



Comparing the effects of various fuel alcohols on the natural attenuation of Benzene Plumes using a general substrate interaction model

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ABSTRACT

The effects of five fuel alcohols (methanol, ethanol, 1-propanol, iso-butanol and n-butanol) on the natural attenuation of benzene were compared using a previously developed numerical model (General Substrate Interaction Module – GSIM) and a probabilistic sensitivity analysis. Simulations with a 30 gal dissolving LNAPL (light non-aqueous phase liquid) source consisting of a range of gasoline blends (10% and 85% v:v alcohol content) suggest that all fuel alcohols can hinder the natural attenuation of benzene, due mainly to accelerated depletion of dissolved oxygen and a decrease in the specific degradation rate for benzene (due to catabolite repression and metabolic flux dilution). Simulations for blends with 10% alcohol, assuming a homogeneous sandy aquifer, inferred maximum benzene plume elongations (relative to a regular gasoline release) of 26% for ethanol, 47% for iso-butanol, 147% for methanol, 188% for 1-propanol, and 265% for n-butanol. The corresponding elongation percentages for blends with 85% alcohol were generally smaller (i.e., 25%, 54%, 135%, 163%, and 181%, respectively), reflecting a lower content of benzene in the simulated release. Benzene plume elongation and longevity were more pronounced in the presence of alcohols that biodegrade slower (e.g., propanol and n-butanol), forming longer and more persistent alcohol plumes. Conversely, ethanol and iso-butanol exhibited the lowest potential to hinder the natural attenuation of benzene, illustrating the significant effect that a small difference in chemical structure (e.g., isomers) can have on biodegradation. Overall, simulations were highly sensitive to site-specific biokinetic coefficients for alcohol degradation, which forewarns against generalizations about the level of impact of specific fuel alcohols on benzene plume dynamics.

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1. Introduction

Groundwater contamination by alcohol-blended gasoline is an emerging concern associated with the increased use of fuel alcohols to meet Clean Air Act [U.S. Environmental Protection Agency, 2009a] and Energy Independence and Security Act requirements [United States Cong. Senate, 2007]. Ethanol is the most commonly used fuel alcohol in North America followed by methanol, which respectively account for 3.4% and 2.3% of the total transportation fuel consumption [U.S. Department of Energy, 2009a; Lynn, 1999]. However,

interest in higher-molecular-weight fuel alcohols such as propanol and butanol has grown recently due to logistic considerations. These higher-molecular-weight alcohols have higher energy density, improving fuel economy [U.S. EPA, 2009b]; they have lower vapor pressure resulting in decreased atmospheric pollution; and their lower hygroscopicity and water solubility allows for storage and distribution using existing infrastructure [U.S. EPA, 2009b] without concern to absorb excessive moisture, which requires special handling of ethanol and dedicated pipelines [U.S. DOE, 2009b].

Benzene is the most toxic of the monoaromatic hydrocarbons, and its presence at gasoline-contaminated sites often governs the need for remedial action [Alvarez and Illman, 2006]. Thus, the effect of fuel alcohols on the transport

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and fate of benzene is of great significance to contaminant hydrogeology. Previous laboratory [Corseuil et al., 1998; Da Silva and Alvarez, 2002; Capiro et al., 2007, 2008], field [Ruiz-Aguilar et al., 2002] and modeling studies [Gomez et al., 2008; Gomez and Alvarez, 2009; Heermann and Powers, 1996; McNab et al., 1999; Molson et al., 2002] showed that ethanol can hinder the natural attenuation of benzene in contaminated groundwater. The principal causes were discerned to be accelerated depletion of molecular oxygen during ethanol degradation, and its preferential metabolism which exerts catabolite repression and metabolic flux dilution – with an overall decrease in the specific consumption rate of benzene [Lovanh et al., 2002; Lovanh and Alvarez, 2004]. This leads to longer benzene plumes and increased risk of exposure to down-gradient receptors [Ruiz-Aguilar et al., 2002; Powers et al., 2001a].

Previous research on the effect of ethanol on benzene plume dynamics suggests the potential for similar impacts by other fuel alcohols, which exhibit similar physico-chemical characteristics as well as other properties that might hinder the natural attenuation of benzene. These include: (1) higher microbial toxicity [Kaiser and Devillers, 1994; Dutka and Kwan, 1981], which could hinder biodegradation; (2) higher cosolvency power, which could result in faster hydrocarbon dissolution and faster migration (i.e., decreased sorption-related retardation) [Poulsen et al., 1991; Paan et al., 2006]; and (3) slower biodegradation rates [Howard et al., 1991], which is conducive to longer and more persistent inhibitory substrate interactions. However, the effect of alternative fuel alcohols on benzene biodegradation and natural attenuation has not been addressed in the literature, and it is unknown whether their presence may increase or decrease the potential for benzene plume elongation relative to ethanol.

An early evaluation of the potential groundwater impacts of alternative fuel alcohols is important for risk assessment and to determine the need to adjust current site management and remediation practices. This paper presents a comparative modeling study of the effects of five fuel alcohols (methanol, ethanol, 1-propanol, iso-butanol and n-butanol) on the natural attenuation of benzene. Reactive transport simulations (20-year long) for eleven different alcohol/gasoline blends were considered: Regular gasoline without fuel alcohol (baseline), 10% ethanol (E10), 85% ethanol (E85), 10% methanol (M10), 85% methanol (M85), 10% 1-propanol (P10), 85% 1-propanol (P85), 10% iso-butanol (IB10), 85% iso-butanol (IB85), 10% n-butanol (B10) and 85% n-butanol (B85). We build on previously developed models: Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW) [Harbaugh et al., 2000], Reactive Transport in 3 Dimensions (RT3D) [Clement et al., 1998] and General Substrate Interaction Module (GSIM) [Gomez et al., 2008; Gomez and Alvarez, 2009], which consider common fate and transport processes (e.g., advection, dispersion, adsorption, depletion of molecular oxygen during aerobic degradation and other electron acceptors during anaerobic biodegradation), as well as substrate interactions that decrease the specific degradation rate of benzene in the presence of fuel alcohols (e.g., metabolic flux dilution and catabolite repression) and LNAPL (light non-aqueous phase liquid) source dissolution dynamics. Resulting microbial population shifts, microbial toxicity at high alcohol concentrations, and cosol-

veny effects are also integrated into the GSIM model. A probabilistic sensitivity analysis of the principal biokinetic parameters used in the model was also conducted, with additional 1-year long simulations, to account for the uncertainty associated with such site-specific variables.

2. Methodology

2.1. Modeling approach

Several numerical models were used to address different processes involved in benzene fate and transport. Groundwater flow velocities were calculated based on domain characteristics (hydraulic gradient, soil porosity and hydraulic conductivity) using the U.S. Geological Survey Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW) model [Harbaugh et al., 2000]. Benzene and fuel alcohol transport was numerically solved using the Reactive Transport in 3 Dimensions (RT3D) model [Clement et al., 1998], based on water flow velocities and chemical properties of the species (e.g., diffusivity, adsorption, solubility).

Contaminant degradation and natural attenuation, substrate interactions between chemical species, microbial population shifts, cosolvency, and toxicity effects were incorporated into the simulations using the General Substrate Interactions Module (GSIM). This previously developed RT3D module, which is extensively described elsewhere [Gomez et al., 2008; Gomez and Alvarez, 2009], considers: (a) decreased specific rate of benzene utilization due to non-competitive inhibition in the presence of an alcohol (i.e., Metabolic Flux Dilution) [Lovanh and Alvarez, 2004]; (b) repression of inducible benzene degrading enzymes by the presence of an alcohol (Catabolite Repression) [Madigan et al., 2005]; (c) lower rates of benzene degradation due to accelerated depletion of available electron acceptors (i.e., oxygen) during alcohol biodegradation; (d) growth and decay of various microbial populations in response to changing electron acceptor and substrate availability; and (e) alcohol cosolvent effects on benzene water–soil partitioning [Da Silva and Alvarez, 2002; Powers et al., 2001b; Groves, 1988] and on benzene source zone dissolution [Heermann and Powers, 1998].

2.2. Model limitations

There are several limitations of the GSIM module as an assessment tool [Gomez et al., 2008], including: (a) all microbial growth is assumed to occur attached to the aquifer matrix with no consideration of detachment kinetics; (b) we assume all substrate biodegradation to take place in the liquid phase (groundwater) and potential decay of sorbed contaminants is conservatively ignored; (c) bacteria are assumed to have complete access to dissolved total organic carbon; (d) complete mineralization of substrates to CO₂ is assumed; (e) degradation byproducts (methanol, acetate, propionate, etc) are not considered in the model; and (f) high alcohol content blends could present deviations in transport behavior not considered by the model, such as alcohol buoyancy and phase partitioning, which could result in complex capillary-zone transport [Sutton et al., 2009]. Our model also assumes all microbial activities to occur in the form of fully penetrated biofilms (i.e., immobile micro-colonies) [Chen et al., 1992]

attached to the aquifer solid matrix, based on the fact that about 99% of subsurface microorganisms are attached [Harvey et al., 1984; Lehman et al., 2001].

2.3. Microbial degradation kinetics

The GSIM model uses multiplicative Monod degradation kinetics, as described by Gomez et al., 2008. Briefly, GSIM consists of a system of equations representing the rate of change of substrates, electron acceptors and microbial populations. The equations involved are alcohol aerobic degradation ($r_{A,Aer}$, Eq. (1)), alcohol anaerobic degradation ($r_{A,An}$, Eq. (2)), benzene aerobic degradation ($r_{B,Aer}$, Eq. (3)), benzene anaerobic degradation ($r_{B,An}$, Eq. (4)), oxygen consumption ($r_{O,Aer}$, Eq. (5)), growth of aerobic alcohol degraders ($r_{X_{A,Aer}}$, Eq. (6)) and growth of anaerobic alcohol degraders ($r_{X_{A,An}}$, Eq. (7)), growth of aerobic benzene degraders ($r_{X_{B,Aer}}$, Eq. (8)) and growth of anaerobic benzene degraders ($r_{X_{B,An}}$, Eq. (9)):

$$r_{A,Aer} = \left[\frac{dA}{dt} \right]_{Aer} = -\frac{f_{SA}^2}{R_A} \left[\frac{\mu_{mA,Aer} X_{A,Aer}}{Y_{A,Aer}} \left(\frac{A}{K_{A,Aer} + A} \right) \left(\frac{O}{K_O + O} \right) \right] \quad (1)$$

$$r_{A,An} = \left[\frac{dA}{dt} \right]_{An} = -\frac{f_{SA}^2}{R_A} \left[\frac{\mu_{mA,An} X_{A,An}}{Y_{A,An}} \left(\frac{A}{K_{A,An} + A} \right) \left(\frac{I_{An,O}}{I_{An,O} + O} \right) \right] \quad (2)$$

$$r_{B,Aer} = \left[\frac{dB}{dt} \right]_{Aer} = -\frac{f_{SB}^2}{R_B} \left[\frac{\mu_{mB,Aer} X_{B,Aer}}{Y_{B,Aer}} \left(\frac{B}{K_{B,Aer} + B} \right) \left(\frac{O}{K_O + O} \right) \right] + r_{A,Aer} (X_{B,Aer}) \quad (3)$$

$$r_{B,An} = \left[\frac{dB}{dt} \right]_{An} = -\frac{f_{SB}^2}{R_B} \left[\frac{\mu_{mB,An} X_{B,An}}{Y_{B,An}} \left(\frac{B}{K_{B,An} + B} \right) \left(\frac{I_{An,O}}{I_{An,O} + O} \right) \right] + r_{A,An} (X_{B,An}) \quad (4)$$

$$r_{O,Aer} = \frac{dO}{dt} = [r_{A,Aer} E_A] + [r_{B,Aer} E_B] \quad (5)$$

$$r_{X_{A,Aer}} = \frac{dX_{A,Aer}}{dt} = -[r_{A,Aer} Y_{A,Aer}] \left(1 - \frac{\eta_{bio}}{\gamma \cdot n} \right) - b_{Aer} X_{A,Aer} \quad (6)$$

$$r_{X_{A,An}} = \frac{dX_{A,An}}{dt} = -[r_{A,An} Y_{A,An}] \left(1 - \frac{\eta_{bio}}{\gamma \cdot n} \right) - b_{An} X_{A,An} \quad (7)$$

$$r_{X_{B,Aer}} = \frac{dX_{B,Aer}}{dt} = -[r_{B,Aer} Y_{B,Aer}] \left(1 - \frac{\eta_{bio}}{\gamma \cdot n} \right) - b_{Aer} X_{B,Aer} \quad (8)$$

$$r_{X_{B,An}} = \frac{dX_{B,An}}{dt} = -[r_{B,An} Y_{B,An}] \left(1 - \frac{\eta_{bio}}{\gamma \cdot n} \right) - b_{An} X_{B,An} \quad (9)$$

where A and B are the concentrations of alcohol and benzene (mg/l), $\mu_{mA,Aer}$, $\mu_{mA,An}$, $\mu_{mB,Aer}$, $\mu_{mB,An}$ are the maximum specific growth rates of aerobic biomass and anaerobic biomass on alcohol and benzene (1/d), $Y_{A,Aer}$, $Y_{A,An}$, $Y_{B,Aer}$, $Y_{B,An}$ are the aerobic and anaerobic biomass yield coefficients (g-biomass/g-

substrate), $K_{A,Aer}$, $K_{A,An}$, $K_{B,Aer}$, $K_{B,An}$ are the half-saturation coefficients under aerobic and anaerobic metabolism (mg/l), $X_{A,Aer}$ and $X_{B,Aer}$ are the aerobic microbial populations (mg/l), $X_{A,An}$ and $X_{B,An}$ are the anaerobic microbial populations (mg/l), b_{Aer} and b_{An} are the aerobic and anaerobic microbial decay rates (1/d), f_{SA} and f_{SB} are the metabolic flux dilution factors (dimensionless), R_A and R_B are the retardation factors (dimensionless), O is the oxygen concentration (mg/l), E_A and E_B are the stoichiometric oxygen use factors (mg/mg), $I_{An,O}$ is an empirical factor representing inhibition of anaerobic processes by oxygen (mg/l), η_{bio} is the total biomass saturation (volume of biomass per volume of pore space), n is the total porosity, γ is the fraction of pore space available for microbial biofilm growth (non-dimensional) and $r_{A,Aer}(X_{B,Aer})$ and $r_{A,An}(X_{B,An})$ are the fortuitous growth rates of benzene degraders on ethanol. Fortuitous growth of benzene degraders while feeding on fuel alcohols can partially offset the negative effects of ethanol [Lovanh et al., 2002; Capiro et al., 2008] on benzene natural attenuation. This process is considered in the GSIM model, as described by Gomez et al. (2008), based on laboratory data from Lovanh et al. (2002). The system considers only aerobic and strongly anaerobic (methanogenic) conditions, which commonly occurs in ethanol-impacted systems as a result of the rapid depletion of thermodynamically-more-favorable electron acceptors such as oxygen, nitrate and sulfate [Da Silva and Alvarez, 2002; Gomez et al., 2008].

Metabolic combinations involved in the simulations use up to 17 different biokinetic coefficients (Table 1), resulting in a highly complex and non-unique system. The literature provides numerous sources for these parameters, which often vary widely due to differences in exposure and environmental conditions. Maximum specific growth rates and microbial biomass yield coefficients were obtained from laboratory studies in the literature (Table 1), which were generally conducted with representative aquifer material and groundwater samples to minimize potential differences between laboratory and field degradation conditions. Aerobic and methanogenic values were available for benzene and ethanol, but Monod coefficients for methanol, n-butanol, iso-butanol and 1-propanol were not available. Thus, the Electron Equivalent Model for Bacterial Yield Prediction (McCarty, 2007) was used to estimate biokinetic coefficients based on thermodynamic data (Supplemental material 2). When unavailable, Monod half-saturation constants (K_s) were estimated with these values using the relationship $\lambda = (\mu_m X / Y K_s)$ (Alvarez and Illman, 2006), where λ is the first-order degradation rate coefficient, obtained from literature sources (Table 1).

2.4. Sensitivity analysis of the GSIM module

Uncertainty in model parameters, primarily those associated with mass transport processes, were addressed in a previous sensitivity analysis [Gomez et al., 2008]. Consistent with water flow being a primary determinant in the fate and transport of contaminants in groundwater, the analysis corroborated that hydraulic parameters such as porosity, hydraulic conductivity, hydraulic gradient and dispersivity were highly influential parameters. However, given the expanded number of substrates considered in this current work, the variability of our biokinetic coefficients is a potential source of uncertainty for the model output that

Table 1
Microbial degradation kinetics.

	First-order degradation rate coefficient, λ (1/d)	Source	Maximum specific growth rate, μ_m (1/d)	Source	Half-saturation constant, K_s (mg/l) ³	Source	Microbial cell yield, Y (g/g)	Source
<i>Ethanol</i>								
Aerobic	0.35	(Powers et al., 2001b)	11.04	(Lovanh et al., 2002)	63.09	Calculated ³	0.50	(Heulekian et al., 1951)
Methanogenic	0.2	(Powers et al., 2001b)	1.10	(Lovanh et al., 2002)	78.86	Calculated ³	0.07	(Lawrence and McCarty, 1969)
<i>Benzene</i>								
Aerobic	0.68	(Alvarez et al., 1991)	3.24	Alvarez et al., 1991	7.63	Calculated ³	0.39	Grady et al., 1989
Methanogenic	0.003	(Wilson et al, 1990; Kazumi et al., 1997)	0.30	(Ulrich and Edwards, 2003)	21.58	Calculated ³	0.05	(O'Rourke, 1968)
<i>Methanol</i>								
Aerobic	0.19	Calculated ¹	1.72	Calculated ²	17.59	Calculated ³	0.52	Calculated ²
Methanogenic	0.11	Calculated ¹	0.09	Calculated ²	10.26	Calculated ³	0.08	Calculated ²
<i>n-butanol</i>								
Aerobic	0.09	Calculated ¹	2.51	Calculated ²	25.03	Calculated ³	1.06	Calculated ²
Methanogenic	0.054	Calculated ¹	0.09	Calculated ²	20.52	Calculated ³	0.08	Calculated ²
<i>Iso-butanol</i>								
Aerobic	1.23	(Pelz et al., 2009)	5.00	Calculated ²	30.58	Calculated ³	0.13	Calculated ²
Methanogenic	0.2	(Pelz et al., 2009)	0.31	Calculated ²	20.49	Calculated ³	0.08	Calculated ²
<i>1-propanol</i>								
Aerobic	0.190	Calculated ¹	2.42	Calculated ²	12.81	Calculated ³	1.00	Calculated ²
Methanogenic	0.108	Calculated ¹	0.09	Calculated ²	10.26	Calculated ³	0.08	Calculated ²
Other parameters		Value		Source				
Aerobic microbial decay rate (b_{Aer})		0.2 1/d		Based on mix culture aerobic systems (McCarty and Brodersen, 1962)				
Anaerobic microbial decay rate (b_{An})		0.03 1/d		Based on methane fermentation (Lawrence and McCarty, 1969)				
O_2 half saturation (K_D)		0.21 mg/l		(Fritzsche, 1994)				
O_2 anaerobic inhibition ($I_{An,o}$)		0.1		Empirical				
Bacterial MC50 (methanol, ethanol, 1-propanol, n-butanol, and iso-butanol)		42,237; 31,000; 9862; 2056; 2500 (mg/l)		(Kaiser and Devillers, 1994; Dutka and Kwan, 1981; Atsumi et al., 2008)				
Alcohol aerobic degraders		10^6 cells/g-soil		(Chen et al., 1992)				
Alcohol anaerobic degraders		10^5 cells/g-soil		10% of alcohol degrading aerobic populations				
Benzene aerobic degraders		10^5 cells/g-soil		10% of total populations				
Benzene anaerobic degraders		10^3 cells/g-soil		1% of benzene degrading aerobic populations				
Maximum pore space utilization factor (γ)		0.2		(Vandevivere et al., 1995; Thullner et al., 2002)				
Biofilm density		10^5 mg/l		High-density biofilm (Freitas dos Santos and Livingston, 1995; Zhang and Bishop, 1994)				

¹First order degradation rates estimated on water half-lives of the compounds. (Howard et al., 1991).²Values estimated using the thermodynamic electron equivalents model for bacterial yield prediction (McCarty, 2007).³Values estimated on the basis of the relationship $\lambda = (\mu X/YK_s)$ (Alvarez and Illman, 2006).

requires consideration. This is particularly important to consider because biokinetic parameters are often subject to significant variability that usually exceeds the accuracy of their quantification. A sensitivity analysis of biokinetic coefficients was conducted to address this uncertainty and identify the parameters requiring the most effort to properly characterize. A formal procedure based on Latin Hypercube sampling and stepwise multiple regression analysis was chosen for this purpose. This approach is suited to complex and intensive (long simulation times) geophysical models [McWilliams, 1987], such as reactive contaminant transport through porous media. The advantage of this method is that it allows to simultaneously vary all variables considered in the analysis, minimizing the number of simulations required on computationally demanding models [McWilliams, 1987], as is

the case with the GSIM module. Numerical details of the implementation of this method using MATLAB (Version R2008a, October 9 2008, The MathWorks, Inc., 3 Apple Hill Drive, Natick, MA) are presented in Supplemental material 3.

A group of 17 variables (V_i) was chosen as input for the GSIM model and grouped in vector form ($\bar{x} = [V_1, V_2, V_3, \dots, V_n]$). A Latin Hypercube Sampling method [MacKay et al., 1979; Stein, 1987], as presented by McWilliams (1987) was used to generate 100 different input vectors (\bar{x}_i) with the aid of MATLAB. Extrapolating from previous work [McWilliams, 1987], a minimum of 34 simulations would be required by this approach to conduct the sensitivity analysis. We chose to expand this number to 100 to enhance the sensitivity analysis. All variables were assumed uncorrelated and to be uniformly distributed over their selected ranges (Supplemental Material 3).

Although some variables might follow different distributions, the benefit of including these non-uniform distributions in the generated vectors is minimal [McWilliams, 1987]. Each input vector was used in a different one-year sensitivity analysis simulation. One-year simulation periods were chosen to avoid long run times involved in a large number (100) of executions. A one-year simulation time was deemed sufficient to allow anaerobic conditions to develop within the plume and account for such processes. Benzene plume length (i.e., the centerline distance from the source to the 5 ppb contour, which represents the drinking water MCL for benzene [U.S. Environmental Protection Agency, 2003]) was used as the indicator output of the GSIM model.

The 17 biodegradation parameters evaluated were: $\mu_{mB,Aer}$, $\mu_{mA,An}$, $\mu_{mA,Aer}$, $\mu_{mB,An}$, $Y_{B,Aer}$, $Y_{A,Aer}$, $Y_{A,An}$, $Y_{B,An}$, $K_{B,Aer}$, $K_{A,An}$, $K_{B,An}$, $K_{A,Aer}$, b_{An} , b_{Aer} , $I_{an,O}$ and γ (see Eqs. (1–9)). The one-year sensitivity analysis simulations yielded a benzene plume length mean of 41 m with a standard deviation of 8.5 m and a 95% confidence interval of 16.4 m. Table 2 lists model parameters in order of most to least relevant for model sensitivity with their associated *p*-value representing the attained level of significance of variable V_i for the model output, as calculated by a stepwise multilinear regression analysis (Supplemental material 3). The most influential parameters are those related to aerobic benzene degradation and anaerobic ethanol degradation. However, for the simulated rapid depletion of molecular oxygen, anaerobic degradation becomes very important to control alcohol plume size and life span. Larger, longer lived alcohol plumes result in longer benzene plumes due to their extended inhibitory effect. The sensitivity analysis also indicates that aerobic benzene degradation, and by association dissolved oxygen concentrations and oxygen recharge rates, play a very important role in controlling benzene natural attenuation. Overall, the sensitivity analysis indicates that the two most important mechanisms that hinder benzene natural attenuation are (1) faster depletion of oxygen due to alcohol degradation, and

(2) extended inhibitory effects associated with the more persistent alcohols (e.g., 1-propanol and n-butanol).

2.5. Initial, boundary, and domain conditions for alcohol simulations

Aquifer material and hydraulic properties for model simulations were based on site characterization of the Hill AFB (Newell et al., 1996; Lu et al., 1999). These properties were implemented on a simulation domain similar to that described by Gomez et al. (2008) and Gomez and Alvarez (2009). The model domain considered for our alcohol evaluation simulations was composed of 3750 cells in a 60 m wide by 200 m long 2D layer with a simulation time of 20 years. A groundwater seepage velocity of 9 cm/d was established by a hydraulic head difference of 0.6 m along the length of the domain. The model considers 6 mg/l of dissolved oxygen (O_2) with a constant recharge through the background groundwater flow into the domain. Direct surface recharge of oxygen from the atmosphere is not considered. Fast depletion of oxygen and other electron acceptors often occurs in aquifers contaminated with ethanol (Da Silva and Alvarez, 2002) and is assumed to take place in our simulations. Simulation and hydrogeological parameters are listed on Table 3. Longitudinal dispersivity can be estimated using empirical models based on plume length (ASTM, 1994; Neuman, 1990). Considering a benzene plume length of 260 ft (80 m), which is the mean length from a survey of benzene plumes at sites contaminated with E10 (Ruiz-Aguilar et al., 2003), we used an improved version of such models (Xu and Eckstein, 1995) to estimate longitudinal dispersivity as 7 m. This value is in agreement with dispersivity values reported for sites with similar hydrogeological characteristics (Lu et al., 1999; Wiedemeier et al., 1996).

To be consistent with previous simulation efforts (Gomez et al., 2008; Gomez and Alvarez, 2009) and avoid potential artifacts, initial microbial concentrations were defined as: (a) 1 mg/l (about 10^6 cells/g-soil) for aerobic ethanol degraders (Chen et al., 1992); (b) 0.1 mg/l (about 105 cells/g-soil), or 10% of total, for aerobic benzene degraders; (c) 0.1 mg/l (about 10^5 cells/g-soil), or 10% of total, for anaerobic ethanol degraders; and (d) 0.001 mg/l (about 10^3 cells/g-soil), or 1% of aerobic benzene degraders, for anaerobic benzene degraders.

Depleting source zone concentrations were calculated assuming an 84 kg mass (30 gal) release of light non-aqueous phase liquid (LNAPL) resting on top of the groundwater table, as described in Gomez and Alvarez (2009). Spill constituents (e.g., benzene and fuel alcohol) are assumed to dissolve into the groundwater at different rates depending on their LNAPL molar fractions and water diffusivity. The composition of E10 (10% ethanol with regular gasoline blend) in mole fractions was used as reference: 0.015 for benzene, 0.172 for alcohol, 0.158 for toluene, ethylbenzene, and xylenes, and 0.655 for other compounds (calculated from Poulsen et al. (1991)). The resulting dissolved concentrations at the groundwater–LNAPL interface can be reasonably estimated using Raoult's law (Mackay et al., 1991) and modified by the cosolvent effects of alcohols using a linear/log linear model developed by Heermann and Powers (1998). Volatilization rates based

Table 2
Sensitivity analysis.

Model parameter	Relevance to model variability ^a	Expected parameter range	Level of significance (<i>p</i> -value)
$Y_{B,Aer}$ (mg/mg)	1	0–1	6.1×10^{-6}
b_{An} (1/d)	2	0–0.5	4.5×10^{-7}
$\mu_{mB,Aer}$ (1/d)	3	0–20	3.6×10^{-6}
$K_{B,Aer}$ (mg/l)	4	0–200	3.2×10^{-6}
$\mu_{mE,An}$ (1/d)	5	0–20	7.3×10^{-6}
$Y_{E,Aer}$ (mg/mg)	6	0–1	6.7×10^{-2}
$K_{E,An}$ (mg/l)	7	0–200	8.8×10^{-2}
$I_{an,O}$ (mg/l)	8	10^{-5} – 10^1	1.4×10^{-1}
$K_{B,An}$ (mg/l)	9	0–200	2.7×10^{-1}
b_{Aer} (1/d)	10	0–0.5	4.1×10^{-1}
K_O (mg/l)	11	0–200	4.4×10^{-1}
$Y_{B,An}$ (mg/mg)	12	0–1	5.1×10^{-1}
$K_{E,Aer}$ (mg/l)	13	0–200	5.8×10^{-1}
$\gamma_{E,An}$ (mg/mg)	14	0–1	6.2×10^{-1}
y (vol/vol)	15	0–0.8	6.8×10^{-1}
$\mu_{mB,An}$ (1/d)	16	0–20	8.1×10^{-1}
$\mu_{mE,Aer}$ (1/d)	17	0–20	8.7×10^{-1}

^a As calculated by the multilinear regression algorithm in MATLAB software – (Supplemental material 3).

Table 3
Simulation parameters.

Parameter	Value	Reference
<i>Hydrogeology</i>		
Hydraulic conductivity (K)	9 m/d	Fine–Medium Sand, LNAST Soils database (Huntley and Beckett, 2002)
Hydraulic gradient (i)	0.003 m/m	(Newell et al., 1996; Lu et al., 1999)
Darcy water velocity (v)	2.7 cm/d	Fine–medium sand, LNAST soils database (Huntley and Beckett, 2002)
Total porosity (n)	0.3	(Newell et al., 1996; Lu et al., 1999)
Groundwater dissolved oxygen (O)	6 mg/l	(Newell et al., 1996; Lu et al., 1999)
<i>Dispersivity</i>		
Longitudinal	7 m	(Xu and Eckstein, 1995)
Transverse	0.7 m	10% of Longitudinal Dispersivity (Newell et al., 1996)
<i>Adsorption and dissolution</i>		
Soil bulk density (ρ_b)	1.7 kg/l	(Newell et al., 1996; Lu et al., 1999)
Retardation factor (R) (methanol, ethanol, 1-propanol, n-butanol, iso-butanol, and benzene)	1.00; 1.01; 1.02; 1.08; 1.04; 1.81	Calculated, $R = 1 + pbKd/n$
Water diffusivity (D_i) (methanol, ethanol, 1-propanol, n-butanol, iso-butanol, and benzene)	1.6×10^{-5} ; 1.3×10^{-5} ; 1.1×10^{-5} ; 9.6×10^{-6} ;	(Hilal et al., 2003)
Water solubility (methanol, ethanol, 1-propanol, n-butanol, and iso-butanol, and benzene)	Miscible; miscible; 0.105; 0.018;	(Hilal et al., 2003)
Cosolvency power (σ_i) (methanol, ethanol, 1-propanol, n-butanol, iso-butanol, and benzene)	0.031; 0.0003 (mole/mole) 2.79; 2.96; 3.18; 3.23; 3.23; n/a	(Poulsen et al., 1991; Paan et al., 2006)
<i>General simulation</i>		
Modeled area length	200 m	
Modeled area width	60 m	
X space discretization	50 units	
Y space discretization	75 units	
Cell width	0.8 m	
Cell length	4 m	
Simulation time	20 years	
Simulation time step (transport)	0.2 days	
Simulation time step (degradation)	0.067 days	
<i>Source zone concentrations at simulation start ($t = 0$)</i>		
Benzene (baseline simulation)	45 mg/l	
Alcohol (10% simulation)	3800 mg/l	
Benzene (10% simulation)	38 mg/l	
Alcohol (85% simulation)	33,000 mg/l	
Benzene (85% simulation)	5 mg/l	

on Fick's first law of diffusion were also considered, as presented by Kim and Corapcioglu (2003). Table 3 provides the initial dissolved groundwater concentrations of benzene and fuel alcohols for three scenarios: baseline (regular gasoline without alcohol), 10% alcohol and 85% alcohol blends. Contaminant concentration values were incorporated in RT3D as a time varying concentration boundary condition at the LNAPL source zone location.

3. Results and discussion

The life cycle of a plume, including longevity and maximum reach, is an important consideration for site investigation and remedial action decisions. Fig. 1 shows the simulated life cycle of benzene plumes for releases of gasoline blended with various alcohols. Benzene plume reach, defined as the distance from the LNAPL source to the 5 ppb down-gradient contour (i.e., the drinking water standard), are plotted as a function of simulation time (Fig. 1). Simulations for E10 corroborate previous laboratory, pilot, field, and modeling studies showing

that the presence of ethanol may hinder the natural attenuation of benzene (Capiro et al., 2007; Corseuil et al., 1998; Da Silva and Alvarez, 2002; Gomez et al., 2008; Ruiz-Aguilar et al., 2003). The model predicts that four years after the 30-gallon release to a sandy aquifer, a regular gasoline spill would emanate a benzene plume with a maximum length of 57 m, compared to 72 m (26% longer) for E10 (Figs. 1a and b). This is in reasonable agreement with a survey of benzene plumes at sites contaminated with regular gasoline versus E10, which found longer benzene plumes for the latter (80 ± 31 m vs. 59 ± 41 m, or 36% longer) (Ruiz-Aguilar et al., 2003).

In all scenarios, benzene plumes expand during the first 2 to 10 years of the simulation, reaching a maximum length, and then recede as the source LNAPL mass is depleted until they disappear. However, both the type and content of the fuel alcohol can have a significant impact on the benzene plume life cycle. For example, maximum centerline benzene plume lengths were 72 m for E10, 84 m for IB10, 141 m for M10, 164 m for P10 and 208 m B10 (Table 4). Furthermore, benzene plumes were smaller and shorter-lived for higher

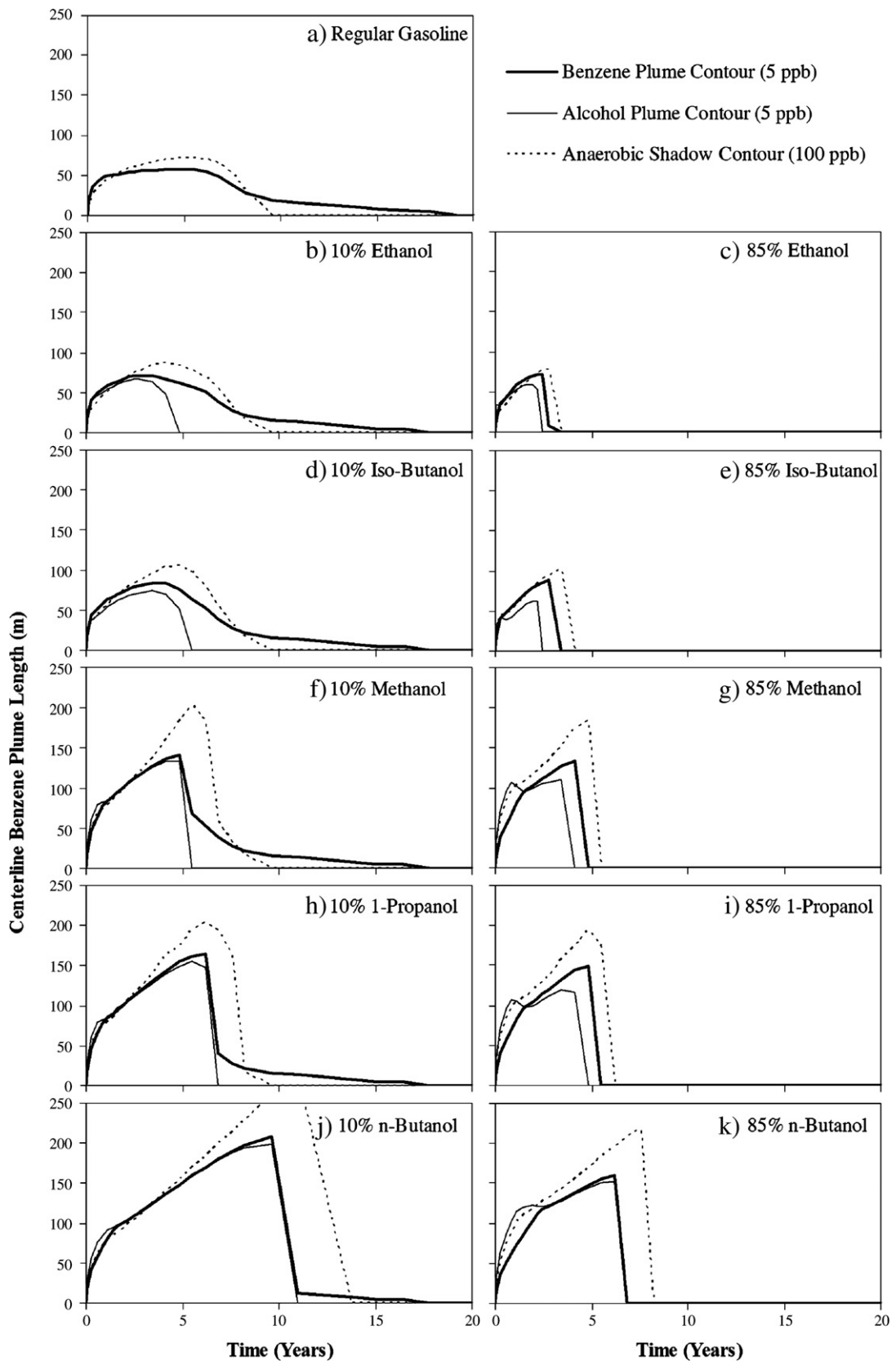


Fig. 1. Simulated benzene plume dynamics (centerline reach) resulting from a 30-gal release of regular gasoline or various fuel alcohol blends.

Table 4
Summary of simulation results.

	Maximum benzene plume length (m)	Percent increase in benzene plume length (%)	Time to maximum benzene plume length (years)	Time to benzene plume depletion (years)	Potential impact index (PII)
<i>Benzene plume length results</i>					
Baseline (regular gasoline)	57	–	4.8	19.2	1.00
10% ethanol (E10)	72	26%	2.8	17.8	1.01
85% ethanol (E85)	71	25%	2.2	3.4	0.26
10% iso-butanol (IB 10)	84	47%	4.1	17.8	1.07
85% iso-butanol (IB85)	88	54%	2.8	3.4	0.34
10% methanol (M10)	141	147%	4.8	17.8	1.35
85% methanol (M85)	134	135%	4.1	4.8	0.69
10% 1-propanol (P10)	164	188%	6.2	17.8	1.58
85% 1-propanol (P85)	150	163%	4.8	5.5	0.86
10% n-butanol (B 10)	208	265%	9.6	17.8	2.47
85% n-butanol (B85)	160	181%	6.2	6.9	1.15
	Near-source zone maximum benzene degrader population (cells/g-soil)	Increase in benzene degrading population (% of baseline)	Near-source zone maximum total degrader population (cells/g-soil)	Benzene degrader population (% of baseline)	
<i>Microbial population results</i>					
Baseline (regular gasoline)	1.6×10^7	–	2.0×10^7	78.28%	
10% ethanol (EB10)	2.4×10^7	52%	4.9×10^9	0.48%	
85% ethanol (E85)	2.1×10^6	–87%	2.4×10^{10}	0.01%	
10% iso-butanol (IB 10)	2.4×10^5	55%	1.5×10^9	1.68%	
85% iso-butanol (IB85)	1.9×10^6	–88%	6.3×10^8	0.30%	
10% methanol (M10)	2.2×10^7	40%	5.5×10^8	4.04%	
85% methanol (M85)	4.4×10^6	–72%	5.4×10^8	0.83%	
10% 1-propanol (P10)	1.7×10^7	8%	6.9×10^8	2.46%	
85% 1-Propanol (P85)	5.5×10^5	–97%	5.1×10^6	10.84%	
10% n-butanol (B10)	5.6×10^6	–64%	2.7×10^8	2.11%	
85% n-butanol (B85)	4.0×10^5	–97%	1.6×10^8	0.25%	

blends of fuel alcohols, due mainly to the smaller content of benzene in the simulated release. The exception was the iso-butanol simulation which produced slightly longer benzene plumes at higher alcohol content (maximum extension of 84 m for IB10 vs. 88 m for IB85). This reflects that although iso-butanol degrades relatively fast (Pelz et al., 2009), it exerts microbial toxicity at levels similar to n-butanol (Atsumi et al., 2008), which inhibits source zone degradation activity for IB85. Life span change due to alcohol content is most pronounced for ethanol and iso-butanol blends, showing a significant decrease in benzene plume duration from 17.8 years for E10 and IB10 (Figs. 1b and d) to 3.4 years for E85 and IB85 (Fig. 1c and e).

The simulated alcohol plumes were relatively short-lived and smaller than the benzene plumes (Fig. 1), reflecting faster degradation rates under the prevailing anaerobic conditions. The anaerobic shadows (defined as the 0.1 mg/l dissolved O_2 contours, which is commonly the limit of detection) are also depicted in Fig. 1. These reflect a geochemical footprint associated with the biochemical oxygen demand of the release, which results in faster oxygen consumption than upgradient recharge. The anaerobic shadow generally reaches a maximum extension shortly after the alcohol plumes, and the contaminated zones remain mainly anaerobic for about 5 to 10 years until natural recharge of oxygen exceeds the decreasing oxygen consumption rate.

Larger benzene plumes and longer life spans were predicted for blends with 1-propanol and n-butanol, which were more

persistent than the other alcohols considered (Fig. 1). Although these alcohols tend to be more toxic and exert higher cosolvency power (Table 3), a sensitivity analysis indicates that anaerobic alcohol degradation rates (and associated persistence) are more influential on benzene plume elongation (Table 2). Specifically, n-butanol and 1-propanol generally exhibit slower dissolution and degradation rates than the other fuel alcohols considered, and persist longer in the aquifer exerting negative substrate interactions (e.g., catabolite repression and metabolic flux dilution) that hinder benzene natural attenuation for longer periods of time (Fig. 1). Note that iso-butanol, which has been reported to degrade relatively fast under both aerobic and anaerobic conditions (Pelz et al., 2009), was inferred to hinder the natural attenuation of benzene to a much lower extent than its isomer n-butanol. This illustrates the significant effect that a small difference in chemical structure can have on biodegradation, and corroborates the high sensitivity of the model to site-specific alcohol biokinetic parameters.

Fig. 2 illustrates how a more persistent alcohol (n-butanol) promotes longer benzene plumes. After 150 days, both n-butanol and benzene plumes are still growing steadily from the LNAPL source zone with high alcohol and benzene concentrations. This stage, where n-butanol strongly hinders benzene degradation (Fig. 2a and b), coincides with the period of benzene plume elongation (Fig. 1j). After about 7 years, n-butanol has been depleted from the LNAPL and a residual butanol plume mobilizes down-gradient, hindering biodegradation of the front end of the benzene plume (Fig. 2c and d). With n-butanol no longer

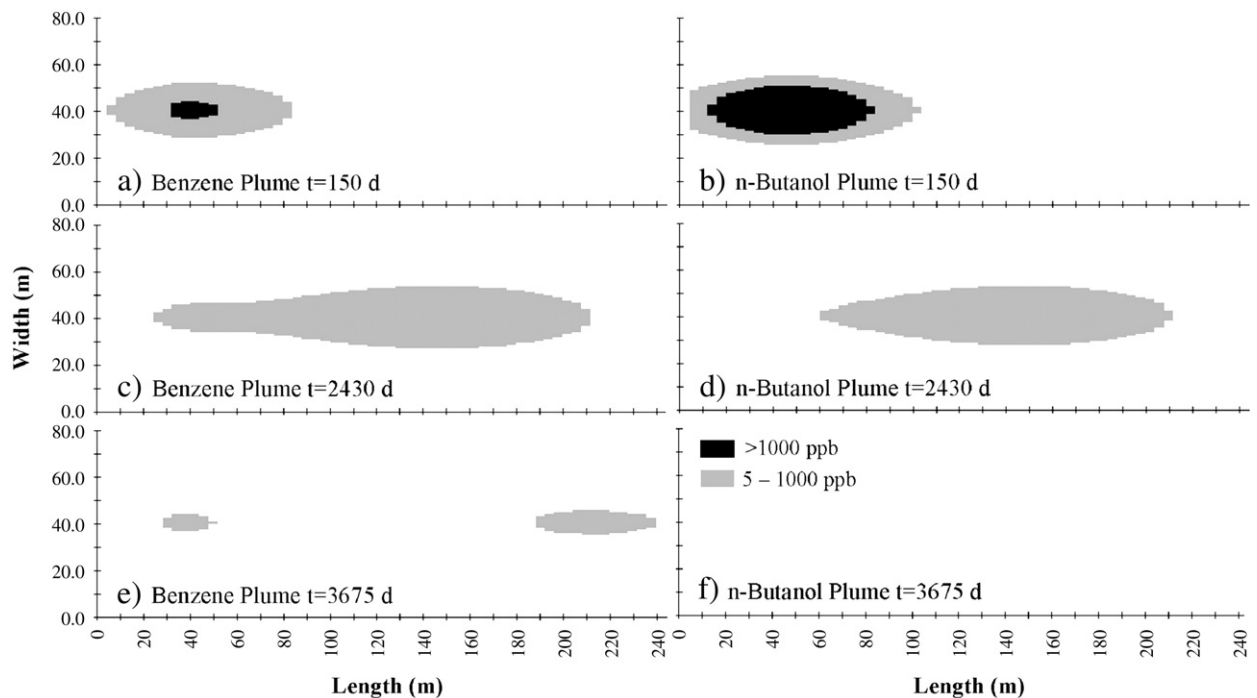


Fig. 2. Simulated benzene and n-butanol contours (5 and 1000 ppb) for a release of a 10% n-butanol blend, after 150, 2430 and 3675 days.

present (Fig. 2f), benzene degradation rates near the source zone increase. Fig. 2e shows a split benzene plume after 9 years, where the central, lower concentration region of the original plume has been completely attenuated and no n-butanol remains in the system (Fig. 2f and 1j). The formation and eventual attenuation of the front end of the discontinued benzene plume results in the sharp decrease in benzene plume length depicted in Fig. 1 (j and k). Faster degrading alcohols like ethanol and iso-butanol are attenuated closer to the source zone and do not form a migrating residual plume. This results in a significantly smaller region of influence and shorter times for inhibition of benzene natural attenuation (Fig. 1b to e). This plume splitting phenomenon is associated with fast groundwater velocities relative to microbial acclimation time, as well as high contaminant concentrations at the source. Due to the acclimation time required by microorganisms to begin degrading the contaminants, the plume front can travel a significant distance before it is attenuated. Increased microbial activity within the plume can result in faster attenuation rates than both at the source zone (where high, possibly inhibitory concentrations prevail) and at the front (unacclimated) edge of the plume. This can result in complete removal of the mid section of the plume, causing an apparent split (Fig. 2e) or a residual contaminant front (Fig. 2d). Naturally attenuated BTEX plumes in a sulfate-reducing aquifer have been reported to show this behavior (Feris et al., 2008).

We previously defined the Potential Impact Index (PII) of a plume as an empirical parameter that considers both plume length (which is related to the possibility of the contaminant reaching a receptor) and lifespan (which relates to the potential duration of exposure) (Gomez and Alvarez, 2009). Briefly, the PII is determined as the area under a given benzene plume life-cycle curve (Fig. 1), normalized to the corresponding area for the regular gasoline baseline plume

(Fig. 1a). The estimated PII values (Table 4) infer that E10 and B10 have relatively low groundwater impacts when considering benzene plume length and persistence, while blends with (more persistent) 1-propanol and n-butanol have a greater impact potential, particularly B10 and P10.

In most simulations, higher alcohol content resulted in higher total microbial populations. For example, near-source zone total bacteria increased from 2×10^7 for regular gasoline to 4×10^9 for E10 and 2×10^{10} cells/g-soil for E85 (Table 4). A similar trend is simulated for other alcohols, although lower population values than for ethanol are obtained despite their higher yield coefficients (Table 1), due to slower degradation rates and toxicity at high alcohol concentrations near the source zone. High concentrations of n-butanol (e.g., for B85) result in the lowest increase in total microbial populations (3×10^8 cells/g-soil), while 1-propanol (85%) results in a reduction in total microbial populations (5×10^6 cells/g-soil), reflecting their higher toxicity as indicated by lower MC50 (midpoint cytotoxicity) values (Table 1).

Although alcohols contribute to the fortuitous growth of benzene degraders (Eqs. 3 and 4), the higher alcohol blends resulted in lower total benzene degrader populations (Table 4). This is due to lower benzene mass available for their growth, which offsets the higher extent of fortuitous growth for higher alcohol content. For example, a 52% increase in benzene degraders is simulated for E10 (38 mg/l initial source zone concentration of benzene) compared to regular gasoline (45 mg/l initial source zone concentration of benzene), due to fortuitous growth on ethanol. However, for E85, the initial concentration of benzene is only 5 mg/l, which supports a smaller benzene degrader population (87% decrease) despite the growth-enhancing effect of ethanol. In all cases, genotypic dilution (Da Silva and Alvarez, 2002; Capiro et al., 2008) was

observed; i.e., benzene degrader populations increase to a lower extent than other commensal microorganisms, and their relative abundance decreases. Genotypic dilution results in a decrease of the percentage of benzene degraders in the total population, from 78% for regular gasoline to 1% for E10, 4% for M10, 3% for P10, 2% for IB10, and 2% for B10 (Table 4).

4. Conclusions

Alcohols present in reformulated fuel blends can have a significant impact on the fate and transport of other gasoline constituents, of which benzene is the most relevant. Model simulations performed using the GSIM model suggest that all five renewable fuel alcohols considered (methanol, ethanol, 1-propanol, iso-butanol and n-butanol) can significantly hinder benzene natural attenuation, mainly due to depletion of available electron acceptors, inhibitory substrate interactions, and microbial toxicity near the source zone. More persistent alcohols (e.g., 1-propanol and n-butanol) have the greatest potential to exert such effects. Simulations infer that ethanol and iso-butanol have a lower propensity to hinder benzene natural attenuation, and that fuels with higher percentage of alcohol will result in smaller, shorter lived benzene plumes. This points to a potential benefit to groundwater pollution mitigation in choosing iso-butanol and ethanol blends with a high percentage of alcohol content. The significant difference between the impacts observed with iso-butanol and n-butanol also highlights the importance of exploring alternative isomers of existing alcohols and new alcohol molecules. Nevertheless, there is considerable uncertainty associated with site-specific biokinetic coefficients for alcohol degradation, which are very influential parameters on simulated benzene plume dynamics as shown by a probabilistic sensitivity analysis. This forewarns against generalizations about the magnitude of the impact fuel alcohols can have on benzene plume elongation, and calls for further laboratory and field research to enable model calibration and validation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jconhyd.2010.02.002.

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