantly affected by MTBE natural attenuation through biodegradation at these and other sites requires further study. In light of its frequent occurrence, high concentrations in groundwater, detection in water supply wells, chemical properties including its potential toxicity and persistence relative to MTBE, and potential presence in ethanol, it is important to consider TBA, not only as a potential degradation product of MTBE, but also as an important component of the gasoline mix.

Acknowledgments

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Supporting Information Available

Discussion of phase equilibrium calculations for VENT3D. Table S1 of the relevant properties of all 39 gasoline compounds used in simulations. Table S2 of parameter values

used in VENT3D simulations. Discussion and plot (Figure S1) of benzene and *p*-xylene response to SVE as compared to MTBE and TBA. Discussion and plot (Figure S2) of sensitivity results. Tables S3 and S4 detailing detections of TBA and MTBE in California public water supply wells. Figure S3A and S3B plotting detected concentrations of TBA and MTBE in California public water supply wells. Site remediation histories (Tables S5 and S6). Plot of MTBE and TBA concentrations and groundwater levels for MW5 (87UT211) (Figure S4). Figure S5 comparing VENT3D model results with observations from well MW8 (00UT038). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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