Modeling the natural attenuation of benzene in groundwater impacted by ethanol-blended fuels: Effect of ethanol content on the lifespan and maximum length of benzene plumes

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[1] A numerical model was used to evaluate how the concentration of ethanol in reformulated gasoline affects the length and longevity of benzene plumes in fuel-contaminated groundwater. Simulations considered a decaying light nonaqueous phase liquid source with a total mass of ~85 kg and a groundwater seepage velocity of 9 cm d^{-1} and corroborated previous laboratory, field, and modeling studies showing benzene plume elongation due to the presence of ethanol. Benzene plume elongation reached a maximum of 59% for 20% ethanol content (E20) relative to regular gasoline without ethanol. Elongation was due to accelerated depletion of dissolved oxygen during ethanol degradation and to a lower specific rate of benzene utilization caused by metabolic flux dilution and catabolite repression. The lifespan of benzene plumes was shorter for all ethanol blends compared to regular gasoline (e.g., 17 years for regular gasoline, 15 years for E10, 9 years for E50, and 3 years for E85), indicating greater natural attenuation potential for higher-ethanol blends. This was attributed to a lower mass of benzene released for higher-ethanol blends and increased microbial activity associated with fortuitous growth of benzene degraders on ethanol. Whereas site-specific conditions will determine actual benzene plume length and longevity, these decaying-source simulations imply that high-ethanol blends (e.g., E85) pose a lower risk of benzene reaching a receptor via groundwater migration than low-ethanol blends such as E10.

1. Introduction

[2] The widespread use of ethanol in gasoline, both as a substitute for the oxygenate methyl-*tert*-butyl ether and to comply with renewable fuel requirements, is likely to result in its increased presence in groundwater. The preferential biodegradation of ethanol and associated accelerated depletion of dissolved oxygen and nutrients in aquifers may hinder the natural attenuation of other fuel constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) [*Corseuil et al.*, 1998; *Da Silva and Alvarez*, 2002; *Cápiro et al.*, 2007]. Decreased natural attenuation would in turn increase the length and lifespan of BTEX plumes, which raises a concern for potential down-gradient receptors [*Powers et al.*, 2001a, 2001b]. This concern is particularly important for benzene, which is the most hazardous of the gasoline constituents and the one that often dictates the need for remedial action [*Alvarez and Illman*, 2006].

[3] The most common ethanol blend used in the United States is currently gasoline with 10% ethanol vol/vol (E10) [*Yacobucci*, 2007], and elongation of benzene plumes due to the presence of ethanol in E10 is inferred by an epidemi-ological study of plume lengths (i.e., 193 ± 135 ft (1 foot = 0.3048 m) for regular gasoline versus 263 ± 103 ft for E10 or 36% longer on a mean basis) [*Ruiz-Aguilar et al.*, 2003], as well as by laboratory experiments [*Da Silva and Alvarez*, 2002; *Lovanh et al.*, 2002; *Lovanh and Alvarez*, 2004; *Ruiz-Aguilar et al.*, 2002] and modeling studies [*Heermann and Powers*, 1996; *McNab et al.*, 1999; *Molson et al.*, 2002]. The mechanisms responsible for benzene plume elongation were also recently analyzed by a general substrate interactions model (GSIM), which considers common fate and transport processes (e.g., advection, dispersion, adsorption, depletion of molecular oxygen during aerobic biodegradation, and anaerobic biodegradation), as well as previously overlooked substrate interactions that decrease the specific utilization rate for benzene in the presence of ethanol (e.g., metabolic flux dilution and catabolite repression) and the resulting microbial populations shifts [*Gomez et al.*, 2008]. However, it is unknown how the content of ethanol in different blends that are rapidly entering the market will affect benzene natural attenuation and the resulting plume lifespan and maximum length, which is important for assessing the potential likelihood and duration of exposure.

[4] This paper builds on the GSIM numerical model to include cosolvency and microbial toxicity exerted by high-ethanol blends near the source zone and evaluates the effect of ethanol content in gasoline on the natural attenuation of benzene plumes. We consider groundwater contamination

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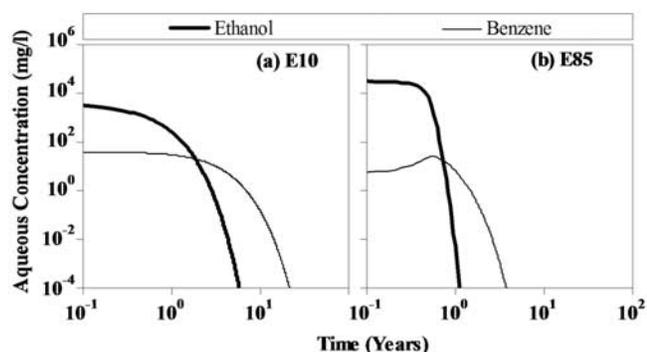
Figure 1. Ethanol and benzene concentrations at the groundwater-LNAPL interface for (a) an E10 release and (b) an E85 release (∼85 kg NAPL total), considering Fick's second law of diffusion and changes in source NAPL composition, enhanced dissolution effect of ethanol, and mass transport due to advection.

by multiple ethanol blends, including E20, which is likely to replace E10 by 2013 in some states [*Kittelson et al.*, 2007] and E85, which is increasingly being used for flexible fuel vehicles or high-compression engines, and report differences in the maximum length and persistence (i.e., lifespan) of benzene plumes relative to regular gasoline without ethanol.

2. Methodology

2.1. Modeling Approach

[5] Advection, dispersion, and adsorption of the dissolved components to aquifer material were simulated using existing models. Reactive Transport in 3 Dimensions (RT3D) was used to numerically solve the 3-D reactive advection-dispersion equation that governs the migration and degradation of the dissolved constituents [*Clement et al.*, 1998]. U.S. Geological Survey flow model Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW) was used to calculate the groundwater flow velocities required by RT3D for transport processes [*Harbaugh et al.*, 2000].

[6] GSIM was used as a custom reaction module for RT3D that considers substrate interactions and microbial population shifts that influence benzene biodegradation kinetics [*Gomez et al.*, 2008]. Various benzene plume elongation mechanisms were considered by GSIM: (1) metabolic flux dilution, which is defined as a decrease in the specific benzene utilization rate due to noncompetitive inhibition when ethanol is present [*Lovanh and Alvarez*, 2004]; (2) catabolite repression, which is defined as the repression of inducible enzymes that degrade the target pollutant (e.g., benzene) by the presence of a preferred carbon source (e.g., ethanol) [*Madigan et al.*, 2005]; (3) accelerated depletion of dissolved oxygen during ethanol biodegradation, which results in slower (anaerobic) benzene degradation; and (4) proliferation of different microbial populations in response to changes in oxygen and substrate availability.

[7] Ethanol may also act as a cosolvent if present in groundwater at concentrations greater than 10,000 mg L^{-1} [*Da Silva and Alvarez*, 2002; *Powers et al.*, 2001b],

increasing BTEX dissolution and mobility [*Groves*, 1988]. This was incorporated into the GSIM model by considering cosolvency effects on both benzene dissolution from a decaying light nonaqueous phase liquid (LNAPL) in the source zone and changes in retardation factor due to the influence of ethanol on the soil-water partitioning coefficient of benzene. The model was also modified to consider ethanol toxicity to microbial populations by simulating inhibition of the growth of both benzene and ethanol degraders when ethanol concentrations in groundwater exceed 39,000 ppm, the average half maximal effective concentration (EC50) for ethanol [*Dutka and Kwan*, 1981].

[8] Although the GSIM model allows consideration of multiple substrates, biological species, and electron acceptors, it has several limitations [*Gomez et al.*, 2008]: (1) microbial activity is assumed to occur while microbes are attached to the soil matrix, and attachment/detachment kinetics are not considered; (2) substrate degradation is conservatively assumed to occur only in the liquid phase, ignoring potential decay of sorbed contaminants; (3) oxygen is the only electron acceptor in the simulations (ignoring nitrate-, iron-, and sulfate-reducing pathways); (4) only ethanol and benzene have been considered for our E10 release case, and no other gasoline components are evaluated; (5) total organic carbon is assumed to be completely available for degradation processes; and (6) the operator splitting solution scheme of the model requires that small time steps be used in the simulations (<0.02 days) because of convergence and stability issues.

2.2. Source Zone Concentrations

[9] Aqueous ethanol–BTEX concentrations at the source zone were calculated by considering a finite mass of LNAPL, with ethanol fractions ranging from 5 to 95%,

Table 1. Source Zone Dissolution Parameters

Parameter	Value
Chemical Properties[a]	
Ethanol density (g cm^{-3})	0.79
Ethanol molecular weight (g mol^{-1})	46.07
Ethanol diffusivity (cm^2 s^{-1})	1.26E-05
Benzene density (g cm^{-3})	0.88
Benzene molecular weight (g mol^{-1})	78.11
Benzene diffusivity (cm^2 s^{-1})	9.60E-06
TEX density (g cm^{-3})	0.87
TEX molecular weight (g mol^{-1})	78.11
Benzene Linear/Log Linear Model[b]	
C_b^{wc}	1780
γ_b^{od}	1.41
$C_b^{\beta}\gamma_b^{o}$	4420
β	0.27
$C_b^{e}f_b^{o}/X_b^{o}$	963,000
Spill Characteristics	
Depth (m)	0.05
Width (m)	4
Length (m)	4
Total NAPL mass (kg)	84
NAPL density (g cm^{-3})	0.74
NAPL volume (L)	113

[a]From *Hilal et al.* [2003].
[b]From *Heermann and Powers* [1998].
[c]Solubility.
[d]Activity.

Table 2. Model Hydrogeological Parameters[a]

Parameter	Value	Source
Hydrogeology		
Hydraulic conductivity K	9.0 m d^{-1}	Fine-medium sand, LNAST soils database[b]
Hydraulic gradient i	0.003 m m^{-1}	*Newell et al.* [1996]
Darcy water velocity v	2.7 cm d^{-1}	Fine-medium sand, LNAST soils database[b]
Total porosity n	0.3	*Newell et al.* [1996]
Groundwater dissolved oxygen O	6 mg L^{-1}	*Newell et al.* [1996]
Pore space utilization factor γ	0.2	*Vandevivere et al.* [1995], *Thullner et al.* [2002]
Dispersivity		
Longitudinal dispersivity	7 m	*Newell et al.* [1996][c]
Transverse dispersivity	0.7 m	
Adsorption		
Soil bulk density ρ_b	1.7 kg L^{-1}	*Newell et al.* [1996]
Ethanol partitioning coefficient K_{dE}	0.001 L kg^{-1}	
Ethanol retardation factor R_E	1.01	Calculated, $R_E = 1 + \rho_b K_{dE}/n$
Benzene partitioning coefficient K_{dB}	0.095 L kg^{-1}	
Benzene retardation factor R_B	1.54	Calculated, $R_B = 1 + \rho_b K_{dB}/n$
General Simulation		
Modeled area length	200 m	
Modeled area width	60 m	
x axis discretization	50 units	
y axis discretization	75 units	
Cell width	0.8 m	
Cell length	4 m	
Cell depth	3 m	
Simulation time	25 years	
Simulation time step	0.02	

[a]For a detailed description of the use of these parameters in the model and a sensitivity analysis of selected parameters, please refer to *Gomez et al.* [2008].

[b]*Huntley and Beckett* [2002].

[c]Modified to fit initial benzene plume lengths measurements of *Ruiz-Aguilar et al.* [2003].

which is dissolved and depleted over time. E10 composition in mole fractions was used as a standard reference for calculating dissolved benzene concentrations at the groundwater-LNAPL interface for other ethanol blends (auxiliary material, Figure S1) and was set as 0.015 for benzene, 0.172 for ethanol, 0.158 for toluene, ethylbenzene, and xylenes (TEX), and 0.655 for other compounds (calculated from *Poulsen et al.* [1991])[1].

[10] Benzene concentration in groundwater equilibrated with the LNAPL source zone was calculated using an Excel spreadsheet model developed for this research. Previous models have considered the changing composition of the source zone as its constituents dissolve (e.g., the American Petroleum Institute's LNAPL Dissolution and Transport Screening Tool (LNAST) [*Huntley and Beckett*, 2002]) but have not considered the cosolvency effects of ethanol on BTEX components. Our model incorporates cosolvency exerted by aqueous ethanol, which enhances benzene dissolution from the LNAPL, as discussed below.

[11] Raoult's law (equation (1)) can provide a reasonable estimate for benzene concentrations in groundwater in equilibrium with regular gasoline LNAPL [*Mackay et al.*, 1991]:

$$C_i = C_i^w X_i^o, \qquad (1)$$

where C_i is concentration of chemical i (e.g., benzene) in the water phase, C_i^w is the maximum solubility of chemical i in

the water phase, and X_i^o is the molar fraction of chemical i in the organic phase. However, in the case of ethanol blends, the presence of high concentrations of ethanol in the water phase makes Raoult's law inappropriate for calculating aqueous benzene concentrations because it does not consider potential phase separation and cosolvent effects that influence mass transfer kinetics [*Heermann and Powers*, 1998]. Thus, a linear/log linear model developed by *Heermann and Powers* [1998] was used to account for these factors and to calculate aqueous benzene concentrations at the groundwater-LNAPL interface:

$$C_b = \left(1 - \frac{f_c}{\beta}\right)C_b^w\gamma_b^o X_b^o + \frac{f_c}{\beta}C_b^\beta\gamma_b^o X_b^o, \qquad f_c < \beta \quad (2)$$

$$\ln C_b = \left(1 - \frac{f_c - \beta}{1 - \beta}\right)\ln\left(C_b^\beta\gamma_b^o X_b^o\right) + \frac{f_c - \beta}{1 - \beta}\ln\left(C_b^e f_b^o\right),$$
$$f \geq \beta, \qquad (3)$$

where C_b is the benzene concentration in the aqueous phase (mg L^{-1}), f_c is ethanol content in the water phase (vol/vol), β is the volume fraction of ethanol in the aqueous phase coinciding with the breakpoint between the two segments of the model (vol/vol), C_b^w is the benzene solubility in pure water (mg L^{-1}), C_b^β is the benzene solubility at β ethanol fraction in water (mg L^{-1}), γ_b^o is the benzene activity coefficient in the organic phase, X_b^o is the benzene molar fraction in the organic phase, C_b^e is the benzene solubility in

Table 3. Model Biodegradation Parameters[a]

Parameter	Value	Source
Ethanol Aerobic		
$\mu_{mE,\text{Aer}}$ (d^{-1})	11	*Lovanh et al.* [2002]
$Y_{E,\text{Aer}}$ (mg mg^{-1})	0.5	Based on mix culture aerobic systems [*Heulekian et al.*, 1951]
$K_{E,\text{Aer}}$ (mg L^{-1})	63.1	Calculated using λ[b]
$\lambda_{E,\text{Aer}}$ (d^{-1})	0.35	*Corseuil et al.* [1998]
Ethanol Anaerobic		
$\mu_{mE,\text{An}}$ (d^{-1})	1.1	*Oonge* [1993]
$Y_{E,\text{An}}$ (mg mg^{-1})	0.07	Based on methane fermentation [*Lawrence and McCarty*, 1969]
$K_{E,\text{An}}$ (mg L^{-1})	78.9	Calculated using λ[b]
$\lambda_{E,\text{An}}$ (d^{-1})	0.2	*Corseuil et al.* [1998]
Benzene Aerobic		
$\mu_{mB,\text{Aer}}$ (d^{-1})	3.2	*Alvarez et al.* [1991]
$Y_{B,\text{Aer}}$ (mg mg^{-1})	0.39	*Alvarez et al.* [1991]
$K_{B,\text{Aer}}$ (mg L^{-1})	7.6	*Alvarez et al.* [1991]
$\lambda_{B,\text{Aer}}$ (d^{-1})	0.68	*Alvarez et al.* [1991]
Benzene Anaerobic		
$\mu_{mB,\text{An}}$ (d^{-1})	0.3	*Ulrich and Edwards* [2003]
$Y_{B,\text{An}}$ (mg mg^{-1})	0.05	Based on methane fermentation [*O'Rourke*, 1968]
$K_{B,\text{An}}$ (mg L^{-1})	21.6	Calculated using λ[b]
$\lambda_{B,\text{An}}$ (d^{-1})	0.003	*Aronson and Howard* [1997]
γ Maximum pore space utilization factor	0.2	*Vandevivere et al.* [1995]; *Thullner et al.* [2002].
b_{Aer} (d^{-1})	0.2	Based on mixed culture aerobic systems [*McCarty and Brodersen*, 1962]
b_{An} (d^{-1})	0.03	Based on methane fermentation [*Lawrence and McCarty*, 1969]
K_O (mg L^{-1})	0.21	*Fritzsche* [1994]
F_E (mg mg^{-1})	1.27	Stoichiometry
F_B (mg mg^{-1})	3.07	Stoichiometry
$X_{\text{Aer},E}$ Aerobic ethanol degraders, initial (mg L^{-1})	1	*Chen et al.* [1992]
$X_{\text{An},E}$ Anaerobic ethanol degraders, initial (mg L^{-1})	0.1	Assumed 10% of aerobes
$X_{\text{Aer},b}$ Aerobic benzene degraders, initial (mg L^{-1})	0.1	Assumed 10% of total
$X_{\text{An},b}$ Anaerobic benzene degraders, initial (mg L^{-1})	0.001	Assumed 1% of aerobes
Biofilm density (mg L^{-1})	105	High-density biofilm [*Freitas dos Santos and Livingston*, 1995; *Zhang and Bishop*, 1994]

[a]For a detailed description of the use of these parameters in the model and a sensitivity analysis of selected parameters, please refer to *Gomez et al.* [2008].

[b]Here λ is the first-order degradation rate coefficient. Values were estimated on the basis of the relationship $\lambda = (\mu X / Y K_s)$ [*Alvarez and Illman*, 2006] for initial microbial populations.

ethanol (mg L^{-1}), and f_b^o is the organic phase volume fraction of benzene (vol/vol).

[12] Equations (2) and (3) require as input the aqueous ethanol concentration at the water interface, as volume fraction (f_c). This cannot be calculated using Raoult's law because ethanol is infinitely soluble in water. Rather, ethanol concentrations were estimated using mass transfer limitation factors leading to concentrations between 0.5 and 5% of the ethanol solubility near the source zone [*Malcolm Pirnie, Inc.*, 1998]. Ethanol has a specific gravity of 0.79 and is completely miscible in water. Thus, the maximum ethanol solubility in water was taken as 790,000 mg L^{-1}, assuming that all of it transfers to the water phase. In the case of E10 (10% ethanol vol/vol), maximum theoretical ethanol concentration would be 79,000 mg L^{-1} (one tenth of the maximum ethanol solubility). Applying 0.5–5% of this value yields 395–3950 mg L^{-1} at the groundwater-LNAPL interface. These estimations can be validated by comparing the water phase concentrations for E22 (estimated at 11,000 mg L^{-1}, assuming 5% of 0.22 × 790,000 mg L^{-1}) with field results reported for Brazilian gasoline [*Corseuil et al.*, 2000], where an E22 release resulted in maximum ethanol concentrations of about 10,000 mg L^{-1} in near–source zone groundwater. With f_c

known, equations (2) and (3) can be used to calculate the dissolved concentration of benzene.

[13] Changes in molar fraction composition of the different LNAPL components over time due to different diffusion coefficients and LNAPL mass depletion were also considered in our dissolution model. Mass transfer rates for the different constituents were used to calculate mass depletion on the basis of Fick's second law and groundwater flow characteristics [*Clark*, 1996]:

$$M_i^w = 2C_i^w \sqrt{\frac{D_i v L t^2}{\pi}}, \qquad (4)$$

where M_i^w is the total mass of BTEX transferred per unit of width of the nonaqueous phase liquid (NAPL) source zone interface with water (mg), C_i^w is the i component water phase concentration at the groundwater-LNAPL interface (mg L^{-1}), D_i is the i component diffusivity (m^2 d^{-1}), v is the groundwater pore space velocity (m d^{-1}), L is the length of the NAPL source zone interface with water (m), and t is time elapsed (days).

[14] As previously reported [*Gomez et al.*, 2008], we assumed that gasoline constituent concentrations just below the water-LNAPL interface decrease rapidly to nondetect-
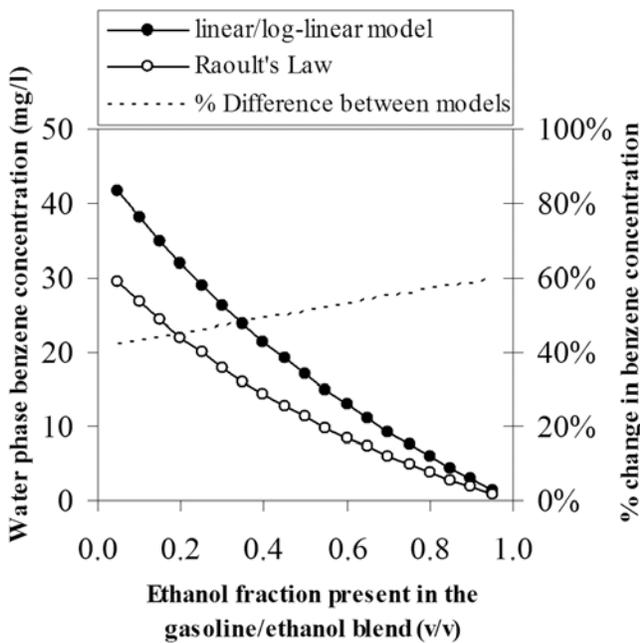
Figure 2. Equilibrium benzene concentrations at the water-LNAPL interface considering *Heermann and Powers'* [1998] linear/log linear model for gasoline-ethanol blends and taking into account fugacity and cosolvency and Raoult's law (without cosolvency) for a range of ethanol blends.

able levels within 2–3 m [*Huntley and Beckett*, 2002]. Thus, we used source cell concentrations that represent the average between the water-LNAPL interface value and zero (i.e., the value at the bottom of the 3 m deep source cells). Figure 1 shows the ethanol and benzene interface concentrations over time for a depleting ~85 kg E10 and E85 source LNAPL, and Table 1 shows the parameters used in these simulations. LNAPLs with higher ethanol content dissolve faster into groundwater than those with lower ethanol content because of the higher diffusivity of ethanol in water and the greater molar fraction of ethanol that leads to higher concentration gradient, resulting in higher mass transfer rates. This leads both to slower ethanol depletion from E10 than from E85 and to ethanol depleting earlier than benzene in both cases.

2.3. Retardation

[15] The GSIM model was modified to incorporate variations in the retardation factor of benzene due to changes in the soil-water partition coefficient resulting from a potential cosolvency effect exerted by ethanol. The effect of a cosolvent on the BTEX components partitioning can be described by the relationship [*Rao et al.*, 1985]

$$\log(K_m) = \log(K_w) - \alpha \sigma f_c, \tag{5}$$

where K_m is the distribution ratio in the presence of the cosolvent, K_w is the distribution ratio with pure water, σ is the cosolvent power of ethanol on any given BTEX compound, and α is the molecular interactions between

the cosolvent and sorbent. This relationship was later refined [*Rao et al.*, 1991] as

$$\log\left(\frac{K_d'}{K_d}\right) = -\alpha \beta_c \sigma f_c, \tag{6}$$

where K_d is the benzene distribution coefficient for pure water, K_d' accounts for the presence of ethanol, f_c is the cosolvent content (i.e., ethanol) as volume fraction in the water phase.

[16] The product of α and β_c in equation (6) depends on various molecular interactions between cosolvent and sorbent (α) and cosolvent and solute (β_c). There is no documented relationship for these values and soil parameters, so they have to be measured experimentally on a case by case basis. In the case of α, the more it deviates from 1, the more the cosolvent interacts with the sorbent (soil). If the soil is relatively inert and low in organic content, then this value should approach unity. The parameters α and β_c were assumed to be 1 for simplicity (conservative approach), and the value for σ for benzene was taken as 2.96 [*Poulsen et al.*, 1991]. Simplifying equation (6) for benzene, assuming inert soil with low organic content ($\alpha \beta_c = 1$),

$$K_d' = K_d \times 10^{-\sigma f_c}. \tag{7}$$

This can be transformed into a retardation factor relationship of the form [*Li et al.*, 2000]

$$R' = \frac{R - 1}{10^{\sigma f_c}} + 1. \tag{8}$$

R can be calculated using the traditional model on the basis of local linear equilibrium ($R = 1 + \rho_b K_d / n$ [*Charbeneau*, 2000]) or using another approach such as the dual equilibrium desorption model [*Chen et al.*, 2002]. In our case, we used the linear equilibrium model to calculate R because this is already incorporated into RT3D. For E10 blends, f_c is usually less than 1% (<10,000 mg L^{-1}), and the resulting reduction of R is negligible (Figure S2), as previously documented in laboratory studies [*Da Silva and Alvarez*, 2002; *Powers et al.*, 2001b].

2.4. Initial, Boundary, and Domain Conditions for Simulations

[17] The simulations domain was the same as described by *Gomez et al.* [2008]. Briefly, the domain consisted of a single 60 m wide by 200 m long layer (2-D) with a seepage water velocity set to a constant 9 cm d^{-1} by establishing a hydraulic head difference of 0.6 m between the two ends of the domain. Tables 2 and 3 list the hydrogeological domain and microbial kinetic parameters used.

[18] The initial dissolved oxygen concentration was set at 6 mg L^{-1}, and background groundwater entering the model domain contained this same dissolved oxygen concentration. The system was assumed to become strongly anaerobic (methanogenic), which commonly occurs in ethanol-impacted systems as a result of the rapid depletion of thermodynamically more favorable electron acceptors [*Da Silva and Alvarez*, 2002]. Similar to previous simulations [*Gomez et al.*, 2008], initial microbial concentrations for aerobic populations that degrade ethanol or benzene were
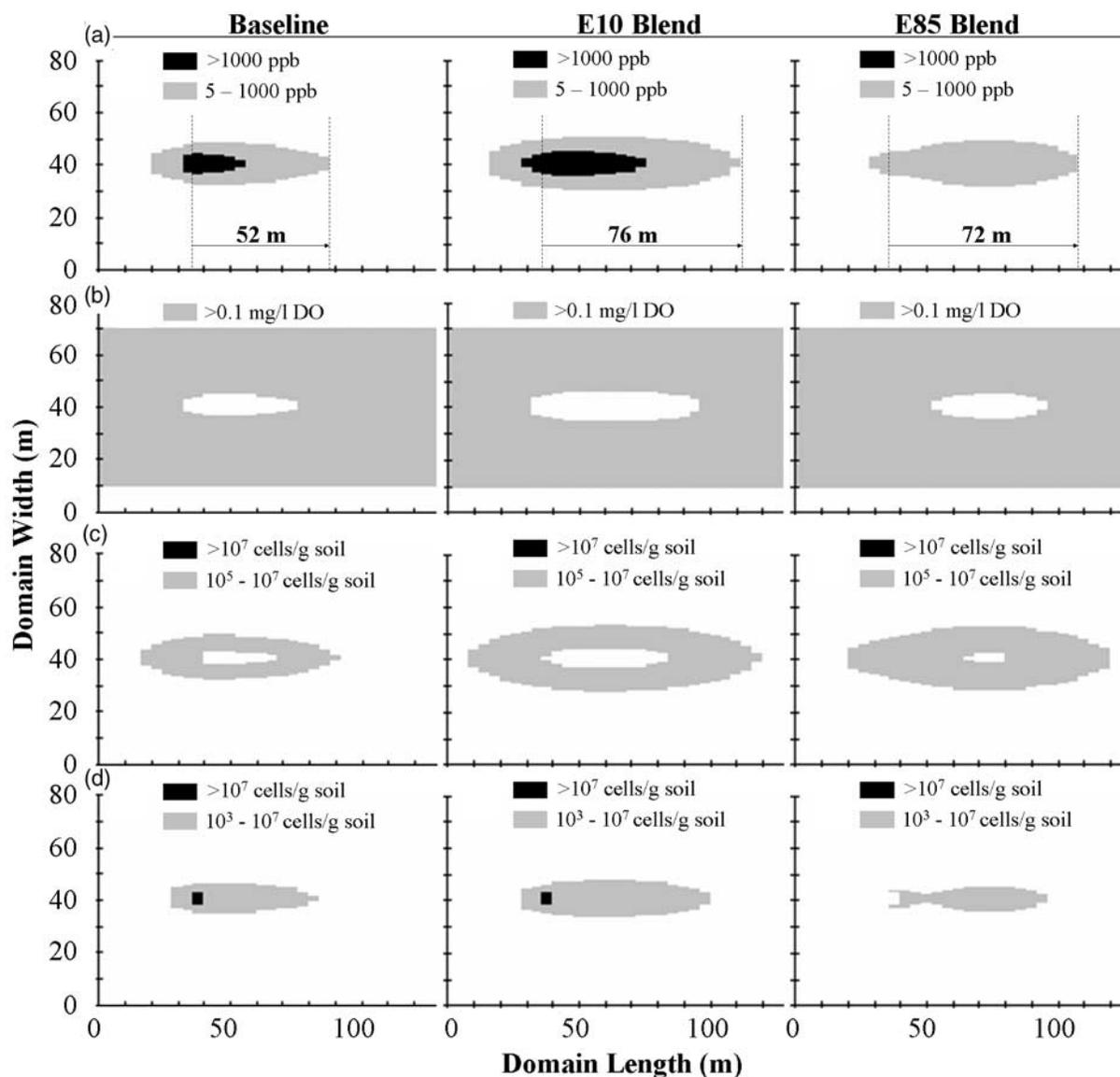
Figure 3. Simulated releases of regular gasoline (baseline), E10, and E85 after 2 years, showing (a) benzene plume (1.0 and 0.005 mg L^{-1} contours), (b) oxygen depletion profile, and the distribution of (c) aerobic and (d) anaerobic benzene degraders.

set at 1 mg L^{-1} ($\sim 10^6$ cells (g^{-1} soil)) [*Chen et al.*, 1992] and 0.1 mg L^{-1} ($\sim 10^5$ cells (g^{-1} soil), 10% of aerobes), respectively. Initial concentrations for anaerobic populations that degrade ethanol or benzene were assumed as 10% of total and 1% of benzene aerobic degraders or 0.1 mg L^{-1} ($\sim 10^5$ cells (g^{-1} soil)) and 0.001 mg L^{-1} ($\sim 10^3$ cells (g^{-1} soil)), respectively.

3. Results and Discussion

[19] Figure 2 shows how the equilibrium concentration of benzene at the water-LNAPL interface changes for different fractions (vol/vol) of ethanol present in the LNAPL, for both the *Heermann and Powers* [1998] linear/log linear model (equations (2) and (3)) and for Raoult's law (equation (1)). Figure 2 also shows that ethanol increases the aqueous concentration of benzene, because of its cosolvent effects,

by more than 40% when considering an E5 spill and up to 60% when E95 is considered. This leads to increased mass transfer rates and faster dissolution when under the effects of ethanol. However, as the ethanol content in the LNAPL increases, both the mass of benzene available for dissolution and the dissolved benzene concentrations decrease.

[20] When using equation (5) to evaluate the cosolvent effect of ethanol on benzene water-soil partitioning (sorption), there is a decrease in retardation for BTEX as the water phase ethanol fraction increases, which could lead to longer BTEX plumes. Xylene and ethylbenzene are the most hydrophobic of the BTEX components and the most impacted by cosolvency with $\sim 2\%$ decrease in retardation for E10, $5-7\%$ for E50, and $8-13\%$ for E85. Benzene, on the other hand, has a change in retardation of $\sim 0.4\%$ for E10, $\sim 1.8\%$ for E50, and 3% for E85 (Figure S2). These calculations consider a sandy soil with 0.2% organic matter.
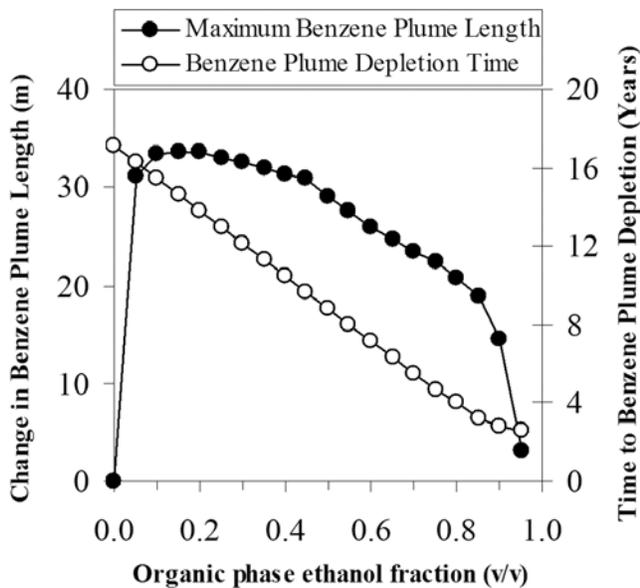
Figure 4. Maximum benzene centerline plume length (to 5 ppb contour) change (% of baseline) and time to benzene plume depletion for blended fuels with varying ethanol fractions (vol/vol organic phase).

[21] Natural attenuation simulations for ethanol blends ranging from E5 to E95 were also performed. Figure 3 shows the benzene plumes formed after 2 years of LNAPL release (regular gasoline, E10, and E85) (Figure 3a), as well as the oxygen depletion profile at 0.1 mg L^{-1} of dissolved oxygen (Figure 3b) and the distribution of aerobic and anaerobic microorganisms that degrade benzene (Figures 3c and 3d, respectively). Simulations show benzene plume elongation by 40% for the common blend E10 relative to the baseline release without ethanol (i.e., 250 versus 180 ft). This is in excellent agreement with a statistical analysis of E10-impacted sites, which reported that the average plume length was 36% longer for benzene than for regular gasoline (i.e., 263 ± 103 ft versus 193 ± 135 ft) [*Ruiz-Aguilar et al.*, 2003].

[22] Aerobic biodegradation of both ethanol and benzene quickly depletes the available dissolved oxygen inside the plume, causing a transition to anaerobic conditions. Then, aerobic benzene degraders prevail only on the fringe of the plume, where oxygen is being recharged by mixing with uncontaminated groundwater. The simulation reflects that the center of the plume harbors a dominantly anaerobic microbial community (Figure 3d), as is commonly observed in hydrocarbon plumes undergoing natural attenuation [*Alvarez and Illman*, 2006].

[23] One important aspect to consider is microbial population changes in response to different ethanol blend releases. Some benzene degraders can grow fortuitously on ethanol, increasing the potential benzene degradation activity [*Cápiro et al.*, 2008]. However, ethanol can stimulate the growth of other bacteria faster than hydrocarbon degraders, which decreases the relative abundance of benzene degraders (i.e., genotypic dilution) [*Da Silva and Alvarez*, 2002; *Cápiro et al.*, 2008]. Benzene degradation in the baseline case without ethanol increases the total microbial concentration near the source (aerobic plus an-

aerobic) to about 5×10^7 cells (g^{-1} soil). When ethanol is present, its consumption increases total microbial concentrations by 2–3 orders of magnitude, reaching ~10^9 cells (g^{-1} soil) for E10 and ~10^{10} cells (g^{-1} soil) for E50 and E85. The latter also results in shorter-lived populations that undergo endogenous decay after the earlier depletion of available substrates (Figure S3).

[24] The maximum benzene plume length for the different ethanol contents in the released fuel was determined as the maximum down-gradient distance from the spill source to the maximum contaminant level (MCL) (5 μg L^{-1}) contour (Figure 4). Ethanol had a significant elongation effect on benzene plumes, which is most pronounced for E10–E20 blends (up to 59% elongation relative to the 56 m baseline). This elongation effect is similar for higher-ethanol blends up to E45, and then plume elongation decreases to almost no impact for E95. This trend reflects competing processes that increase elongation versus those that offset it. As the ethanol content increases, processes that hinder the natural attenuation of benzene because of the presence of ethanol are accentuated, such as electron acceptor depletion, metabolic flux dilution, and catabolite repression [*Gomez et al.*, 2008]. At the same time, the mass of benzene available for dissolution decreases for higher-ethanol blends because of the higher content of ethanol, resulting in lower benzene concentrations. Furthermore, higher ethanol concentrations result in larger overall microbial populations that contribute to benzene degradation (Figure 3). Between E10 and E45 these competing plume elongation and attenuation processes are in relative balance. Above E45 ethanol content, a decrease in the mass of benzene released and increased biodegradation dominate, and the maximum plume length decreases more abruptly (Figure 5).

[25] A comparison of benzene plume life cycles for four different blends (E10, E50, E95, and no ethanol) shows that although all ethanol blends resulted in longer plumes than the baseline scenario for regular gasoline without ethanol, the benzene plume life span (time until plume is degraded below MCL) decreases almost linearly as ethanol content in the blend increases (and thus the mass of benzene released decreases) (Figure 5).

[26] Benzene transport may be influenced by site-specific heterogeneity. Thus, additional simulations were conducted to consider how heterogeneity in hydraulic conductivity (*K*) influences the effect of ethanol on benzene plume elongation. Spatially correlated hydraulic conductivity random fields were generated using an existing model, HYDRO_GEN [*Bellin and Rubin*, 1996], with a correlation scale of 5 times the spatial cell size in the *x* and *y* directions. HYDRO_GEN was run using a Gaussian distribution with a mean of 9 m s^{-1} and a variance ranging from 0 (baseline, homogeneous) to 8 m^2 d^{-2} (most heterogeneous case). Heterogeneity decreased simulated benzene plume lengths relative to the homogeneous baseline by 7% (E10) to 9% (E85) for 2 m^2 d^{-2} of variance, 10% (E10) to 14% (E85) for 4 m^2 d^{-2}, and 19% (E10) to 20% (E85) for 8 m^2 d^{-2}. However, benzene plume elongation exerted by ethanol was not significantly affected by heterogeneity compared to the homogeneous baseline (Figure S4).

[27] Since the potential for exposure to benzene in groundwater depends on both plume length and persistence (i.e., lifespan), we arbitrarily combined these factors into an
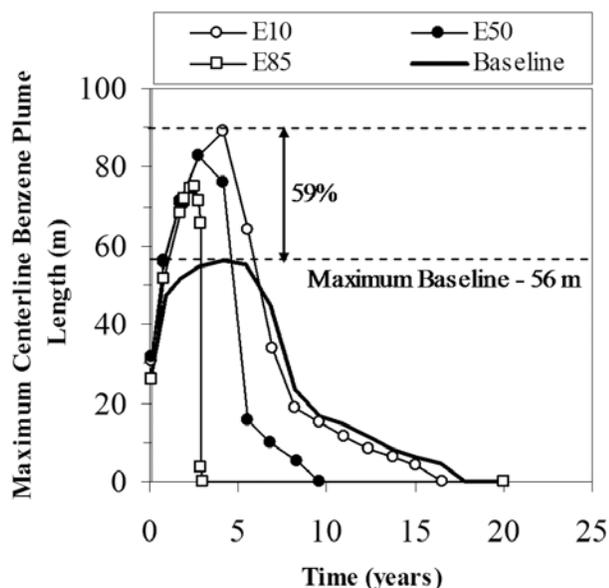
Figure 5. Effect of ethanol volumetric content (10% for E10, 50% for E50, and 85% for E85) in released fuel on resulting benzene plume life cycle compared to regular gasoline without ethanol (baseline).

empirical index to compare the risk associated with groundwater contamination by different ethanol blends. This potential impact index (PII) was defined as the area under the plume length versus lifespan curve (Figure 5) normalized to the corresponding area for the baseline case without ethanol. The PII is 1.16 for E10, 1.07 for E20, 0.78 for E50, and 0.29 for E85. Thus, E10 and E20 spills represent a greater potential for benzene exposure (i.e., length times persistence) than regular gasoline without ethanol. Interestingly, E50 and E85 releases represent a lower PII than the baseline, even though their maximum benzene plume lengths are larger. In this case, longer plumes are offset by a shorter lifespan. A similar inference can be made by considering the maximum benzene plume area of influence for a given spill, normalized to the corresponding area for the baseline, as a metric of potential exposure. This ratio increases from 1.60 for E10 to 1.70 for E20 and then decreases to 1.50 for E50 and 0.91 for E85, inferring that E85 releases would result in a smaller maximum benzene plume area of influence than both E10 and regular gasoline spills.

4. Conclusions

[28] A previously developed custom reaction module for RT3D, GSIM [*Gomez et al.*, 2008] was modified to consider cosolvency and toxicity of ethanol and was used to evaluate the impact of different ethanol blends on benzene plume dynamics. The influence of ethanol content on maximum benzene plume length, plume life span, and microbial populations was evaluated.

[29] Model simulations suggested that the ethanol content in the released blend has a significant impact on benzene fate and transport, with longer benzene plumes (up to 59% for E20) compared to releases of regular gasoline without ethanol. Higher ethanol content led to shorter-lived benzene

plumes because of higher microbial concentrations and enhanced biodegradation rates for both benzene and ethanol, decreased mass of benzene present in the source zone LNAPL, and increased benzene dissolution rates in the source zone LNAPL due to cosolvency.

[30] When considering both negative and positive processes affecting benzene plume elongation, simulations infer that blends with more than 50% ethanol (vol/vol) are likely to experience significantly shorter benzene plume life spans relative to regular gasoline. This leads, within the assumptions and limitations of this model [*Gomez et al.*, 2008], to the conclusion that high−ethanol content blends (e.g., E85) might have a lower and shorter-lived impact on benzene groundwater contamination compared to low−ethanol content blends like E10.

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