API American Petroleum Institute

DECEMBER 2005 NO. 23

THE IMPACT OF GASOHOL AND FUEL-GRADE ETHANOL ON BTX AND OTHER HYDROCARBONS IN GROUND WATER: EFFECT ON CONCENTRATIONS NEAR A SOURCE

RESULTS FROM BENCH-SCALE PARTITIONING AND COLUMN STUDIES

WILLIAM G. RIXEY, XIAOHONG HE, AND BRENT P. STAFFORD
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, UNIVERSITY OF HOUSTON

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

This technical bulletin summarizes the results of batch equilibrium and continuous-flow column experiments to assess the enhancement of BTX (benzene, toluene and xylenes) and other hydrocarbon concentrations in ground water near ethanol releases. The experiments were conducted to approximate worst-case scenarios in which either gasohol or highly concentrated ethanol (e.g., fuel-grade ethanol, which is typically denatured with 5% gasoline) comes in direct contact with ground water. Enhancements of BTX [1,2,4-trimethylbenzene (TMB) and n-octane were included for comparison with BTX] concentrations in the aqueous phase due to ethanol were investigated.

Principal conclusions from this research are as follows:

- *Batch equilibrium experiments indicate that BTX & other hydrocarbon concentrations can be significantly enhanced when ethanol concentrations in the aqueous phase are greater than 10 vol%.* Benzene is enhanced by a factor of 1.2 at 10 vol% ethanol. Enhancements increase in proportion to ethanol concentration and are much greater for lower solubility compounds (e.g., enhancement for 1,2,4-trimethylbenzene >> benzene). These results are consistent with previous studies (Heerman and Powers, 1998).

- *It is unlikely that gasohol spills (described herein as Scenario 1) create sufficiently high ethanol concentrations near the source to produce a noticeable increase in hydrocarbon concentrations.* Phase equilibrium data indicate that high concentrations of ethanol in water are possible for very low water/NAPL phase ratios. In the field, however, NAPL occurs in contact with relatively larger amounts of water, and therefore, high concentrations will not be realized. In column experiments with 15% ethanol initially in a NAPL mixture, a maximum concentration of 34,700 mg/L ethanol with maximum aqueous concentration enhancement factors of 1.3 to 1.4 for BTX were observed. For comparison, the predicted enhancements were less, 1.09 and 1.19 for benzene and m-xylene, respectively, for the same peak ethanol concentration. These results are consistent with the modest increase in plume lengths reported for several field sites affected with gasohol (Ruiz-Aguilar et al., 2003).

- *Higher peak ethanol concentrations and therefore more BTX concentration enhancement can be expected for fuel-grade ethanol spills with or w/o existing NAPL contamination (described herein as Scenarios 2 & 3) than for gasohol (Scenario 1).* Measured concentration enhancements for fuel-grade ethanol were up to 10 and 130 times for benzene and m-xylene, respectively (peak ethanol concentration was 557,000 mg/L), compared to 1.3 to 1.4 maximum enhancements for gasohol (peak ethanol concentration of 34,700 mg/L).

- *Fuel-grade ethanol released into aquifers without existing NAPL yields lower maximum BTX concentrations than releases onto existing NAPL.* For neat ethanol spilled onto existing NAPL (Scenario 2), the maximum BTX and other hydrocarbon concentrations that were observed were controlled by equilibrium dissolution from NAPL into the concentrated ethanol pulse. For fuel-grade ethanol spilled without an existing NAPL source (Scenario 3), the maximum BTX and other hydrocarbon concentrations observed were determined by the dilution of the fuel mixture in water as the ethanol pulse became dispersed.

- *Phase separation of hydrocarbon can occur from spills of fuel-grade ethanol resulting in a residual NAPL source.* Thus, sites that did not previously have BTX will potentially become affected with a persistent source of BTX. For the E95 spill experiment, 40% of the hydrocarbon remained as trapped NAPL after ethanol passed through the

column. This phase-separated NAPL yielded similar longer-term dissolved BTX concentrations comparable to an existing NAPL.

- *Migration of NAPL due to immiscible displacement was not observed for spills of neat ethanol onto existing NAPL.* This is likely due to the low initial NAPL saturation (0.05) in these experiments. Mobilization is anticipated for higher NAPL saturations when ethanol concentrations are high.

What was the overall purpose of the project?

Recently, considerable research has been conducted related to the impact of ethanol on ground water quality. Two of the principal concerns related to ethanol spills are 1) what impact does ethanol have on the natural attenuation of BTX, and 2) what impact does ethanol have on enhancing ground water concentrations of BTX near the source area.[1] The purpose of the research reported in this bulletin was to better understand the factors that control the latter through bench-scale laboratory experiments.

What were the specific objectives of the study?

- Determine the maximum enhancements in concentrations of BTX and other hydrocarbons in ground water that may be expected near a source of contamination for the following spill scenarios:

    - Scenario 1: Gasohol
    - Scenario 2: Neat ethanol onto existing NAPL
    - Scenario 3: Fuel-grade ethanol w/o existing NAPL

- Determine the maximum ground water concentrations of ethanol that can be expected for each of these scenarios.

- Determine the longer-term impact on source BTX and other hydrocarbon concentrations once ethanol has been depleted from the source region.

- Determine the potential for the hydrocarbons in fuel-grade ethanol to phase-separate and generate a long-term residual NAPL source for sites that do not have existing NAPL.[2]

Overview of the Experiments

Batch equilibrium experiments were conducted to determine the enhancement in BTX, 1,2,4-trimethylbenzene, and n-octane partitioning for a given ethanol concentration in water. Batch equilibrium experiments were also conducted to determine the partitioning of ethanol between NAPL and water.

Continuous-flow, water-saturated column experiments were conducted to simulate a spill of ethanol in direct contact with ground water. Experimental results were compared with equilibrium dissolution models.

Batch Equilibrium Experiments

Equilibrium measurements are important for determining the maximum dissolved aqueous concentrations of BTX and other hydrocarbons resulting from ethanol spills. Equilibrium hydrocarbon concentrations in water are a function of the aqueous ethanol concentration and the composition of the NAPL. Thus, if the ethanol concentration in water is known, then the equilibrium (maximum) concentrations of the hydrocarbons for a given NAPL can be determined.

Equilibrium measurements were also conducted to determine what ethanol levels are possible when a NAPL containing ethanol (e.g., gasohol) contacts water.

How were the batch experiments conducted?

For these experiments, a NAPL mixture with the following composition (in weight fraction) was prepared: ethanol, 0.15[3]; benzene, 0.004; toluene, 0.05; m-xylene, 0.13; 1,2,4-trimethylbenzene (TMB), 0.32; and n-octane balance. This synthetic NAPL mixture was contacted with varying amounts of water, and equilibrium aqueous concentrations for BTX, TMB and n-octane were measured for various equilibrium ethanol concentrations. Each batch experiment was conducted in triplicate. The aqueous phases of each vial were then analyzed by direct aqueous injection GC/FID for BTX, 1,2,4 trimethylbenzene (TMB), n-octane and ethanol in duplicate.

How were the concentration enhancements determined?

Enhancements in concentrations were determined by the ratio of the measured aqueous concentration to the concentration in the absence of ethanol as follows:

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[1] A recent API technical bulletin provides a comprehensive summary of the major issues regarding ethanol impacts to ground water (Buscheck, 2003).

[2] The potential for enhancing the migration of existing NAPL due to immiscible displacement (mobilization) is also an important concern for spills of E95 or gasohol; however, this was not addressed in this research. The experiments in this summary were focused on miscible displacement (dissolution) and were designed to minimize mobilization.

[3] 15 wt.% ethanol corresponds to 15 vol.% ethanol for this NAPL mixture. Ethanol-blended gasoline will typically contain 10 vol.% ethanol.

$$C_i^w/C_{io}^w \qquad [1]$$

where:

C_i^w = measured equilibrium concentration of the component in the aqueous phase (g_i/cm^3-w)
C_{io}^w = calculated equilibrium concentration of the component in the aqueous phase (ethanol-free) (g_i/cm^3-w)

The ethanol-free aqueous concentrations were calculated as

$$C_{io}^w = \gamma_i^o x_i^o S_i^w \qquad [2]$$

where:

S_i^w = pure component solubility in water (g/cm^3-w)
x_i^o = mole fraction in NAPL
γ_i^o = activity coefficient of the component in NAPL

In Equation 2 the mole fractions used were the initial mole fractions in the NAPL prior to equilibration. Activity coefficients were calculated using solubility parameters for each component and regular solution theory (Garg and Rixey, 1999).

How much enhancement can be expected in BTX concentrations?

The batch experiments illustrate the maximum enhancement in aqueous concentrations that could occur when existing NAPL is contacted with ethanol. Figure 1 shows enhancements for various hydrocarbons (concentration in ethanol-water normalized by the concentration in ethanol-free water) vs. equilibrium ethanol concentration in water. These results indicate an exponential increase in enhancements with increasing ethanol concentration. However, the benzene concentrations are not enhanced appreciably until the ethanol concentrations reach approx. 10 vol.%. Benzene is enhanced by a factor of 1.2 and TMB is enhanced by a factor of 1.8 at 10 vol% ethanol. The enhancement is greater for less soluble NAPL components. The enhancement is thus dependent on the concentrations that can be expected for ethanol. Gasohol under most conditions is likely to generate relatively low concentrations of ethanol (see discussion below). However, depending on the size of the release, spills of neat or fuel-grade ethanol could generate ethanol concentrations sufficient to significantly enhance BTX concentrations.

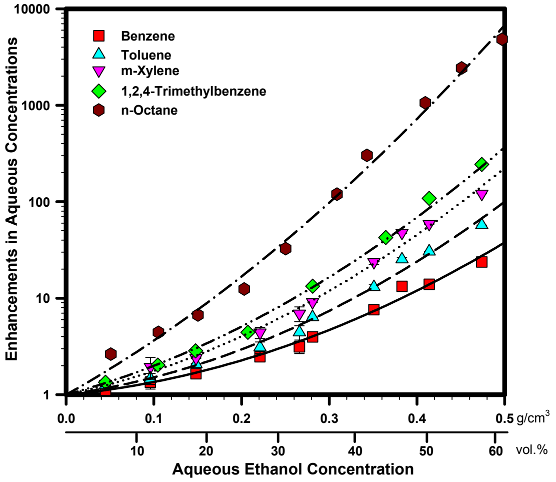

Figure 1. Enhancement in the equilibrium aqueous concentrations for BTX, 1,2,4-trimethylbenzene (TMB), and n-octane vs. equilibrium aqueous ethanol concentration. The curves represent empirical regressions of the data for each compound.

What concentrations of ethanol can be expected for gasohol and E95?

Gasohol: Concentrations will depend on the amount of spilled NAPL. For small spills, ethanol can be absorbed by the moisture content in the unsaturated zone, thereby limiting the amount that reaches ground water (Heermann and Powers, 1998). For larger spills, after the unsaturated zone is saturated with ethanol, the amount present in ground water near a spill can be estimated from the amount of water that is in contact with the NAPL. Figure 2 shows the equilibrium aqueous concentrations for a given NAPL/water volume ratio.

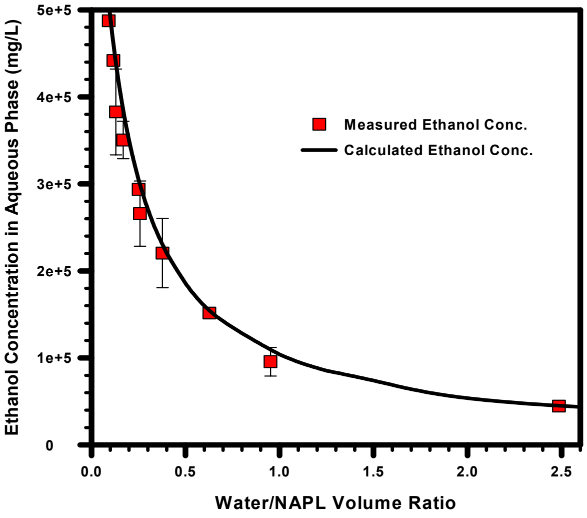

Figure 2. Equilibrium aqueous concentrations of ethanol for a NAPL containing initially 15 vol.% ethanol (E15). The experiments simulate a gasohol contacting various amounts of water. The symbols are measured values, and the curve is based on calculations assuming all of the ethanol initially in the NAPL partitions into the aqueous phase at equilibrium.

For NAPL that reaches the water table, maximum ethanol concentrations in ground water near a NAPL source will critically depend on how the source is generated. For a large gasohol spill that generates a NAPL pool, ethanol concentrations could be quite high in ground water in the immediate vicinity of the spill. Figure 2 shows that for very low water/NAPL ratios, the ethanol concentration in ground water for gasohol containing 15% ethanol approaches 500,000 mg/L (> 60 vol.%). For such ethanol concentrations, the benzene concentrations are enhanced by more than a factor of 20. (Figure 1).

However, for a NAPL at residually trapped levels as a “smear zone,” the maximum concentrations of ethanol in the pore water in direct contact with residual NAPL will be much lower. From Figure 2, a water/NAPL ratio of 2.5 (would correspond to a NAPL saturation of 29%) yields an ethanol concentration of 45,000 mg/L (5.7 vol.%) for NAPL containing initially 15% ethanol. For such conditions, only a slight enhancement of BTX and TMB concentrations can be expected in ground water (Figure 1.) Lower NAPL saturations would yield even lower ethanol concentration and corresponding enhancements in BTX and TMB concentrations.

E95: For E95 spills, ethanol concentrations could be significantly greater because ethanol is completely miscible with water. However, ethanol is likely to mix with water in the capillary fringe, thereby reducing the amount that enters ground water. Also, ethanol has a much lower density than water and will tend to remain on top of the water table, despite its high miscibility, until equilibrated with water. The rate at which it enters ground water will be slow if mixing does not occur, as dissolution will then be limited by diffusion. More research is needed to determine what concentrations of ethanol are likely to be generated for a given size spill of fuel grade ethanol.

Column Experiments

How were the experiments conducted?

Experiments were conducted in continuous-flow, water-saturated columns to assess the impact of spill Scenarios 1 through 3 on BTX and other hydrocarbon concentrations in ground water near a spill source. The experiments were conducted with volumes of spilled fuel ranging from 10 to 40 ml in columns with a pore volume of 95 ml (corresponds to a range of spill volumes of 0.1 to 0.4 column pore volumes). This range of pore volumes was chosen to represent a practical range of spill volumes relative to the volume of affected ground water in the immediate vicinity of a spill. These experiments were designed to represent direct contact of the ethanol fuel with ground water, i.e., assume that 100% of the spill enters the saturated zone. Thus, the experiments can be considered to represent a worst-case scenario for ground water impacts for spills of gasohol and fuel-grade ethanol. The conditions for each of the experiments and the compositions of the gasohol and fuel-grade ethanol mixtures are summarized in Table 1.

In Scenarios 1 and 2, the fuel was placed into water saturated columns as a NAPL, and then eluted with water at constant flow rate. In Scenario 3 the fuel was injected as a pulse at the inlet of a column that contained no NAPL.

A diagram of the experimental setup is shown in Figure 3.

Figure 3. Diagram of the experimental setup for the laboratory column experiments. A NAPL source region was placed in the columns for Experiments 1 to 4. No trapped NAPL was present prior to the initiation of flow for Experiments 5 and 6. Neat or fuel-grade ethanol was injected for Experiments 3 to 6 only.

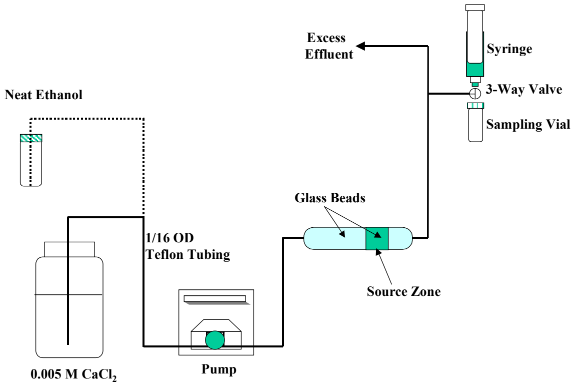

Table 1. Conditions for Ethanol Column Experiments.

	Scenario 1		**Scenario 2**		**Scenario 3**	
	Gasohol		**Neat Ethanol onto Residual Gasoline**		**Fuel-Grade Ethanol**	
Column Experiment	**#1**	**#2**	**#3**	**#4**	**#5 - E97.5**	**#6 - E95**
Volume of Ethanol pulse (ml)	0	0	**20**	**40**	**40**	**40**
Volume of HC in Ethanol (ml)	0	0	0	0	1.0	2.0
Volume of NAPL (ml)	**10**	**20**	1.0	1.0	0	0
Volume of Ethanol in NAPL (ml)	1.5	3.0	0	0	0	0
NAPL sat. in source region	0.50	0.50	0.05	0.05	0	0
Flow rate (ml/day)	144	144	144	144	144	144
v, interstitial velocity (cm/d)	30	30	30	30	30	30
Vol. column pore space (ml)	95	95	95	95	95	95
Ethanol density (g/cm^3)	0.79	0.79	0.79	0.79	0.79	0.79
NAPL density (g/cm^3)	0.78	0.78	0.78	0.78	0.77(1)	0.77(1)
NAPL MW	94	94	113	113	114(1)	114(1)
NAPL composition (wt. fraction)						
Benzene	0.007	0.005	0.004	0.007	0.005(1)	0.005(1)
Toluene	0.06	0.05	0.065	0.068	0.06(1)	0.06(1)
m-xylene	0.12	0.12	0.14	0.14	0.12(1)	0.12(1)
1,2,4-trimethybenzene	0.30	0.30	0.35	0.35	0.30(1)	0.30(1)
ETHANOL	**0.15**	**0.15**	**0.00**	**0.00**	**0.00(1)**	**0.00(1)**
Octane	0.37	0.38	0.44	0.43	0.51(1)	0.51(1)

Note: (1) properties and composition of hydrocarbon (HC) in fuel-grade ethanol, if HC completely phase separated from ethanol.

Table 2. Peak Effluent Concentrations Observed for Ethanol Column Experiments.

	Gasohol		**Neat Ethanol onto Residual Gasoline**		**Fuel-Grade Ethanol**	
Column Experiment	**#1**	**#2**	**#3**	**#4**	**#5 - E97.5**	**#6 - E95**
ETHANOL	**18,700**	**34,700**	**186,000**	**557,000**	**557,000**	**602,000**
Benzene	25.1	16.9	18.3	220	62	150
Toluene	48.5	51.7	118	1,400	790	1,600
m-xylene	26.7	41.5	126	3,400	740	4,000
1,2,4-trimethybenzene	24.8	38.6	86	8,500	1,600	10,400
Octane	<1	<1	3.2	5,400	3,200	18,400

Table 3. Enhancement in Peak Concentrations Relative to Ethanol-free Water Dissolution of NAPL.(1)

	Gasohol		**Neat Ethanol onto Residual Gasoline**		**Fuel-Grade Ethanol**	
Column Experiment	**#1**	**#2**	**#3**	**#4**	**#5 - E97.5**	**#6 - E95**
Benzene	1.2	1.3	1.7	10	5(2)	10(2)
Toluene	1.1	1.4	2.5	30	20(2)	40(2)
m-xylene	1.1	1.4	3.0	130	35(2)	180(2)
1,2,4-trimethybenzene	1.2	1.4	3.1	400	90(2)	570(2)
Octane	-	-	9.8	16,000	8,500(2)	46,000(2)

Notes: (1) Enhancements were calculated based on the ratio of the peak measured concentrations to the calculated concentrations for equilibrium with ethanol-free water with NAPL of the composition shown in Table 1.

(2) Concentrations in Table 2 and enhancements shown in Table 3 are likely controlled by dilution of the fuel-grade ethanol components by water, not by solubility in ethanol/water.

Column Preparation:

The overall length of the column was 19 cm and the diameter was 4 cm. For Experiments 1 through 4, the column was packed with a NAPL source region (≈4 cm in length) that was sandwiched between clean glass beads. In Experiments 5 & 6, no NAPL was placed in the column.

For Experiments 5 & 6, glass beads of size 35-50 μm were used to pack the entire column. The pore volume of the columns was 95 cm^3. For Experiments 1-4, glass beads of diameter 105-150 μm were used for preparing the NAPL source region and glass beads of size 35-50 μm were used to pack the remainder of the column.

What experiments were run?

Experiments 1 and 2
Scenario 1: Spills of gasohol. Continuous-flow, water-saturated column experiments were conducted with different volumes of gasohol (NAPL with 15 vol.% ethanol). For each experiment, a certain amount of the ethanol/hydrocarbon mixture was first packed into a water-saturated column to act as a residually trapped, gasohol source. Ethanol-free water was then introduced. Amounts of 10 ml and 20 ml of gasohol were used in Experiments 1 and 2, respectively. Effluent samples were collected and concentrations of ethanol and each NAPL component were measured vs. time.

The columns were packed with glass beads and were then oriented horizontally for the experiments. Note for these experiments, the NAPL saturation was prepared at a high level (above residual saturation) to minimize the amount of dilution of ethanol in the pore water. After packing, the NAPL saturation in the source zone was approximately 50% of the pore space. The NAPL source zone was placed in the first half of the column to allow for displacement of the NAPL when the water flow was initiated. The flow rate was 144 ml/day during and after the ethanol injection.

Experiment 3 and 4
Scenario 2: Spills of neat ethanol onto existing NAPL contamination. Continuous-flow, water-saturated column experiments with different size pulses of ethanol were conducted. For each experiment, a certain amount of ethanol-free NAPL mixture was first packed into a water-saturated column to act as a residually trapped NAPL source, and then a pulse of neat ethanol was introduced into the column to simulate a neat ethanol spill, followed by ethanol-free water. A 20-ml pulse was used in Experiment 3 and a 40-ml pulse was used in Experiment 4 to simulate different spill sizes. Effluent samples were collected and concentrations of ethanol and each NAPL component were measured vs. time.

Similar to Experiments 1 and 2, the columns were packed with glass beads and were then oriented horizontally for the experiments. The residual NAPL saturation in the source region was 5% of the pore space in Experiments 3 and 4. The NAPL source region was placed in the second half of the column to minimize dispersion from the downstream edge of the NAPL zone to the effluent. The flow rate was 144 ml/day during and after the ethanol injection. The compositions of the NAPL mixture are shown in Table 1.

Experiment 5 and 6
Scenario 3: Spills of fuel-grade ethanol without existing contamination. Continuous-flow, water-saturated column experiments were conducted to simulate a spill of fuel-grade ethanol into the subsurface that does not have existing NAPL. The fuel-grade ethanol was created by mixing pure ethanol and a synthetic NAPL mixture at different volume ratios. Two different concentrations of ethanol/NAPL in the fuel-grade ethanol were used. One contained 95 vol.% ethanol and 5 vol.% NAPL, and the other contained 97.5 vol.% ethanol and 2.5 vol.% NAPL. The composition of the NAPL mixture is shown in Table 1. In these experiments, fuel-grade ethanol pulses were injected into the inlet of the water-saturated columns packed with clean glass beads, and the concentrations of ethanol and each NAPL component were measured in the effluent vs. time. The materials, apparatus and experimental setup for the fuel-grade ethanol spill experiments were similar to those for the neat ethanol experiments. A similar column experiment was also conducted with pure ethanol (100% ethanol) with no existing NAPL to compare effluent ethanol behavior (comparable results were obtained but are not reported in this bulletin).

Results

Results of these experiments are shown in Tables 2 and 3 and Figures 4 through 7. The results are discussed in terms of the following: 1) peak concentrations generated (Tables 2 and 3) and comparisons with equilibrium predictions (Tables 4 through 6); 2) curves of effluent concentrations vs. pore volumes eluted (Figures 4 through 7, and 3) NAPL phase separation.

Observed Peak Concentrations and Comparison with Equilibrium Dissolution

A comparison of maximum concentrations of ethanol and hydrocarbons observed is shown in Table 2 (previous page) for each of the experiments.

Gasohol: For the gasohol experiments, the ethanol concentrations were 18,700 and 34,700 mg/L, respectively, for the two volumes of NAPL used (10 ml and 20ml). (As indicated in Figure 2, higher ethanol concentrations are possible when very small amounts of water are contacted with gasohol. From Figure 2, a NAPL saturation of 0.25, i.e., a NAPL/water ratio = 3, would yield an ethanol concentration of 34,700 mg/L.) The hydrocarbon concentrations were increased only slightly above the ethanol-free water concentrations. Enhancements in peak concentrations ranging from 1.3 to 1.4 for benzene to TMB were observed. The small enhancements were due to the relatively low ethanol concentrations (34,700 mg/L or less). Comparisons with equilibrium predictions are shown in Table 4 and discussed below.

The equilibrium predictions yielded enhancements of 1.09 for benzene and 1.24 for TMB. The experimental values reported are above these values, but can be considered within experimental error (± 20%) of the predicted values.

Table 4. Peak Enhancements for Gasohol – Experiment 2.

	Experiment	Equilibrium Dissolution Model	Equilibrium (Figure 1)
Benzene	1.3	1.09	1.09
Toluene	1.4	1.12	1.12
m-Xylene	1.4	1.19	1.19
1,2,4-TMB	1.4	1.24	1.24
Octane	-	1.54	1.54

Table 5. Peak Enhancements for Neat Ethanol – Experiment 3.

	Experiment	Equilibrium Dissolution Model	Equilibrium (Figure 1)
Benzene	1.7	1.7	1.8
Toluene	2.5	2.0	2.1
m-Xylene	3.0	2.5	2.7
1,2,4-TMB	3.1	3.2	3.3
Octane	9.8	8.8	8.4

Table 6. Peak Enhancements for Neat Ethanol – Experiment 4.

	Experiment	Equilibrium Dissolution Model	Equilibrium (Figure 1)
Benzene	10	9	75
Toluene	30	53	232
m-Xylene	130	204	572
1,2,4-TMB	400	633	964
Octane	16,000	22,900	23,600

(Peak ethanol concentrations are shown in Table 2.)

Neat ethanol on existing NAPL: For these experiments, the peak ethanol concentrations were 186,000 and 557,000 mg/L, respectively, for the two volumes of ethanol used (20 ml and 40 ml). Higher peak ethanol concentrations were observed than for the gasohol experiments. This is primarily because, for the same volume of neat ethanol or gasohol, more ethanol (6.7 times) was used vs. that in the gasohol experiments. Hydrocarbon concentrations increased substantially as predicted by Figure 1. Enhancements in peak concentrations ranging from 1.7 to 3.1 for benzene to TMB were observed for Experiment 3 (20 ml ethanol). Enhancements in peak concentrations ranging from 10 to 400 for benzene to TMB were observed for Experiment 4 (40 ml ethanol). Comparisons with equilibrium predictions are shown in Tables 5 and 6. Experimentally derived and predicted concentrations were similar. This suggests that the observed enhancements can be described in terms of equilibrium dissolution. There was no evidence of immiscible displacement of the trapped NAPL in these experiments.

Note that for Experiment 4, the experimentally observed peak enhancements for benzene and toluene, in particular, were much lower than that predicted from Figure 1. This is because there was depletion of benzene and toluene from the trapped NAPL as dissolution occurred during the ethanol pulse. This effect is captured in the equilibrium dissolution model and shows that peak enhancements in concentrations of hydrocarbons for large volume ethanol spills are dependent on the amount of existing NAPL that comes into contact with the spilled ethanol.

Fuel-grade ethanol: Experiments 5 and 6 both yielded peak ethanol concentrations (≈600,000 mg/L) similar to Experiment 4 (neat ethanol onto existing NAPL). This was expected, as the size of the ethanol injected was the same. However, the peak concentrations for the hydrocarbons in Experiment 5 were lower than those for Experiment 4, i.e., the benzene peak concentration was 3.5 times lower and the TMB peak concentration was 5 times lower, despite the same amount of hydrocarbon present for the two scenarios. (In Experiment 4, 1 ml of HC was present as existing trapped NAPL, while in Experiment 5, 1 ml of HC was already dissolved in the ethanol). Experiment 6 generated comparable peak hydrocarbon concentrations to Experiment 4, but twice the amount of hydrocarbon was used for Experiment 6. Comparable peak hydrocarbon concentrations occurred because during dissolution of the NAPL by ethanol (in Experiment 4), ethanol contacted a separate phase NAPL and, at the leading edge, a small of amount of ethanol with very high HC concentrations was generated from solubilization of the NAPL; whereas, in the fuel-grade ethanol case, the hydrocarbons were already dissolved in the ethanol, and their peak concentrations were limited by either 1) dilution of the original fuel-grade ethanol composition, or 2) solubility, based on the compound. For Experiments 5 and 6, the peak BTX, TMB, and n-octane concentrations appear to be controlled by dilution rather than by solubility at this high ethanol concentration. Experiments with smaller amounts of ethanol (not conducted) and corresponding lower peak ethanol concentrations would likely have had peak hydrocarbon concentrations that were limited by the solubility of the compounds. (See following discussion regarding phase separation.)

Effluent Concentration Curves and Longer-term Source Concentration Behavior

Effluent concentration curves are shown in Figures 4 to 7 (Page 11) for the neat ethanol and fuel-grade ethanol experiments.[4] The figures show the same results presented in the previous section with respect to peak concentrations for ethanol and hydrocarbons. (See Table 2.)

Neat ethanol on existing NAPL: In Figures 4 and 5, the curves further illustrate the comparison of observed concentrations with those predicted from an equilibrium dissolution model. The curves also show the BTX concentrations emanating from residual NAPL after ethanol concentrations have been depleted. For Figure 4, although there is some enhancement in peak concentrations observed with ethanol, the hydrocarbon concentrations following the peaks are largely determined from dissolution by ethanol-free water. We see that benzene depletes to low concentrations after 4.5 column pore volumes (PVs) (22 PVs through the NAPL source zone within the column) have been eluted. In Figure 5 the ethanol volume was doubled, and we not only see a large increase in the peak concentrations, from 186,000 to 557,000 mg/L, but a much faster depletion of benzene from the NAPL occurs. Figure 5 indicates that benzene could be removed selectively from the existing NAPL, resulting in a greater transfer of benzene into ground water through dissolution. In addition, after ethanol is depleted, NAPL is left behind that is depleted in benzene. Thus, multiple spills of neat ethanol may result in faster, selective depletion of existing NAPL, i.e., faster depletion of benzene over time than would occur without ethanol. For this to have a significant effect on long-term benzene concentrations, however, the amount of ethanol spilled would have to be large relative to the amount of NAPL present. It should also be noted that downstream NAPL could be formed (that also contains some of the previously dissolved benzene) as the ethanol plume attenuates and the less soluble compounds (e.g., TMB, octane) phase separate. Thus, spreading of existing NAPL sources by dissolution/phase separation (vs. mobilization by immiscible displacement) could occur. (See also discussion regarding phase separation of fuel-grade ethanol.) The experiments reported here were not designed to verify the potential for redistribution of existing NAPL.

Fuel-grade ethanol without existing NAPL: The curves in Figures 6 and 7 also show the same results presented in the previous section with respect to peak concentrations for ethanol and hydrocarbons. (See Table 2). The curves also show the BTX, TMB, and octane concentrations emanating from some trapped NAPL after ethanol concentrations have reduced to low levels. It was stated in the previous section that, for the fuel-grade experiments reported here, the concentrations appear to be controlled by dilution of the hydrocarbon components in the ethanol fuel rather than by solubility. However, from the observed concentrations of BTX and TMB, it is clear that a residual NAPL remains after the ethanol has been depleted from the column, i.e., some hydrocarbon phase separated from the ethanol.

Phase Separation, Entrapment of NAPL, and Generation of a Long-term Source

Why did the NAPL phase separate in the fuel-grade ethanol experiments? Although the peak concentrations of ethanol were high enough such that phase separation should not have occurred at the *peak* concentrations, the ethanol concentrations in the trailing edge of the ethanol pulse reduced to the point that the solubilities were exceeded for some of the hydrocarbons. This resulted in phase separation of some hydrocarbon as NAPL.

The NAPL then acted as a new longer-term source of BTX and TMB. For Experiment 6, 40% of the original hydrocarbon in E95 remained in the column as NAPL after 3 PVs of ethanol was eluted. Comparing Figure 6 and 7 (fuel-grade ethanol) with Figure 4 (neat ethanol onto existing NAPL), similar hydrocarbon concentrations in water were observed for the two scenarios after 1.5 PVs of ethanol were eluted. Thus, a spill of fuel-grade ethanol at a site without existing NAPL could produce similar, longer-term concentrations to that from an existing NAPL. It should be pointed out that more phase separation would likely occur as the ethanol pulse dilutes further. (In Experiment 6, a separate NAPL phase was observed in the effluent samples for which ethanol concentrations were near peak concentrations. The amount of NAPL collected was 20% of the amount of the hydrocarbon in the E95.) Thus, for fuel-grade ethanol spills, there exists the potential for generation of NAPL even further downstream of a spill as the ethanol attenuates and the solubility of the HC mixture continues to be exceeded. Eventually ethanol will dilute to the point that no further NAPL will phase separate. Sorption may also play a role here as the various hydrocarbons will be selectively retarded and separated as the concentrated plume migrates. Additional experiments and model simulations are needed to better quantify what fractions of each of the individual compounds, e.g., BTX, TMB, ultimately move with the dissolved, attenuated ethanol plume vs. remain behind in a phase-separated NAPL.

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[4] Curves are available but not included here for gasohol Experiments 1 and 2. (See He, 2002; Rixey and He, 2001.) The enhancements were less than those shown for Figure 4. Peak concentrations and enhancements for Experiments. 1 and 2 are shown in Tables 2 and 3.

Migration of NAPL

In the Scenario 2 (ethanol onto existing NAPL) experiments (Experiment 3 and 4) the potential for mobilization of the NAPL existed as a result of immiscible displacement as well as from solubilization. There was no indication of mobilization of NAPL in Experiment 3, however in Experiment 4 (for which the maximum ethanol concentration was much higher) there was evidence of a small amount of separate phase in the effluent. This occurred in samples where the peak concentrations were observed. The separate phase was observed because of the presence of a hydrophobic red dye (Sudan IV) in the NAPL; however, the amount of NAPL collected was too small to be quantified. The presence of a negligible amount of separate phase, coupled with the agreement between the dissolution curves and the experimental data (see Figures 4 & 5), indicated that dissolution of the NAPL vs. mobilization was the dominant removal mechanism in these experiments. This is likely the result of the low initial NAPL saturation (5%) used for these experiments.

Utility of this Study and Issues to be Addressed

The results presented here are useful for anticipating potential enhancements in source BTX and other hydrocarbon concentrations and what type of longer-term source concentration behavior to expect at sites when gasohol or fuel-grade ethanol spills occur.

It should be emphasized that the experiments approximate possible worst-case scenarios in which gasohol or highly concentrated ethanol comes in direct contact with the saturated zone. *Predicting ethanol concentrations is key to determining enhancements in BTX source concentrations.* If the amount of ethanol that gets into ground water can be predicted, it should then be possible to estimate the near source dissolved concentrations of BTX and other hydrocarbons. In the experiments described in this report, 100% of the ethanol or gasohol was injected (forced) into a continuous flow column saturated with water (a confined system). In practice, spills will be unconfined. Additional research is needed to determine just how sources are generated for spills of fuel-grade ethanol (E95) and gasohol (E10) in more realistic unconfined systems and their impacts on ground water concentrations near the source. Recent research has already provided important insight into the generation of spills of neat ethanol and the impact on existing pools of gasoline and on residual gasoline in the unsaturated zone (McDowell et al., 2003). However, investigations of spills in unconfined systems (at both the bench and larger scales), coupled with comprehensive measurements of ground water concentrations of ethanol and BTX, are still needed to be able to quantitatively link spills of E95 or gasohol to levels of dissolved concentrations in ground water near the spill source.

Key issues to be addressed:

1) *Amount of ethanol that enters ground water*. Some of the important questions are: 1) how much ethanol remains trapped in the capillary fringe due to its low density and how much is absorbed by moisture in the capillary zone; 2) does ethanol that enters ground water migrate downstream near the water table as a concentrated, lower-density plume; and 3) what are the peak and the longer-term concentrations of ethanol that can be expected in ground water near the source of a spill?

2) *Migration and generation of NAPL and resulting BTX and other hydrocarbon*[5] *ground water concentrations.* The key questions are: 1) what happens to the hydrocarbons when E95 or gasohol contacts the water table, i.e., where does phase separation occur, within the capillary fringe or at the water table; 2) what corresponding levels of hydrocarbon concentrations in ground water near the source that can be expected; and for E95 spills, how much NAPL is formed downstream and what fractions of each of the individual compounds, e.g., BTX, TMB, etc., ultimately move with the dissolved, attenuated ethanol plume vs. what remains behind in a phase-separated NAPL?

Ultimately, we are usually most interested in what impact ethanol will have at some point downstream of the source of a spill. Such an assessment of plume *evolution* can best be accomplished with field studies and the use of appropriate ground water transport models (e.g., Molson et al., 2002) that account for the combined effects of enhanced source concentrations and reduced bioattenuation. Because such modeling also requires a proper description of the ground water concentrations near the source, the results of this source *generation* study can be considered complementary to these other efforts. Taken together, descriptions of maximum dissolved concentrations near a source and plume evolution will produce improved assessments of the overall impact of ethanol on hydrocarbon plumes at affected sites

Relationship to Other Ethanol Studies

Additional studies investigating the impact of ethanol are underway at the University of Waterloo, Rice University, and the University of Houston. In 2004, University of Waterloo began field studies at Borden AFB to assess the *evolution* of plumes from spills of E10 and E95. To

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[5] Additional research is also needed on the effect of ethanol on other less soluble chemical of concern found in gasoline (e.g., naphthalene).

complement the Waterloo field studies, Rice University and University of Houston are conducting pilot-scale experiments, coupled with additional bench-scale experiments that focus on the *generation* of ethanol, BTX and other hydrocarbons in ground water near the source for spills of E95 and E10. Preliminary results for a pilot-scale experiment for an E95 spill have been reported recently (Capiro, et al., 2004).

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Acknowledgements

API wishes to acknowledge the API Soil and Groundwater Technical Task Force (S/GTTF), for their contributions to this document

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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Scenario 2: Neat ETOH
onto existing NAPL

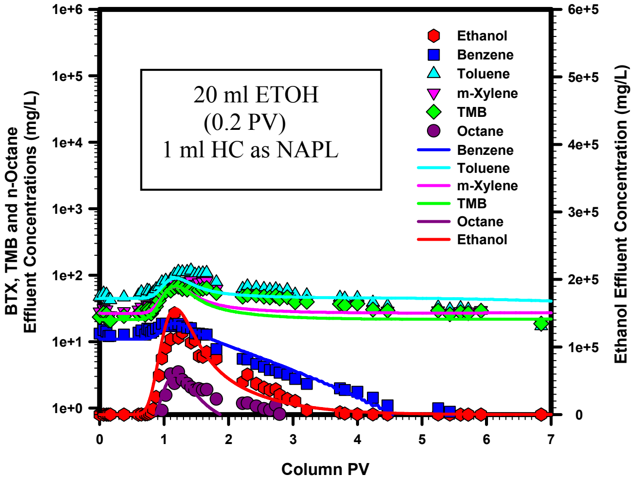

Figure 4. Effluent concentrations for ethanol, BTX, 1,2,4-trimethylbenzene, and n-octane for Experiment 3 (small, neat ethanol spill onto existing NAPL: 0.2 pore volumes (PV) neat ethanol).

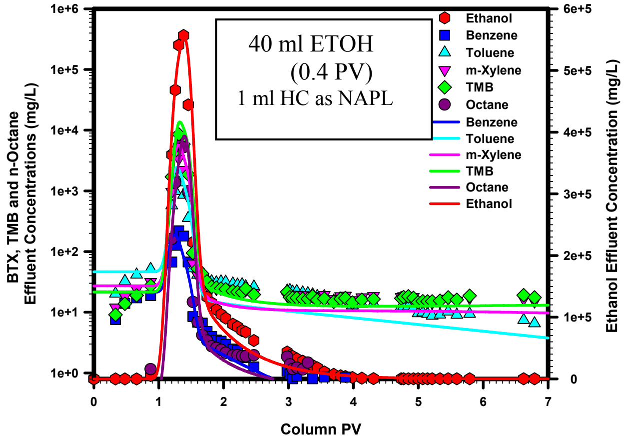

Figure 5. Effluent concentrations for ethanol, BTX, 1,2,4-trimethylbenzene, and n-octane for Experiment 4 (large, neat ethanol spill onto existing NAPL: 0.4 PV neat ethanol).

Scenario 3: Fuel grade ETOH
no existing NAPL

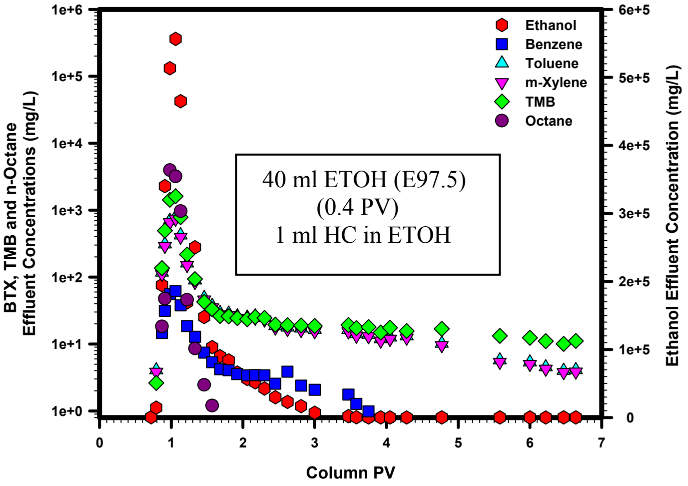

Figure 6. Effluent concentrations for ethanol, BTX, 1,2,4-trimethylbenzene, and n-octane for Experiment. 5 (large, fuel-grade ethanol spill – no existing NAPL: 0.4 PV 97.5% ethanol).

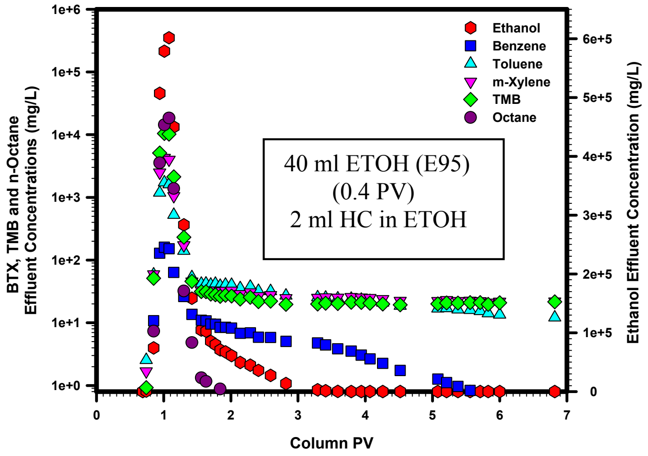

Figure 7. Effluent concentrations for ethanol, BTX, 1,2,4-trimethylbenzene, and n-octane for Experiment 6 (large, fuel-grade ethanol spill – no existing NAPL: 0.4 PV 95% ethanol).

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