

# DISSOLUTION OF MTBE FROM A RESIDUALLY TRAPPED GASOLINE SOURCE

## A SUMMARY OF RESEARCH RESULTS

WILLIAM G. RIXEY AND SUSHRUT JOSHI, UNIVERSITY OF HOUSTON

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

### SUMMARY

Laboratory studies were conducted to investigate the dissolution of methyl tertiary butyl ether (MTBE) relative to benzene, toluene, ethylbenzene, xylenes (BTEX) by advection of groundwater through a source region containing residually trapped gasoline. These laboratory studies were quantitatively analyzed with a multicomponent dissolution model. The results of these studies are summarized herein, and indicate what MTBE groundwater concentrations immediately downstream from a residually trapped gasoline source could be expected under both equilibrium and mass transfer limited dissolution conditions.

It is shown how the duration of the source even under equilibrium conditions can be significant depending on the groundwater velocity, the source length, and the non-aqueous phase liquid (NAPL) saturation within the source zone. Moreover, under field conditions a significantly larger number of pore volumes of water through the source may be needed to remove MTBE to acceptable concentrations, due to soil heterogeneity, enhanced mixing and mass transfer limited processes that can occur at the field scale vs. that at the laboratory scale. Mass transfer limitations in the source can be important for MTBE, even when not significant for BTEX, and could result under certain conditions in MTBE source groundwater concentrations from NAPL sources that are as long-lived as benzene source concentrations. Mass transfer limitations in the source may be one explanation why detached MTBE plumes are seldom found at field sites.

### What was the overall purpose of the project?

Recently, there has been considerable research related to the impact of MTBE on groundwater quality. MTBE is more soluble than other environmentally regulated compounds, e.g., benzene, found in gasoline. Because of this higher solubility, it has been anticipated that NAPL sources of MTBE contamination (e.g., gasoline) should deplete relatively faster than sources of other, less soluble contaminants. The purpose of this research was to better understand the factors that control the duration of MTBE sources of contamination, specifically when NAPL is present.

### What were the specific objectives of the study?

- Obtain experimental dissolution behavior of MTBE leaching from a residually trapped gasoline source over a wide aqueous concentration range under equilibrium dissolution conditions and directly compare this behavior with that for other compounds, e.g. benzene, toluene, etc., present in the NAPL.
- Obtain partition coefficients for MTBE and other compounds for partitioning between a multicomponent NAPL and water. Accurately assess the effects of multicomponents on MTBE and other components' partitioning and compare these effects with calculated values using Raoult's Law.
- Quantitatively compare experimental equilibrium dissolution behavior of MTBE and other compounds with appropriate multicomponent dissolution models.
- From the quantitative analysis of the dissolution and the partitioning experiments, determine the duration of an MTBE source (from the initial aqueous concentration of MTBE in water down to 50 µg/L).
- Perform a preliminary assessment of the impact of mass transfer limitations in the source on MTBE concentrations relative to that for BTEX.

### METHODOLOGY

- I. Batch equilibrium experiments were conducted to determine partition coefficients for MTBE, BTEX, and 1,2,4 trimethylbenzene (TMB) to be used in subsequent modeling of column dissolution data.
- II. Column dissolution experiments were conducted to determine the dissolution characteristics of MTBE (as well as BTEX and 1,2,4 trimethylbenzene for comparison) from laboratory-prepared model and actual gasoline mixtures residually trapped in porous media. Experimental results were compared with numerical and analytical equilibrium dissolution models.

III. A preliminary assessment of the impact of mass transfer limitations was made using a numerical multicomponent dissolution model.

$$K_i^{o-w} = \frac{MW_i}{\gamma_i^o S_i^w MW_o} \quad [2]$$

## I. Determining Partition Coefficients

### Why determine these experimentally?

Partition coefficients are important for determining source groundwater concentrations and the duration of the source concentrations. In this research project, the partition coefficients were determined experimentally, so that they would be known with accuracy for quantitatively analyzing the results of the dissolution experiments. They were also compared with Raoult's law calculated values to see how valid the assumption of Raoult's law might be for MTBE in gasoline mixtures. Deviations from Raoult's law can be expressed in terms of NAPL phase activity coefficients which were determined from the experimentally measured values.

Once partition coefficients are known they can be used with a model (analytical or numerical) to predict MTBE dissolution from NAPL.

### How were the batch experiments conducted?

Experiments were conducted for two different equilibrium MTBE concentrations, a high concentration (7.4 wt.% or 7.6 vol.%), and a lower concentration (1.7 wt.% or 1.8 vol.%). In the model oil experiments 51.5 ml of water was equilibrated with 3 g of the model NAPL mixture. Each batch experiment was conducted in triplicate. The aqueous phases of each vial were then analyzed by purge and trap GC/PID for MTBE, BTEX, and 1,2,4 trimethylbenzene (TMB), also in triplicate. BTEX and 1,2,4 trimethylbenzene were also analyzed by HPLC with UV detection. Consistent results were obtained from both analytical methods.

### How are partition coefficients determined?

Experimental partition coefficients can be determined from batch experiments as follows:

$$K_i^{o-w} = \frac{w_i}{C_i^w} \quad [1]$$

where:

- $K_i^{o-w}$  = partition coefficient of component in the gasoline phase ( $\text{cm}^3\text{-w/g-oil}$ )
- $C_i^w$  = equilibrium concentration of the component in the aqueous phase ( $\text{g}/\text{cm}^3\text{-w}$ )
- $w_i$  = equilibrium weight fraction of the component in the NAPL ( $\text{g}/\text{g-oil}$ )

The partition coefficients are defined theoretically in terms of component and NAPL properties as follows:

where:

- $S_i^w$  = aqueous solubility of the component as a pure liquid ( $\text{g}/\text{cm}^3\text{-w}$ )
- $MW_i$  = molecular weight of the component ( $\text{g}/\text{mole}$ )
- $MW_o$  = average molecular weight of gasoline at equilibrium ( $\text{g-oil}/\text{mole-oil}$ )
- $\gamma_i^o$  = activity coefficient of the component in the gasoline phase (unitless)

Equation 2 can be used to determine activity coefficients from measurements of  $K_i^{o-w}$ . Note that when  $\gamma_i^o = 1.0$ , Equation 2 becomes the expression for the Raoult's Law based partition coefficient expressed in units of  $\text{cm}^3\text{-w/g-oil}$ :

$$K_i^{RL} = \frac{MW_i}{S_i^w MW_o} \quad [3]$$

Thus, the activity coefficient for a compound in the NAPL is equal to the ratio of the Raoult's Law partition coefficient divided by the actual or measured partition coefficient, i.e.

$$\gamma_i^o = \frac{K_i^{RL}}{K_i^{o-w}} \quad [4]$$

Note from Equation 4 that if the measured partition coefficient is less than the Raoult's law partition coefficient, then the activity coefficient is greater than 1.0, i.e., positive deviations from Raoult's law. Measured partition coefficients are compared with Raoult's Law calculated values in Tables 1 and 2. The corresponding measured activity coefficients are also shown in Tables 1 and 2.

### Can Raoult's law be used to calculate partition coefficients?

Tables 1 and 2 show that MTBE behaves ideally in this model gasoline mixture containing BTEX, 1,2,4 trimethylbenzene, and octane. The measured activity coefficients for MTBE varied from  $0.92 \pm 0.07$  -  $1.00 \pm 0.04$  for mixtures containing equilibrium concentrations of 1.7 and 7.4 wt.% MTBE, respectively. These results indicate that Raoult's Law is a good assumption for MTBE in gasoline mixtures.

Measured activity coefficients for benzene were somewhat non-ideal, with values ranging from 1.18-1.19. Thus, for the NAPL mixture used in these experiments, Raoult's law underpredicted partitioning to the aqueous phase. Although not that significant for estimating purposes in the field, this difference in activity coefficients was important in this study for quantitatively comparing the dissolution behavior of MTBE relative to that for benzene, since the dissolution comparisons based on Raoult's law predictions would have then been in error by at least 20% for this NAPL mixture.

The partition coefficient values reported here are similar to previously published values (Groves, 1988; Cline *et al.*, 1991).

**Table 1.** MTBE Concentrations and Gasoline-Water Partition Coefficients for Low MTBE Concentration Case with Model Gasoline (25 °C).

	$w_i$ (g/g-o)	$K_i^{o-w}$ ( $\text{cm}^3\text{-w/g-o}$ ) measured	$K_i^{RL}$ ( $\text{cm}^3\text{-w/g-o}$ ) calculated	$\gamma_i^o = K_i^{RL}/K_i^{o-w}$ measured
Benzene	0.011	335±9	395	1.18±0.03
Toluene	0.063	1,530±25	1,608	1.05±0.02
m-Xylene	0.117	6,035±90	5,891	0.98±0.02
Ethylbenzene	0.060	NA	6,279	NA
1,2,4-TMB	0.237	18,220±500	18,955	1.04±0.03
<b>MTBE</b>	<b>0.017</b>	<b>17.3±1.2</b>	<b>15.9</b>	<b>0.92±0.07</b>
n-Octane	0.495	NA	5.1 x 10 <sup>8</sup>	NA
MW <sub>o</sub>	111.1			
$\rho_o$ @ 20°C	0.779			

**Table 2.** MTBE Concentrations and Gasoline-Water Partition Coefficients for High MTBE Concentration Case with Model Gasoline (25 °C).

	$w_i$ (g/g-o)	$K_i^{o-w}$ ( $\text{cm}^3\text{-w/g-o}$ ) measured	$K_i^{RL}$ ( $\text{cm}^3\text{-w/g-o}$ ) calculated	$\gamma_i^o = K_i^{RL}/K_i^{o-w}$ measured
Benzene	0.010	337±20	400	1.19±0.06
Toluene	0.057	1,500±75	1,632	1.09±0.05
m-Xylene	0.110	5,715±100	5,978	1.05±0.02
Ethylbenzene	0.056	NA	6,372	NA
1,2,4-TMB	0.225	17,350±750	19,236	1.11±0.05
<b>MTBE</b>	<b>0.074</b>	<b>16.1±0.6</b>	<b>16.1</b>	<b>1.00±0.04</b>
n-Octane	0.468	NA	5.1 x 10 <sup>8</sup>	NA
MW <sub>o</sub>	109.4			
$\rho_o$ @ 20°C	0.777			

**Table 3.** Conditions for MTBE Dissolution Experiments 1 through 4.

Dissolution Experiment	#1	#2	#3	#4
Flow Rate ( $\text{cm}^3/\text{day}$ )	165	144	144	144
Mass of NAPL (g)	0.40	0.85	0.46	0.73
Source Zone Length (cm)	2.5	4.0	4.1	4.0
Source Zone Diameter (cm)	4.0	4.0	4.0	4.0
Source Zone Media Type	Glass Beads 105-150 $\mu\text{m}$	Glass Beads 105-150 $\mu\text{m}$	Glass Beads 105-150 $\mu\text{m}$	Silty Loam Soil
NAPL Type	Model Mixture	Model Mixture	Gasoline	Model Mixture
Porosity, $\phi$ ( $\text{cm}^3/\text{cm}^3$ col.)	0.39	0.37	0.38	0.41
$\rho_s$ (g dry beads/ $\text{cm}^3$ beads)	2.55	2.55	2.55	2.47
$\rho_b$ (g dry beads/ $\text{cm}^3$ column)	1.56	1.58	1.59	1.41
$S_o$ ( $\text{cm}^3\text{-o}/\text{cm}^3$ pores)	0.043	0.059	0.032	0.023
$S_w$ ( $\text{cm}^3\text{-w}/\text{cm}^3$ pores)	0.957	0.941	0.968	0.977
$v$ , source interstitial velocity ( $\text{cm}/\text{d}$ )	36	33	31	27
$v/L$ , source $N_{PV}$ per day ( $\text{d}^{-1}$ )	14	8.3	7.7	6.7
NAPL density (in source)	0.78	0.78	0.74	0.76
NAPL MW (in source)	111	111	125	112
NAPL Comp. (wt. Fraction)				
Benzene	0.005	0.005	0.005	0.007
Toluene	0.050	0.050	0.048	0.025
m-xylene	0.118	0.120	0.134	0.092
Ethylbenzene	0.058	0.061	0.069	0.060
1,2,4-trimethylbenzene	0.248	0.254	-	0.216
<b>MTBE</b>	<b>0.029</b>	<b>0.030</b>	<b>0.025</b>	<b>0.012</b>
n-Octane	0.492	0.480	-	0.588
Other Components (gasoline)	0.000	0.000	0.719	0.000
Partition Coefficients, $K_i^{o-w}$				
<b>MTBE</b>	<b>17.3</b>	<b>17.3</b>	<b>14.1</b>	<b>17.1</b>
Retardation Coefficient, $R_i$				
<b>MTBE</b>	<b>1.61</b>	<b>1.85</b>	<b>1.35</b>	<b>1.58</b>

## II. Dissolution of Residually Trapped NAPL

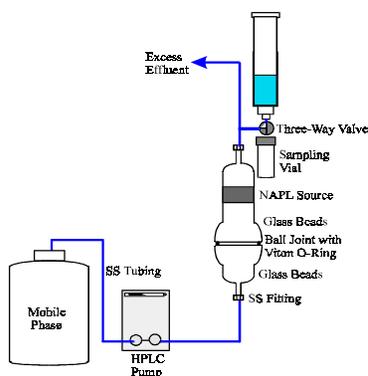
Experiments were conducted to determine the dissolution characteristics of MTBE from gasoline residually trapped in porous media. These experiments were conducted with model MTBE/gasoline mixtures and with a retail-grade MTBE/gasoline. Experimental conditions for the experiments and the compositions of the NAPL are presented in Table 3.

The porous media used in this study was glass beads. Experiments were conducted in an apparatus similar to that used in previous API dissolution studies of crude oils and model NAPLs residually trapped in glass beads and soils. The procedure for using this apparatus is described in detail elsewhere (Rixey et al., 1999; Garg and Rixey, 2000).

### How were the experiments conducted?

#### Experimental Procedure:

A diagram of the experimental setup is shown in Figure 1.



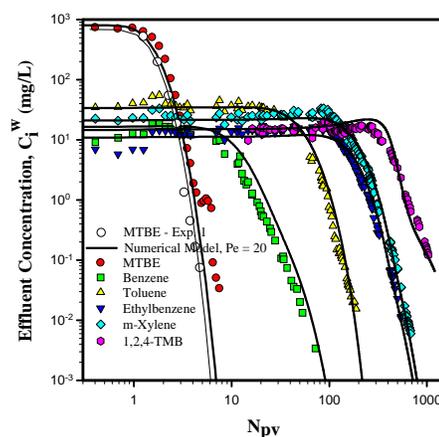
**Figure 1.** Diagram of the column experimental setup for the dissolution experiments.

#### Column Preparation:

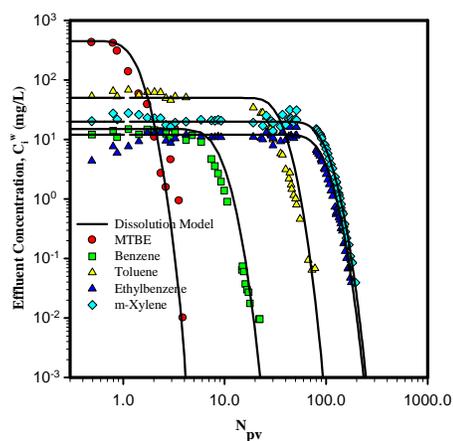
The overall length of the column was 19 cm and the diameter was 4 cm. The column was packed such that a NAPL source region of 2.5 cm to 4.0 cm length was sandwiched between clean glass beads. Glass beads of diameter 105-150  $\mu\text{m}$  (or soil) were used for preparing the source region, and glass beads of size 35-50  $\mu\text{m}$  were used to pack the remainder of the column. For preparation of the source, dry glass beads (or soil) and the desired volume of NAPL (to achieve a target NAPL saturation of 5% after placement within the column) were stirred with a stainless-steel spatula in order to achieve uniform distribution of the NAPL in the column. The NAPL and glass beads (or soil) mixture was packed in the column in small alternating increments with water to ensure that the source region was saturated. The initial composition used for the column calculations was modified to incorporate changes from the initial NAPL composition resulting from

volatilization during pre-mixing of the NAPL and equilibration of the NAPL with pore water during packing of the column. Since the partition coefficients were known from the batch experiments, the concentrations of benzene and toluene in the NAPL in the column at the start of dissolution could be determined accurately from the initial effluent aqueous concentrations. The glass beads, soils, glass columns and fittings and aqueous feed solutions were all autoclaved prior to the dissolution experiments.

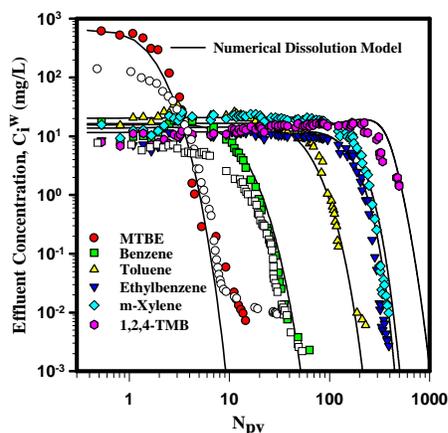
The results of these dissolution experiments are shown in Figures 2-4.



**Figure 2.** Dissolution curves for MTBE, BTEX and 1,2,4-TMB from a model NAPL mixture residually trapped in glass beads (Experiment 2). Open symbols are the MTBE data for Experiment 1.



**Figure 3.** Dissolution curves for MTBE and BTEX from gasoline residually trapped in glass beads (Experiment 3).  $Pe=20$ .



**Figure 4.** Dissolution curves for MTBE, BTEX and 1,2,4-TMB from a model NAPL mixture in soil. Filled symbols – two weeks aged (Experiment 4a). Open symbols – seven months aged (Experiment 4b).  $Pe=20$ .

### What experiments were run?

Experiments 1 and 2: *Synthetic NAPL mixture residually trapped in glass beads.* Dissolution data for MTBE for

Experiments 1 and data for benzene, toluene, ethylbenzene, m-xylene and 1,2,4-trimethylbenzene for Experiment 2 are shown in Figure 2. The curves shown in Figure 2 were determined from a multicomponent dissolution model using the independently measured partition coefficients. This multicomponent dissolution model is described in the following section. The model calculations provide a good representation of the data. Experiment 2 was similar to Experiment 1 except that the NAPL source length and saturation were greater.

The number of pore volumes is independent of source length, but is dependent on the source saturation, which was 0.059 in Experiment 2 vs. 0.043 in Experiment 1. For the theoretical curves a Peclet number ( $Pe$ ), which describes the amount of dispersion in the source region, was used to fit the curves to the data. For Experiments 1 and 2,  $Pe = 20$  was used. The dissolution data for MTBE for Experiment 1 are shown as open symbols in Figure 2. The data points are shifted to the left of those for Experiment 2, as would be expected due to the lower saturation for Experiment 2.

#### How does one translate $N_{pv}$ to time?

The data for Experiments 1-4 are shown in Figures 2-4 as effluent concentrations vs. the number of pore volumes,  $N_{pv}$ , of water flushed through the source. It is convenient to plot these data vs. pore volumes, since the results can be readily scaled for a particular contact time of water through the source (time for one pore volume of fluid to pass through the source, or  $L/v$ , where  $L$  is the length of the source, and  $v$  is the interstitial or pore water velocity). To translate to time,  $t$ , for these experiments, divide  $N_{pv}$  by the  $v/L$  values given in Table 4 for the various experiments.

Experiment 3: *Actual gasoline mixture residually trapped in glass beads.* Dissolution data for MTBE and BTEX dissolving from an actual gasoline are shown for Experiment 3 in Figure 3. The gasoline was blended with pure MTBE to a composition of 15 wt.% MTBE prior to pre-mixing with the glass beads. The MTBE composition in the source after mixing was 2.5 wt.%. This was determined from the initial aqueous concentrations during dissolution and the partition coefficient for MTBE, based on Raoult's Law. Good agreement between model calculations and experimental results was observed indicating that MTBE dissolution in model porous media behaves generally as expected for actual gasoline, as well as model gasoline mixtures.

Experiment 4: *Synthetic NAPL mixture residually trapped in a silty loam soil.* Dissolution data for MTBE, BTEX, and 1,2,4-TMB for Experiments 4a and 4b are shown in Figure 4. For these experiments, the NAPL was aged in soil for two weeks (Expt. 4a) and seven months (Expt. 4b). It was anticipated, based on previous desorption research for BTEX that had been aged with dissolved

components only (using this same soil), that non-equilibrium desorption from the soil might be observed. Figure 4 indicates that there is an effect of rate limited desorption from these soils at low MTBE concentrations, and the effect is more pronounced as the aging time increases. (This effect of aging is being studied further in ongoing experiments.) Although potentially significant at low MTBE groundwater concentrations, the effects of mass transfer limited desorption of MTBE from soil must be weighed against potential larger-scale mass transfer limitations that may arise from groundwater bypassing a NAPL pool or a fraction of the residually trapped NAPL in the source zone. (See Section III.)

#### How were the MTBE source dissolution experiments modeled?

In Experiments 1 and 2 in Figure 2 and Experiment 4

#### Volatilization of MTBE from the source and its significance

During the preparation of the source for these experiments, some losses from the NAPL due to volatilization and equilibration with the pore water occurred for MTBE and benzene. This resulted in lower initial column effluent concentrations in the dissolution experiments than if volatilization had not occurred.

The initial pore water concentration for MTBE was 735 mg/L for Experiment 1 vs. 9,300 mg/L if volatilization had not occurred – a 13 fold reduction. By contrast, benzene's initial concentration was 16 mg/L vs. 30 mg/L if volatilization had not occurred.

This result may help explain the common field observation that initial MTBE concentrations in the pore water near a source of contamination are frequently significantly lower than the predicted equilibrium concentrations (based on typical concentrations in fresh gasoline) while BTEX concentrations can be closer to predicted values.

in Figure 4, a multicomponent dissolution model was used to characterize the dissolution of MTBE, BTEX, and TMB. This numerical model is one-dimensional and accounts for changes in partition coefficients and NAPL saturation during dissolution in addition to the effects of finite dispersion. The model also can account for mass transfer limited dissolution. This model is similar to that of Borden and Kao (1992) used to analyze the multicomponent dissolution of BTX from residually trapped gasoline. For these experiments it was necessary to use such a model for BTEX and TMB, because the NAPL saturation decreased significantly during dissolution of these compounds. For MTBE and benzene dissolution, the saturation did not decrease significantly, and a numerical model is not necessary for modeling the experimental data provided equilibrium dissolution conditions exist. For these experiments, equilibrium conditions were generally observed. (It should be noted, that some mass transfer limitations were inferred from the data for Experiment 2 which affected the shape of the dissolution curves somewhat at low concentrations for MTBE, BTEX, and 1,2,4 trimethylbenzene.)

When the volume of the NAPL phase and the component partition coefficients do not change significantly during dissolution under equilibrium conditions, it is convenient to use the following analytical solution (modified from the Bastian and Lapidus [1956] solution for sorption in finite columns) to describe dissolution:

$$C^* = 2 \sum_{n=1}^{\infty} \frac{\lambda_n \sin \lambda_n}{\lambda_n^2 + \left(\frac{Pe}{2}\right)^2 + Pe} \exp \left[ \frac{Pe}{2} - \left( \frac{Pe}{4} + \frac{\lambda_n^2}{Pe} \right) t^* \right] \quad [5]$$

where  $\lambda_n$  are the roots of

$$\lambda_n \cot \lambda_n + \frac{Pe}{4} = \frac{\lambda_n^2}{Pe} \quad [6]$$

and where  $C^* = C_i^w/C_{i0}^w$  is a non-dimensionalized (normalized) effluent concentration,  $C_{i0}^w$  is the initial aqueous concentration in the effluent from a column,  $Pe$  is the Peclet number which characterizes the component's mass transfer rate due to dispersion relative to that due to advection in the source zone, and  $t^*$  is a non-dimensionalized time (expressed in terms of pore volumes and normalized by partitioning) given by:

$$t^* = \frac{tv/L}{R_i} = \frac{N_{PV}}{R_i} \quad [7]$$

where  $N_{PV}$  is the number of pore volumes eluted,  $t$  is the time (day),  $L$  is the length of the source (ft),  $v$  is the interstitial groundwater velocity (ft/day), and  $R_i$  is the retardation coefficient given by:

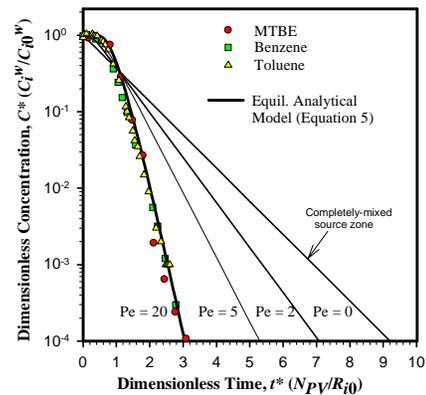
$$R_i = 1 + \frac{S_o}{S_w} K_i^{o-w} + \frac{\rho_b}{\phi S_w} K_i^{s-w} \quad [8]$$

where:

- $K_i^{o-w}$  = partition coefficient between gasoline and water ( $\text{cm}^3\text{-w}/\text{cm}^3\text{-o}$ )
- $K_i^{s-w}$  = partition coefficient between soil and water ( $\text{cm}^3\text{-w}/\text{g soil}$ )
- $S_o$  = oily phase saturation ( $\text{cm}^3\text{ oil}/\text{cm}^3$  interstitial pores)
- $S_w$  = aqueous phase saturation ( $\text{cm}^3\text{ water}/\text{cm}^3$  interstitial pores)
- $\rho_b$  = bulk density of the oil free solid ( $\text{g}/\text{cm}^3$  media)
- $\phi$  = porosity of the media ( $\text{cm}^3\text{ pores}/\text{cm}^3$  media)

Equation 5 also more readily illustrates the important parameters that determine dissolution of MTBE, BTEX, and other components in source regions under equilibrium conditions. This equation shows that plots of  $C^*$  vs.  $t^*$  should yield dissolution curves that are independent of chemical partition coefficients and NAPL saturation in the source zone and are only dependent on the Peclet number in the source zone as shown in Figure 5.

The MTBE data for Experiment 1 and the benzene and toluene data from a previous experiment for which NAPL saturations and partition coefficients were constant (Garg and Rixey, 2000) are plotted in dimensionless form in Figure 5.



**Figure 5.** Non-dimensionalized dissolution curves for MTBE, benzene, and toluene. Effect of dispersion (Peclet number) on source dissolution curves (Equation 5) is also shown.  $R_{i0}$  is the initial retardation coefficient.

## How does one adjust column dissolution data to the field scale? Effect of source dispersion.

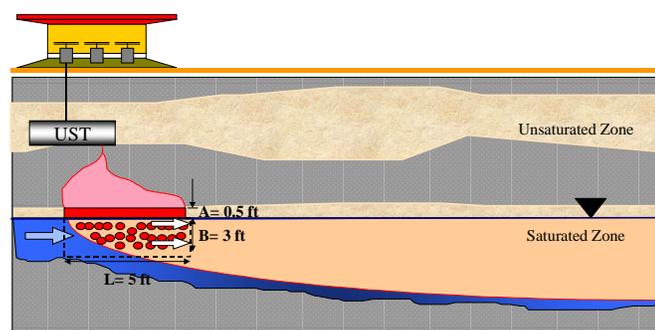
Dispersion in the source zone can have a significant effect on the number of pore volumes required to achieve a desired aqueous concentration near the source. For field conditions dispersion in the source zone will be more pronounced, i.e., the Peclet number will be lower, than for typical laboratory conditions. Figure 5 also illustrates the effect of increased dispersion on the change in concentrations with time. These curves are also plotted in dimensionless units of concentration and time in order to show that data for various chemicals and levels of source zone NAPL saturation can be generalized.

The curve for  $Pe=0$  is more representative of what would be expected for source zones in the field. This case corresponds to complete mixing in the source zone. According to Figure 5, to achieve a 10,000-fold reduction in concentration for  $Pe=0$  requires three times the number of pore volumes than for  $Pe=20$ .

### III. Mass Transfer Limited Dissolution

#### What is the potential impact of mass transfer limitations on dissolution of MTBE relative to BTEX?

Figures 6 (a) and (b) illustrate one potential scenario for which equilibrium dissolution of MTBE from a source zone can be followed by mass transfer limited dissolution.



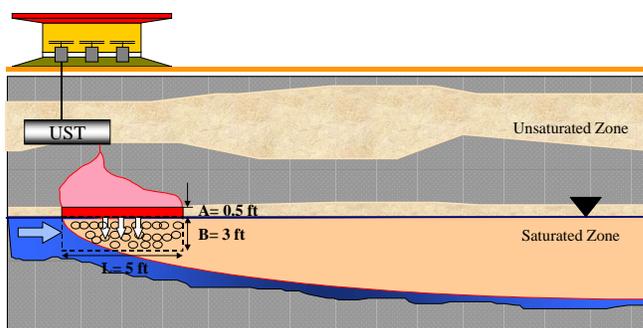
(a)

#### Laboratory Dissolution Results

In these column studies, the observed MTBE dissolution for both the model and actual MTBE/gasoline mixtures followed essentially equilibrium dissolution behavior over an aqueous concentration range that varied over four orders of magnitude. For MTBE this concentration range was from an initial effluent concentration of the order of 1000 mg/L to less than 0.10 mg/L.

Approximately 10 pore volumes of water were required to achieve a concentration of less than 0.10 mg/L for a NAPL saturation of 0.06. This would correspond to 30 pore volumes for a completely mixed source. For higher source saturations, the number of pore volumes would increase in proportion to the source zone retardation coefficient,  $R$  (Equation 8).

Figure 5 is a graphical representation of Equation 5, that can be used for estimating the number of pore volumes required to achieve a desired MTBE concentration under equilibrium dissolution conditions.



(b)

**Figure 6.** Diagrams illustrating a scenario for which equilibrium dissolution from the source zone can be followed by mass transfer limited dissolution. (a) Initially equilibrium dissolution occurs due to advection of groundwater directly through a residually trapped NAPL region. (b) Following depletion of MTBE from this region, subsequent dissolution from the NAPL pool to the groundwater underneath can be mass transfer limited. The dimensions shown in this figure are used as a basis for calculations to illustrate the effect of mass transfer limited dissolution.

Figure 6 depicts a situation where both a LNAPL pool and a source region containing well dispersed droplets of NAPL are present. This situation is likely when water table fluctuations occur following a spill.

The scenario suggested in Figure 6 was used to estimate a mass transfer rate constant for mass transfer limited dissolution. Assuming a groundwater velocity,  $v = 1$  ft/day, an effective diffusivity,  $D_{eff} = 1.5 \times 10^{-4}$  ft<sup>2</sup>/day, and using the dimensions for the source zone shown in Figure 6, a value of  $kL/v=0.03$  was estimated for mass transfer from the bypassed NAPL, where  $k$  is a mass transfer rate constant (day<sup>-1</sup>) and  $L$  and  $v$  were defined previously. The quantity  $kL/v$  is a dimensionless quantity which represents the rate of mass transfer limited dissolution relative to the rate of advective mass transfer. Note a value of  $kL/v < 1$  results in mass transfer limited dissolution, while for  $kL/v > 1$  equilibrium dissolution is approached. The mass transfer rate constant for mass transfer from the NAPL pool into the source region defined by the dotted lines in Figure 6b was estimated using the following expression:

$$k = \frac{2}{B\phi S_w} \sqrt{\frac{D_{eff}v}{\pi L}} \quad [9]$$

where  $B$  is the thickness of the source zone.  $B=3$  ft. was used for these calculations. Values of  $\phi=0.4$  and  $S_o=0.15$  were also assumed for the source region containing residually trapped NAPL. With the additional assumption that 50% of the NAPL in the source is by-passed by the groundwater flow (50% of the NAPL is in direct contact, and equilibrium dissolution occurs for this fraction, i.e.,  $F=0.5$ ), calculations were made using a multicomponent dissolution model that includes mass transfer limited dissolution for a fraction of the NAPL. This model is similar to that described by Garg and Rixey (1999)

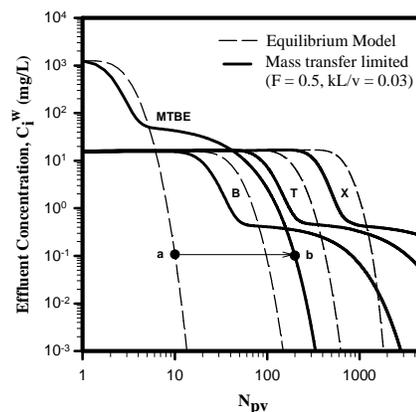
but has been modified to include longitudinal dispersion in the source region. The results of these calculations are shown in Figure 7.

For these calculations it was assumed that the mass transfer rate constant was the same for all compounds. Comparing the number of pore volumes to achieve a MTBE groundwater source concentration of 0.1 mg/L, Figure 7 indicates (see path a-b) that for the scenario presented in Figure 6 mass transfer limitations could increase the number of pore volumes (or time) to achieve acceptable concentrations by more than an order of magnitude over that assuming equilibrium dissolution.

Figure 7 also presents an interesting comparison of MTBE and benzene dissolution. For the region from 10 to 100 pore volumes, benzene and MTBE concentrations decrease by the same relative amounts for the mass transfer limited case. In this region, MTBE dissolution is mass transfer limited, but the effect of mass transfer limited dissolution for benzene is not yet very significant. The impact of mass transfer limited dissolution for benzene does not become significant until a larger number of pore volumes has been eluted. Also, by the time (concentration) that mass transfer limitations become important for benzene, degradation near the source would likely begin to take a predominant role in controlling source concentrations. This would occur when mass transfer rate constants are less than first order pore water degradation constants. For example, in the case considered here a mass transfer rate constant of  $0.006 \text{ day}^{-1}$  was calculated. This is less than typical first order degradation constants observed for benzene. Thus, mass transfer limitations could be observed for MTBE but not observed for BTEX. This comparison of MTBE and benzene may offer a possible explanation for the field observation that MTBE source concentrations sometimes drop off by only roughly the same amount as benzene source concentrations when NAPL is present. Mass transfer limitations in the source may also help explain why detached MTBE plumes are seldom found at field sites.

Figures 6 and 7 illustrate the possible effect that mass transfer limitations can have on MTBE source dissolution relative to that for BTEX. In addition to the scenario shown in Figure 6, there are certainly other ways in which bypassing of NAPL in source regions can occur and potentially limit the mass transfer of MTBE to groundwater. The extent of mass transfer limitations will in general be dependent on the relative dimensions of the source and of the bypassed regions, the amounts of the bypassed NAPL, and the groundwater velocity near the source. In the field, actual behavior will range from less to more severe bypassing than that indicated in this hypothetical example, and a distribution of mass transfer rate constants (see Garg and Rixey, 1999) can be expected rather than the simplified two-site (an equilibrium region and a mass transfer limited region described with a single rate constant) case presented here.

Additional scenarios that may lead to long-lived MTBE source concentrations include diffusion into and out of low hydraulic conductivity regions (Durrant *et al.*, 1999), as well as, MTBE transport to groundwater from small continuous or intermittent leaks from underground storage tanks in the unsaturated zone (Lahvis and Rehmann, 1999).



**Figure 7.** An illustration of the potential effect of mass transfer limitations on the dissolution of MTBE relative to that for BTEX.  $N_{pv}$  refers to the number of pore volumes of groundwater passing through the source region (region bounded by dotted lines in Figure 6).

## CONCLUSIONS

Conclusions from this research can be summarized as follows:

- In these 1-D laboratory column studies, the observed MTBE dissolution for both the model and actual MTBE/gasoline mixtures followed essentially equilibrium dissolution behavior over a concentration range of four-to-five orders of magnitude.
- Experimental partition coefficients for MTBE in the model NAPL were within 10% of the Raoult's Law values, thereby indicating that Raoult's Law is a good assumption for MTBE in gasoline mixtures.
- These dissolution experiments demonstrated that it would take approximately 10 pore volumes to reduce the MTBE source pore water concentrations from 1000 mg/L to <0.1 mg/L for a source NAPL saturation of 0.06. For higher source saturations the number of pore volumes required would increase in proportion to  $R=1+S_o/S_w * K_1^{0-w}$ . Note that for these laboratory experiments the dispersion in the source is not as great as would be expected in the field. For a completely mixed source, the number of pore volumes required to reduce the MTBE source pore water concentrations from 1000 mg/L to <0.1 mg/L would increase from 10 to 30.

- Calculations using a mass transfer limited dissolution model indicated that mass transfer limitations could significantly increase the number of pore volumes (or time) necessary to achieve acceptable MTBE concentrations.
- Volatilization of MTBE occurred relative to BTEX during source preparation, and the effect of volatilization on source concentrations was accurately accounted for in the experiments using the model mixture. Relative rates of volatilization coupled with equilibration of the residually trapped gasoline with the source pore water may help explain the common field observation that initial MTBE concentrations in the pore water near a source of contamination are frequently significantly lower than the predicted equilibrium concentrations (based on typical concentrations in fresh gasoline) while BTEX concentrations can be closer to predicted values. The importance of volatilization will be determined by site-specific factors such as the release scenerio and soil type.

## KEY IMPLICATIONS FOR RISK-BASED DECISION MAKING

- These results indicate that MTBE is not necessarily released instantaneously from a NAPL source as has been commonly suggested. The duration of the source even under equilibrium conditions can be significant depending on the groundwater velocity, the source length, and the NAPL saturation in the source zone.
- Mass transfer limitations in the source can be important for MTBE even when not significant for BTEX, and could result under certain conditions in MTBE source groundwater concentrations from NAPL sources that are as long-lived as benzene source concentrations.

## Relationship to Related API Dissolution Models

Huntley and Beckett (1997) developed an approach to predict temporal changes in concentration of soluble hydrocarbon constituents (including MTBE) due to dissolution from groundwater flowing through and below light non-aqueous phase liquid (LNAPL) sources. The model assumptions and equations for groundwater flowing through an LNAPL source are consistent with the experimental equilibrium dissolution results reported in this summary for a given LNAPL saturation and groundwater velocity through the source zone and when the source zone is considered to be well-mixed.

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## AUTHOR BIOGRAPHICAL SKETCH

**Bill Rixey** is an associate professor in the Department of Civil and Environmental Engineering at the University of Houston. He has a B.S. in chemical engineering from Lehigh University and a Ph.D in chemical engineering from the University of California, Berkeley. Prior to joining the faculty at UH in 1993, he was a research engineer in the Environmental Research and Development directorate of Shell Development Co. His primary research focus is the characterization of the release of chemicals from subsurface multicomponent sources of contamination and how that impacts the exposure of chemicals to groundwater and other environmental exposure pathways.

**Sushrut Joshi** is a M.S. candidate in environmental engineering at the University of Houston. The focus of his research is the dissolution/desorption characteristics of MTBE from gasoline-impacted soils.

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