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Impact of New Diesel Fuels Used in Port Operations on Subsurface Quality

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DISCLOSURE

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ABSTRACT

Diesel is widely used as fuel for operations in the port of Los Angeles - Long Beach as well as for transport of goods to and from the port. Conventional diesel fuel contributes disproportional to air pollution (particulate matter, NO_x, CO, and hydrocarbons). The arrival of low-sulfur diesel, which is already widely available in Japan and Europe, and other improvements in fuel and engine technology should greatly decrease the adverse impact of diesel on air quality. Examples of modifications are the use of diesel with ethanol as oxygenate ("diesohol"), biodiesel, and diesel with catalytic additives. Each fuel has some merits that need to be weighed against potential disadvantages. This proposal considers diesohol. Diesohol is already used in Europe and Brazil and is being investigated for wider use in the United States and Australia. In the past, scientists and decision makers were mainly concerned with the impact of diesel and gasoline on air quality. However, even under the best of circumstances release of diesel and fuel additives to the surface and subsurface environment cannot be ruled out. Accidental spillage and leakage may occur during production, transport, storage, handling, or use.

In this study we quantified the impact of the release of a potential new diesel fuel on the movement and fate of contaminants in the aqueous phase of the unsaturated (vadose) and saturated zone of the subsurface. Existing software was modified to model subsurface flow in the vadose zone. The model accounts for the effect of surfactants (ethanol and other fuel additives) on flow properties, and the dissolution of diesel components (benzene in this case). The impact of ethanol on dissolution and degradation of fuels compounds and pre-existing organic contaminants in the groundwater has been analyzed using a model based on analytical solutions.

The results of the study for the unsaturated zone suggest that, for the most common scenario of a particular water flux at the surface, water and dissolved substances will move somewhat farther in the underground. Ethanol reduces the amount of water that is retained by the porous medium. Furthermore, the concentration of contaminants such as benzene may be greatly increased due to the enhanced aqueous solubility. The analysis conducted for the saturated zone illustrated changes in contaminant plumes due to enhanced solubility and reduced biodegradation caused by ethanol. Contaminants such as benzene are more persistent in groundwater and the plume area exhibits a moderate increase if ethanol is present.

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1. INTRODUCTION

1.1. Ethanol as Fuel Oxygenate

Diesel is widely used as fuel for operations in the port of Los Angeles - Long Beach as well as for transport of goods to and from the port. Diesel engines tend to operate more efficiently than those using conventional fuel. However, conventional diesel fuel contributes disproportional to air pollution (particulate matter, NO_x, CO, and hydrocarbons). For this reason, the sudden popularity of diesel-powered passenger cars in the U.S. after the 1970s oil crisis did not last long. The arrival of low-sulfur diesel, which is already widely available in Japan and Europe, and other improvements in fuel and engine technology should greatly decrease the adverse impact of diesel on air quality. Recent increases in the price of oil should further spur the interest in diesel as an alternative to conventional gasoline.

Examples of modifications are the use of diesel with ethanol as oxygenate ("diesohol"), biodiesel, and diesel with catalytic additives. Each fuel has some merits that need to be weighed against potential disadvantages. The focus of this project is on diesohol. Diesohol is already used in Europe and Brazil and is being investigated for wider use in the United States and Australia. Several pilot programs are underway for bus and truck fleets such as the use of E-15 OxyDiesel by the Chicago Transit Authority and the Archer Daniels Midland Corporation, and of O_2 Diesel by Lincoln Star Tran in Nebraska and Pepsi Cola in New York City.

1.2. Potential Adverse Effects of Ethanol on the Environment

In the past, scientists and decision makers were mainly concerned with the impact of diesel and gasoline on air quality. However, even under the best of circumstances release of diesel and fuel additives to the surface and subsurface environment cannot be ruled out. Accidental spillage and leakage may occur during production, transport, storage, handling, or use. Partly due to problems with the use of MTBE as fuel oxygenate, there is growing awareness that improvements in air quality should not be achieved at the expense of soil and water quality. MTBE was quickly introduced in the marketplace because of its success to reduce air emissions but was found later to be a persistent and troublesome contaminant of aquifers. Similarly, ethanol may become the predominant contaminant at sites where a diesel spill occurs due to the high concentrations of ethanol in fuel mixtures and to the infinite solubility of ethanol in water.

Because diesel and ethanol do not mix well, additional compounds are needed to obtain stable blends. The presence of ethanol and other additives is likely to affect the solubility and degradation of diesel components such as BTEX (Benzene, Toluene, Ethylbenzene, Xylene) and naphthalene. Some of these compounds are highly toxic: the maximum contaminant levels (MCLs) for drinking water are 5 µg/L for benzene and 3 µg/L for toluene according to the EPA. Their aqueous solubilities are much higher (1780 and 515 mg/L, respectively). In this study we will consider the impact of ethanol on the fate and transport of benzene, which is commonly present in diesel fuel and a known carcinogen (Dean, 1985). It is the most recalcitrant mono-aromatic under anaerobic conditions. The use of ethanol as fuel oxygenate for gasoline, i.e., gasohol, has already received considerable scrutiny (Rice and Cannon, 1999). Less work has been done on diesohol (Corseuil and Kulkamp, 2003).

Ethanol and additives are organic compounds whose presence in the aqueous phase will lower the surface tension at the air-water interface. They are therefore considered surfactants (i.e., surface active agents). Commercial surfactants have many industrial applications (cf. Schwarzenbach et al., 1993) and they are also used to remediate the subsurface environment after contamination with nonaqueous phase liquids (NAPLs). The latter are typically highly toxic compounds, which may reside in a residual liquid phase for many years. In addition to ethanol, many other natural organic compounds have nonpolar (hydrophobic) and polar (hydrophilic) parts and will hence lower surface tension. Such compounds may be acids, alcohols, amines, esters, aliphatics, and aromatics. The use of surfactants has been widely investigated for the petroleum industry to enhance oil recovery (e.g., Pope and Wade, 1995) and, as mentioned, for subsurface remediation (e.g., Oostrom et al., 1999). In the former case, the change in interfacial tension between oil and water is of interest whereas for the latter the change in aqueous solubility of DNAPLs (NAPLs with a greater density than water) is often of primary concern

1.3. Scope of Project

The purpose of this project is to quantify how the release of a potential new diesel fuel – diesohol in this case, but the results of this study may also be useful for other reformulated fuels – might affect the movement and fate of contaminants in the aqueous phase of the subsurface. We will review the findings on the use of ethanol as oxygenate for regular gasoline and the effect of surfactcants on vadose flow (e.g. Rice and Cannon 1999, Smith and Gillham, 1999). METRANS has an interest in objectively evaluating and managing potential adverse effects of (candidate) diesel fuels to meet the transportation needs such those at the port of Los Angeles – Long Beach. Groundwater represents a significant source of drinking water in Southern California. Restoring contaminated groundwater to EPA standards could be difficult and costly.

Spillage of ethanol on the surface or leakage from underground storage tanks may impact the fate and transport of other diesel components or pre-existing contaminants in several ways. We will consider this impact by examining the behavior of a contaminant (e.g., benzene) in the aqueous phase for idealized scenarios. We will not consider movement in the nonaqueous phase or interaction of different contaminant species in the aqueous phase. The processes that determine the impact are reviewed in Chapter 2. Ethanol will typically be released in the unsaturated or vadose zone. Chapter 3 of this study is devoted to the potential impact on the vadose zone. This chapter is the most extensive due to the nonlinear nature of water flow in the vadose zone and the variety of boundary and soil conditions that may occur. We will examine changes in the hydraulic properties of porous media due to ethanol. Existing software is modified for this purpose and the numerical code is used to model flow and transport that accounts for the presence of ethanol (and potentially any other surfactant such as fuel additives). Eventually, if the conditions are right, ethanol may reach the groundwater table and spread in the saturated zone of the subsurface (aquifers). Chapter 4 presents analytical solutions for two different contamination scenarios in the saturated zone due to transport from a diesel spill or dissolution from a pre-existing contaminant pool of a dense nonaqueous phase liquid (DNAPL). These solutions can be used to determine how ethanol might affect the development of contaminant plumes in aquifers. For the scenario of the diesel contamination we examine changes in solubility and biodegradation due to ethanol, for the DNAPL scenario we will examine changes in mass transfer between contaminant pool and aquifer.

2. BACKGROUND

2.1 Introduction

In this chapter we will present a review of the physical processes that are responsible for changes in subsurface flow and transport due to the presence of ethanol. We start with the impact on the hydraulic properties due to the dependency of surface tension and viscosity on ethanol concentration. An overview of research in this area will be presented in Chapter 3 on the vadose zone. In section 2.3 we review the impact of ethanol on the aqueous solubility of organic contaminants and we review published data on cosolvency. We conclude this chapter with a discussion on possible changes in biodegradation of organic contaminants (diesel compounds or other pre-existing contaminants) due to ethanol being present in the subsurface environment.

2.2. Surface Tension and Viscosity

The retention of water in porous media is typically explained based on the work on capillarity by Young and Laplace (cf. Pomeau and Villermaux, 2006). The pressure difference across the air-water interface in a circular tube yields the following estimate for the soil water pressure head (similar to capillary rise equation):

$$h = \frac{2\sigma \cos\phi}{\rho g r} \tag{2.1}$$

where σ is the surface tension (about 72 mN/m for pure water at room temperature), ϕ is the contact angle where solid, air, and water meet, ρ is solution density [M/L^3], g is gravitational acceleration [L/T^2], r is the pore radius of an equivalent circular tube [L]. The pressure head is negative for unsaturated conditions as the water is under suction by the porous medium. The actual shape of pores will be rather different and a correction is sometimes used. However, the major effects of surfactants on water retention may be adequately explained with Eq. (2.1). A surfactant such as ethanol will lower the surface tension with a commensurate decrease in pressure for a particular pore size (water content) and – although not considered here – alter the contact angle. In other words, there is less suction to retain water in the presence of ethanol.

Figure 2.1 shows the surface tension at the air-water interface as a function of the amount of ethanol dissolved in water reported by Powers and Heermann (1999). Water has a relatively high surface tension due to its polarity. The surface tension drops considerably when adding ethanol. The surface tension of pure ethanol is approximately 22.4 mN/m. Because ethanol is highly soluble in water, the presence of other gasoline components will not greatly affect the surface tension (Powers and Heermann, 1999).

The ability of a soil to transmit water is characterized by its hydraulic conductivity, the unsaturated conductivity for the vadose zone tends to be lower than the hydraulic conductivity (permeability) of aquifers because not all pore space is occupied by water. The unsaturated hydraulic conductivity function is indirectly affected by the reduced capillary pressure as discussed for the water retention. At given pressure head, surfactants will lower the water content and hence the hydraulic conductivity at that particular pressure. There is a considerable body of literature on the effect that surfactants may have on the conductivity of porous media that are saturated with water.

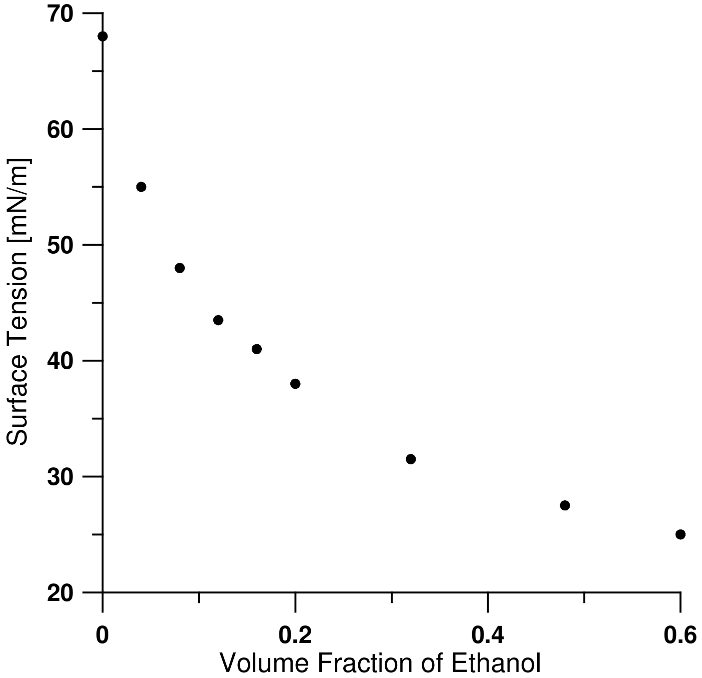

Figure 2.1. Surface tension as a function of ethanol fraction (after Powers and Heermann, 1999).

The saturated hydraulic conductivity may be defined as:

$$K_s = \frac{g}{\nu} k \tag{2.2}$$

where K_s is the saturated hydraulic conductivity [L/T], k is intrinsic permeability [L^2], and ν is the kinematic viscosity [L^2/T]. For an inert porous medium – with constant k – the surfactant will increase the viscosity and hence lower K_s.

2.3. Aqueous Solubility

An important consideration for the use of fuel oxygenates such as MTBE or ethanol and any other additives, is their effect on the dissolution of organic fuel components in water. Considerable work has been done on co-solvency effects for ethanol-blended gasoline (cf. Rice and Cannon, 1999). Ethanol increases the solubility of organics, which enhances transfer of organics from the nonaqueous to the aqueous phase and leads to greater organic contaminant plumes in the aqueous phase.

Diesel fuel is comprised of compounds with similar chemical properties and low aqueous solubilities for the pure compound. Raoult's law may hence be used to estimate the maximum dissolved concentration:

$$C_i = x_i C_{si} \tag{2.3}$$

with C_i as aqueous concentration [M/L^3], x_i as the mole fraction of i in the diesel fuel, and C_{si} as the solubility of pure component i in water. However, ethanol has dissimilar properties than diesel components and is highly soluble in water. Raoult's law will no longer be valid to predict the solubility of diesel component. Ethanol acts as a co-solvent. By reducing the polarity of the aqueous phase, it facilitates dissolution of hydrophobic organic compounds (Groves, 1988; Schwartzenbach et al., 1993).

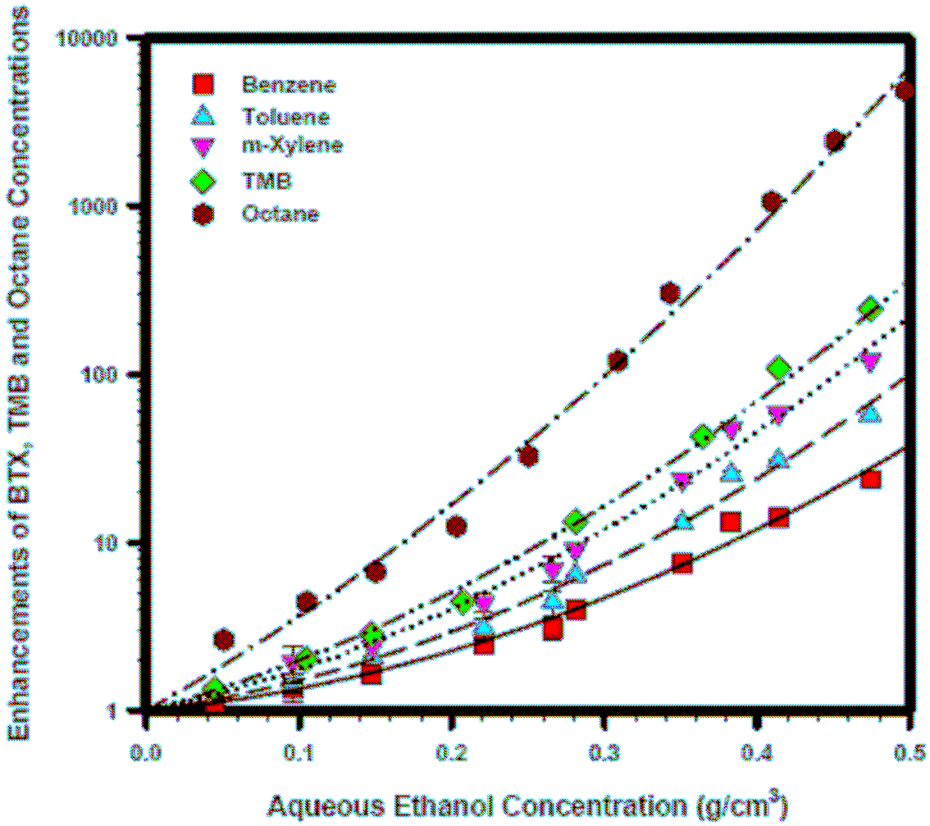

Figure 2.2. Normalized aqueous solubility of organics as a function of ethanol concentration in the aqueous phase (He, 2002)

Most studies dealing with the cosolvent effect of ethanol pertain to regular gasoline. He (2002) reported data for BTX (benzene, toluene, xylene), 1,2,4-trimethylbenzene (TMB), and n-octane, which are al components of diesel fuel. Figure 2.2 shows the aqueous solubility of various organics, in a mixture of water and the aforementioned compounds, normalized to the solubility in pure water, referred to as enhancement, as a function of ethanol concentration. The data shows considerable enhancement of the solubility due to the presence of ethanol. The cosolvency effect is greater for more hydrophobic compounds such as xylene or octane than for the less hydrophobic benzene, which is the compound of most concern as it was proved to be carcinogenic (cf. Heermann and Powers, 1998). He (2002) also described the data with an empirical function for the enhancement factor.

Corseuil and Fernandez (1999) studied the solubility of BTEX compounds in water aqueous phase equilibrated with gasoline containing 22% ethanol. From their experiments conducted by varying the water to fuel ratio from 20:1 to 1:1, they reported that the maximum ethanol concentration in water was about 15%. The study revealed that ethanol concentration in the aqueous phase corresponding to 10% will enhance the solubility of BTEX compound by 30%.

Heermann and Powers (1998) analyzed the cosolvency effect for water-gasoline mixture containing ethanol. Their experiments were performed using simple and complex gasoline as well as two commercial reformulated gasolines. The partition coefficients of the organic compounds increased with increasing ethanol concentration, but while on a semi-log scale the data showed a linear trend for aqueous ethanol volume fractions greater than 0.2, a different trend was observed for lower ethanol contents. This behavior was further analyzed by comparing the results from three models to simulate the relationship between the partition coefficients of BTEX compounds as a function of ethanol aqueous concentration. Heerman and Powers (1998) employed a log-linear model (Yalkowsky et al., 1972), a linear/log linear model (Banerjee and Yalkowsky, 1988), both modified for multicomponent mixtures, and the UNIFAC model. The authors observed that the log-linear and the UNIFAC model correctly described the observed overall increase of BTEX aqueous concentrations with increasing ethanol levels. However, the two models failed to describe the observed trend in the data and generally overestimated the BTEX concentrations. The piecewise linear/log linear model that included a linear relationship for low ethanol levels and a log-linear function for higher levels, fitted using the laboratory data, accurately described the observed trend in the data. The authors concluded that this model may be useful to predict BTEX concentrations at the lower ethanol levels that are likely top occur for spills of commercial gasoline.

Brederode et al. (2001) analyzed the enhanced concentration and aqueous solubility of 12 organic compounds in gasoline with increasing ethanol levels. They used Raoult's law and the log-linear cosolvency model to describe the experimental data. The experimental and model-predicted results for the solubility in water with increasing water to gasoline ratio, were in good agreement for compounds with relatively high aqueous solubilities. For compounds with a lower solubility, the aqueous concentrations were too low. The results of the study confirmed that the cosolvency effect was significant only when the volume fraction of ethanol in water exceeded 10%.

The percentage of ethanol in the aqueous phase and thus the cosolvency effect is determined by the mass transfer rate. Powers and Hermann (1999) noted that greater ethanol concentrations, and an increased cosolvency effect, will transpire at high rates of ethanol mass transfer. The processes that govern movement of ethanol and other compounds through gasoline are molecular diffusion and free convection. While molecular diffusion has been extensively studied and modeled, studies on free convection are limited.

From the analysis of the results reported by Heerman and Powers (1998), Corseuil and Fernandez (1999), and Brederode et al. (2001), we may infer that the cosolvency effect of ethanol will not be significant when spillage of gasoline occurs because the aqueous concentration of ethanol will be relatively low. However, when pure ethanol is spilled – during transport or at a production or blending facility – cosolvency will substantially alter the solubility of organic contaminants.

2.4. Biodegradation

A third area of concern is the effect of ethanol on the biodegradation and natural attenuation of organics. Bioremediation is used to deal with persistent contaminants in the subsurface environment. *In situ* bioremediation minimizes disturbance of the environment and is often expedient and cost effective (Lee et al., 1988). Microorganisms are supplied to degrade contaminants into harmless daughter products. The process may be facilitated by adding fertilizers and oxygen to provide additional nutrients and electron acceptors. Intrinsic bioremediation involves the degradation of contaminants by natural attenuation. The presence of ethanol in the subsurface may hamper bioremediation and attenuation of more persistent and/or toxic contaminants. The preferential degradation of ethanol involves microorganisms, electron acceptors, and nutrients that would otherwise be available for the attenuation of diesel components (Corseuil and Kulkamp, 2003). Since ethanol represents a carbon and energy source, the microbial population that can degrade BTEX may actually grow. If nutrients and electron acceptors are not depleted, this may result in faster degradation of BTEX after ethanol has been degraded as observed by Corseuil et al. (1998) for toluene.

BTEX compounds are recalcitrant to microbial degradation (cf. Alvarez and Hunt, 1999). Their aerobic degradation has been widely reported. Anaerobic degradation proceeds slower. Anaerobic degradation of toluene is easier than that of more toxic benzene. In addition to the availability of nutrients and electron acceptors (such as nitrate, sulfate, and carbon dioxide for anaerobic degradation), temperature, pH, and moisture content will affect biodegradation. Ethanol is highly biodegradable provided that the concentration does not reach levels toxic for microorganisms (between 40 and 100 g/L). It is also widely available because it is completely miscible with water. Degradation of diesel components and ethanol may be described as a first-order process:

$$\frac{dC_i}{dt} = -\lambda_i C_i \tag{2.4}$$

where C_i is the concentration of organic compound i [M/L^3] with degradation coefficient λ_i [1/T] where λ_i is not constant but will vary in time and space. For aerobic aquifer conditions, a typical value would be λ=0.3 1/d with a corresponding half-life of 2.31 days. In moving surface waters, the degradation will proceed even faster. For the degradation of benzene in aquifers, the value of λ may reportedly vary between 0.0001 and 0.087 1/d. For our simulations we will use lower, more conservative, values.

Da Silva and Alvarez (2002) performed experiments to investigate the impact of ethanol and MTBE on the natural attenuation of BTEX compounds. They concluded that while MTBE did not hinder the degradation of the BTEX compounds and that of ethanol, ethanol adversely affected the degradation of the BTEX compounds because the oxygen in the system was depleted by the degradation of ethanol. In this environment, degradation of benzene, the contaminant of concern, is greatly impacted. However, the authors noted, the persistence of ethanol in the subsurface is limited to short duration and the impact of ethanol would be less significant than that of MTBE.

The impact of ethanol on benzene plume lengths was investigated by Deeb et al. (2002). They performed experimental studies to quantify the effect of ethanol on the rates of benzene biodegradation under aerobic conditions and developed a two-dimensional model based on the Domenico (1987) solution. The experimental results confirmed previous finding that the presence of ethanol inhibited the biodegradation of benzene. In accordance with the experimental results, the model predicted a 16% to 34% increase in benzene plume length in the presence of ethanol. The authors also reported that the plume length increased with the water velocity and organic carbon content. The modeling results were in agreement with those reported by Malcom Pirnie (1998).

Ulrich (1999) employed MODFLOW (McDonald and Harbaugh, 1988) and MT3D (Zheng, 1990) software to determine the impact of ethanol on benzene plume lengths.

The extent of a benzene plume for a scenario where no ethanol was present was compared to results obtained for a spillage of gasoline containing ethanol. The modeling results showed that ethanol will enhance the length of the benzene plume. The author pointed out that the persistence of ethanol in the environment is not likely to extend to long periods of time due to its rapid biodegradation and therefore its impact maybe limited.

In a study conducted by the Institute for Groundwater Research (2000) the impact of ethanol on benzene and other BETX compounds was investigated through a numerical model that was applied to two different scenarios; the first one pertaining to the spillage of gasoline, containing either a 10% volume fraction of ethanol or none, in a pristine aquifer and the second to the spillage of pure ethanol in an aquifer with pre-existing gasoline contamination. In the first scenario, cosolvency effects were neglected and only biodegradation was considered whereas both effects were included for the spillage of pure ethanol. For the first scenario, the study confirmed that the length of the benzene plume was longer for spillage of oxygenated than for ethanol-free gasoline. This increase, which in case of a single spill amounts to about 30%, is significant when multiple spillages occur. For the case of pure ethanol spillage the model predicted an enhancement of the contaminant plume between 30 to 140%. Significantly higher length increases could be obtained in scenarios where multiple ethanol/gasohol spillages occur.

3 VADOSE ZONE

3.1. Introduction

As mentioned in the Introduction, fuel spills typically impact the vadose zone first. Remediation and other corrective or preventive actions will be most successful when the contaminant still resides in the vadose zone. This is the zone between the soil surface and the groundwater table. The pore space of this "unsaturated" zone is partly filled with water and partly with air; flow and transport proceed at a relatively slow rate. Furthermore, soil organic matter is most prevalent near the surface and can retard organic contaminants by adsorption. The vadose zone can be rather extensive in the Southwestern United States. Relatively little research has been done on the effect of surfactants on the vadose zone because most bioremediation deals with heavier organics that reside in the "saturated" zone and because of experimental difficulties. However, there is an urgent need to consider the impact of surfactants in the vadose zone. Ethanol in regular gasoline or diesel fuel constitutes an important representative of a compound that may affect hydraulic properties of the vadose zone. As was stated earlier, the ability of porous media to retain and transmit water is quantified by the water retention and hydraulic conductivity functions, respectively. Both these functions are highly nonlinear and hysteretic. They are also affected by the presence of surfactants in water as will be briefly discussed in the following.

3.2. Governing Equations

One-dimensional flow in the vadose zone is governed by the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left(K \frac{\partial h}{\partial z} \right) - \frac{\partial K}{\partial z} \tag{3.1}$$

where θ is the volumetric water content of the soil [L^3/L^3], h is the soil water pressure head [L], K is the soil hydraulic conductivity function [L/T], z denotes depth [L], and t is time [T]. In vadose zone hydrology, negative values are often used for h to convey that water is under suction. In unsaturated soils the water content and the pressure head are related through the retention function. Several relationships have been developed in the past to describe the relationship between θ and h. In this study we use the following relationship (van Genuchten, 1980)

$$\Theta = \frac{\theta - \theta_r}{\theta_s - \theta_r} = (1 + |\alpha h|^n)^{-m} \qquad (m = 1 - 1/n) \tag{3.2}$$

where Θ is the effective saturation, θ_r is the residual water content, θ_s is the saturated water content, and α [1/L], m, and n are soil-specific curve fitting constants with m often defined in terms of n. The hydraulic conductivity for an unsaturated soil can be calculated from the van Genuchten retention function using (Mualem, 1986):

$$K(\Theta) = K_s \Theta^{\ell} [1 - (1 - \Theta^{1/m})^m]^2 \tag{3.3}$$

where $K(\Theta)$ is the unsaturated hydraulic conductivity [L/T] and ℓ is a fitting parameter.

Ethanol or other surfactants will impact the constitutive relationships between θ, h and K, as will be discussed shortly in more detail. In order to quantify this impact, we need to know the surfactant concentration. Transport of the surfactant may be modeled with the following well-known advection-dispersion equation for solute transport:

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial \theta V C}{\partial z} - \lambda \theta C \tag{3.4}$$

where C is solute (surfactant) concentration [M/L^3]. The terms on the right-hand side account for dispersion, advection, and first-order degradation with dispersion coefficient D [L^2/T], pore-water velocity V [L/T], and degradation factor λ [1/T]. It is assumed that the surfactant is linearly degraded, is completely miscible with water, and is not adsorbed at the soil-water or air-water interfaces. We further assume that surfactant transport is not affected by other solute species (e.g., diesel components).

The decrease in capillarity due to surfactants will have several ramifications for flow and transport in the vadose zone (Henry and Smith, 2003). The so-called "air entry" value of a soil, h_e=1/α (cf. Eq.(3.2)), will become smaller leading to additional drainage of water. The zone above the groundwater table with appreciable water (the capillary fringe) will be reduced. Introduction of surfactants into the subsurface changes the hydraulic equilibrium, there will be water flow from regions contaminated with surfactants – where the capillary pressure will increase (i.e., less negative) – toward cleaner regions with the original lower pressure head (higher suction). Surfactants may even affect the saturated and residual water contents (i.e., the maximum and minimum of the retention curve), but these effects are beyond the scope of this project.

The water retention curve of water with a surfactant concentration C may be predicted from the (known) retention determined at a reference concentration C_o (such as zero for pure water). According to the scaling procedure by Leverett (1941) – at a given water content – the pressure head for an arbitrary concentration and tension is expressed in terms of the pressure head h_o for the reference surface tension σ_o of pure water according to:

$$h(\theta, C) = \frac{\sigma}{\sigma_o} h(\theta, C_o) \tag{3.5}$$

The scaling is straightforward but requires that the relationship between σ and C is known (cf. Fig. 2.1). Smith and Gillham (1994, 1999) and Smith (1995) fitted the surface tension concentration data as function of the concentration using a relationship proposed by Adamson (1990):

$$\frac{\sigma}{\sigma_o} = 1 - b \ln\left(\frac{C}{a} + 1\right) \tag{3.6}$$

where a and b are fitting parameters characteristic for the surfactant of interest, and C is the concentration of the surfactant, which in the studies by Smith and Gillham (1994, 1999) and Smith (1995) was butanol.

The hydraulic conductivity also depends on the viscosity of the solution (cf. Eq. (2.2)). A somewhat similar logarithmic expression as (3.6) was employed by Smith (1995) and Henry et al. (2001) to describe the dependency of the viscosity on the surfactant concentration:

$$\frac{\nu}{\nu_o} = \left(1 - e \ln\left(\frac{C}{d} + 1\right)\right)^{-1} \tag{3.7}$$

where ν is the kinematic viscosity at concentration C, ν_o is the reference kinematic viscosity for pure water, and e and d are surfactant-dependent constants

3.3. Impact of Surfactants on Vadose Flow

Henry et al. (1999) experimentally studied the effect of a butanol solution on water flow in the vadose zone. They found that the surfactant induced water flow from high concentrations to low concentration regions. The authors also employed the HYDRUS 1-D Version 5 code (Vogel et al., 1996) to simulate the experimental data. The water retention data were scaled and then fitted with the van Genuchten relationship (3.2). The numerical results poorly described the experimental findings for butanol and the authors attributed this discrepancy to the inability of their model to account for the changes in the soil hydraulic properties as the surfactant moves through the soil.

Henry *et al*. (2001) used relationships (3.6) and (3.7) in an unsaturated flow and transport model, based on a modification of the existing version 5 of the HYDRUS 1D model, that incorporated both hysteresis and concentration dependent hydraulic functions. The model was applied to simulate the surfactant induced flow of a butanol solution in a horizontal column and to investigate the effect of hysteresis. The model satisfactorily described the laboratory results reported by Henry et al. (1999). The sensitivity analysis revealed that dispersivity is an important factor in the flow behavior. In particular sharper surfactant concentration gradients were observed for low dispersivity values. This generated large capillary pressure gradients that induced higher fluxes near the solute front.

Subsequently Henry and Smith (2002, 2006) incorporated the butanol effects on the hydraulic properties into the HYDRUS-2D model (Simunek et al., 1999) to analyze the surfactant impact on the infiltration of water into a laboratory model of a sand aquifer at residual moisture content. The authors compared the numerical results with the laboratory data reported by Henry and Smith (2002). The numerical results were consistent with the experimental data and showed that the surfactant concentrations gradients cause capillary pressure gradients, which induced flow from regions at high level of contamination toward less contaminated areas. The authors point out that standard numerical codes that simulate flow and transport in the vadose zone without incorporating the surfactant effect on the soil hydraulic properties are still useful whenever the effect of the surfactant on the water retention and hydraulic conductivity properties is small. In addition they noticed that when later-time infiltration behavior is important the standard numerical models where the hydraulic properties in the entire domain are those of the porous medium uniformly wetted with the surfactant solution produce accurate results. However they fail to represent the behavior of the system during transient, early time infiltration.

Typically, the solid phase of the medium will not be inert. The surfactant may be sorbed by the medium. Surfactants may enhance dissolution of particles or precipitation of minerals. Some surfactant will affect the diffuse double layer around clay minerals and promote swelling. Due to the complexity of the processes that are involved and the lack of consensus in the literature on how they affect hydraulic conductivity, it is difficult to quantify the impact of surfactants on the conductivity function and therefore we did not incorporate this effect in our project.

Recently, Silva and Grifoll (2007) presented results from a one-dimensional numerical model that incorporates the dependence on density, viscosity, surface tension, molecular diffusion coefficient in the liquid-phase, and the gas-liquid and solid-liquid partition coefficients on the concentration of the surfactant. In addition the model included the decrease in the gas-liquid partition coefficient caused by high capillary pressure values according to the Kelvin's equation for multi-component mixtures. The authors applied their model to simulate the infiltration and redistribution of water containing butanol and methanol in the vadose zone in two different types of soils. Their results showed that the volumetric water content and the concentration profiles together with the volatilization and evaporation fluxes were highly affected by the methanol concentration. A sensitivity analysis showed that at relatively high values of the dispersivity, solute dispersion was the main factor that affected the transport of the methanol solution. At low dispersivities, liquid flow was induced by changes in surface tension due to concentration changes and the most significant transport mechanism was advection. The authors also noted that the reduction in the gas partition coefficient has a significant impact on the transport. Ignoring the Kelvin effect produced a low gas-phase diffusion; the water evaporation flux was lower and the volumetric water content was higher. The authors emphasized the importance of the Kelvin effect on the accurate prediction of flow and transport behavior especially in arid regions.

3.4. Numerical Simulations

3.4.1. General Information

In this study we will use the relationship, Eq. (3.6), proposed by Smith and Gillham (1994, 1999) and employed by Henry et al. (2001) to describe the surface tension as function of the ethanol concentration. The parameters *a* and *b* in the equation were obtained by fitting the data from Powers and Heermann (1999) and unpublished data obtained from our own surface tension experiments. Figure 3.1 includes the data set used to obtain *a* and *b* as well as the fitted curve. The fitted values for *a* and *b* were 2.401%, and 0.204 respectively. It should be noted that these values and Eq.(3.6) lead to an underestimation of the surface tension of pure ethanol; other parameterizations may yield more accurate estimates for high ethanol concentrations.

Vol % ethanol	σ [mN/m]
0	71.5
0.1	70.6
0.2	69.9
0.3	69.7
0.4	69
0.5	68.7
1	66.7
2	63.8
5	57.2
10	45
20	38.5
32	31.5
48	27.5
60	25

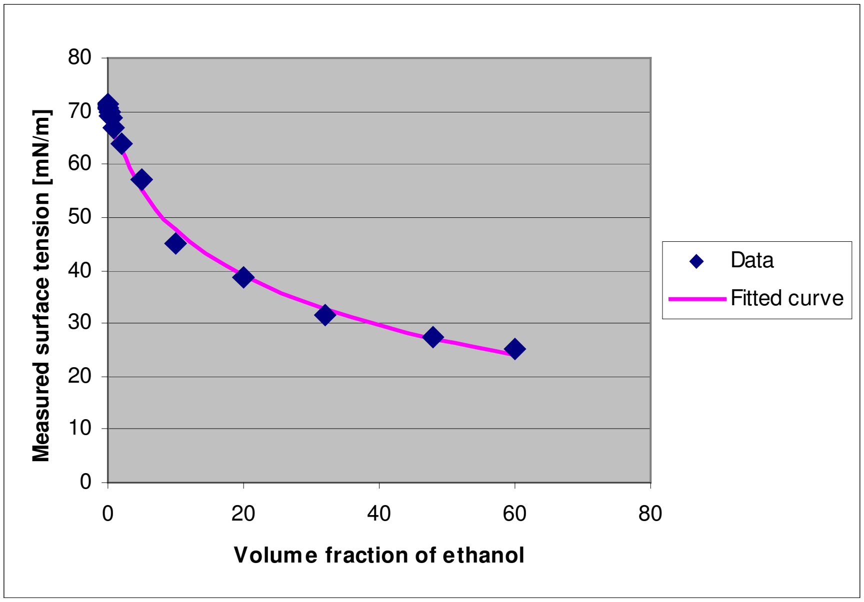

Figure 3.1. Measured and fitted surface tension values of aqueous solution as function of the volume fraction of ethanol

The HYDRUS 1D version 6 code (Simunek et al., 1996) for simulating one-dimensional water flow and solute transport in the unsaturated zone was modified to incorporate the dependency of the water retention curve on the surfactant concentration according to Eq. (3.5). The code solves the one-dimensional Richards equation and the unsaturated transport equation using the Galerkin finite element method. We modified the code so that at every time step, it evaluates the surfactant concentration profile and then uses this information to modify the water retention function as prescribed by Eqs. (3.5) and (3.6). Our measurements showed that ethanol has a negligible effect on the viscosity of the aqueous solution, hence no correction of the hydraulic conductivity according to Eq. (3.7) was implemented. The model was employed to simulate water flow and benzene transport due to infiltration resulting from ponding or a prescribed surface flux. All scenarios were compared with the reference case involving no ethanol. The soil profile is 200 cm long with a surface condition that depends on the type of scenario being simulated (h =0 for ponding or a prescribed flux for the flow problem, surface concentration equal to solubility for benzene transport) and free drainage at the bottom. The initial pressure head in the entire soil is given by h=–1000 cm, which indicates reasonably dry conditions.

3.4.2. Ponding

We selected a silt loam soil from the UNSODA database (Leij et al. 1996). The hydraulic parameters, used to parameterize the retention and conductivity functions according to Eqs. (3.2) and (3.3), are given in Table 3.1. For the simulation of ethanol and benzene transport, we used a (longitudinal) dispersivity of 2 cm. Degradation is neglected due to the short duration of the transport (flow) process of up to one day.

The parameters in Table 3.1 were used to compute the retention curve. The retention curve for pure water was scaled according to Eqs. (3.5) and (3.6) to obtain a curve for a soil in equilibrium with an aqueous solution with 10% ethanol as well as with pure ethanol. The three retention curves are shown in Figure 3.2. Figure 3.3 shows the relationship between the hydraulic conductivity K and the volumetric water content θ according to Mualem equation (Eq. (3.3)) for 0%, 10%, and 100% volume fractions of ethanol. The figures show that for the same value of the pressure head (energy status of the soil), the volumetric water content and the hydraulic conductivity of the soil in the presence of ethanol are lower than the corresponding values for pure water indicating a drier and less permeable soil. The fraction of pores that is filled with liquid is inversely related to the ethanol content of the equilibrating solution. We already discussed in section 3.2 the impact of changed hydraulic properties induced by the ethanol on water flow and contaminant transport in the vadose zone.

Table 3.1. Soil Parameters for the Silt Loam used in Ponding Simulations

θ_r [-]	θ_s [-]	α [cm^{-1}]	n [-]	K_s [cm/hr]
0.102	0.526	0.0278	3.59	1.042

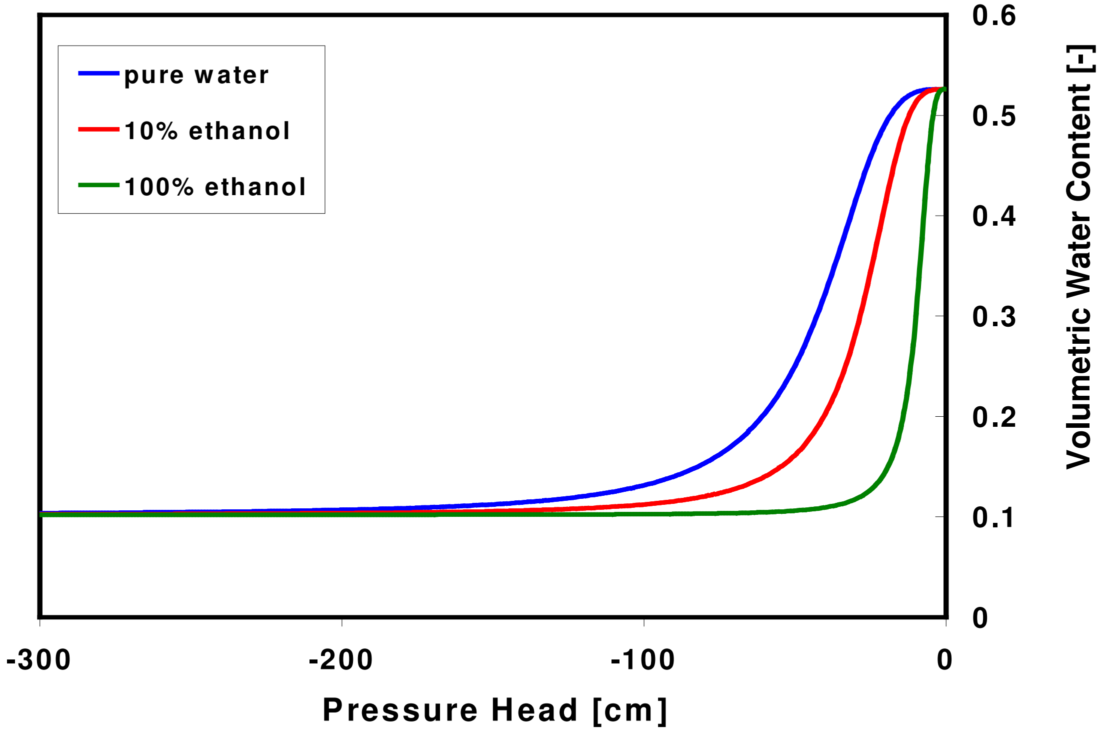

Figure 3.2. Retention curves for silt loam soil in equilibrium with 0%, 10%, and 100% ethanol solutions.

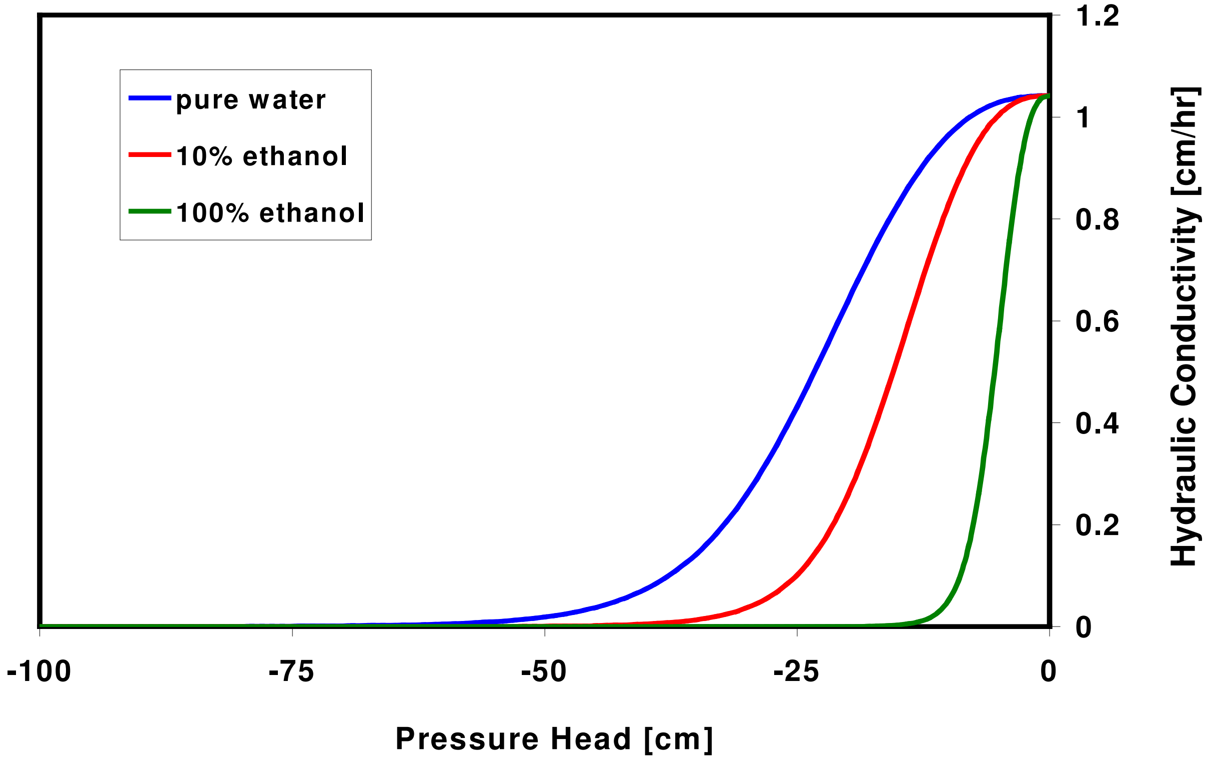

Figure 3.3. Hydraulic conductivity curves for silt loam soil in equilibrium with 0%, 10%, and 100% ethanol solutions.

Scenario 1: Ponding of an Ethanol-free Soil

The simulated pressure head, volumetric water content, and water flux profiles, which developed 6 and 24 hours after the onset of ponding, are shown in Fig. 3.4-3.6. The profiles are for ponding with 0%, 10%, and 100% ethanol. In the last two cases, the ethanol fraction of the resident and ponding solution are different. It is worth repeating that we had to simultaneously simulate the ethanol concentration (shown in Fig. 3.7) in order to determine the precise retention curve. The value for α in Eq. (3.2) changes with position and time depending on the ethanol concentration. The pressure head h is negative since the soil is unsaturated (Fig. 3.4), the negative water flux denotes downward movement (Fig. 3.6).

The simulations suggest that ethanol reduces infiltration. The soil moisture front travels more slowly when ethanol is present (Fig. 3.5). The soil water flux is an important parameter for the water balance and for the transport of dissolved substances. The water flux is consistently lower when the surface tension is reduced by the ethanol and the soil retains less water at a particular pressure head (Fig. 3.6). Even though the ethanol front is behind the wetting front – there is initially no ethanol but there is water – the impact of ethanol on the water flux at smaller depths is clearly manifested near the wetting front. It should be noted that this is a simple infiltration scenario where the soil only experiences wetting, there is no hysteresis or any reverse effect of the ethanol.

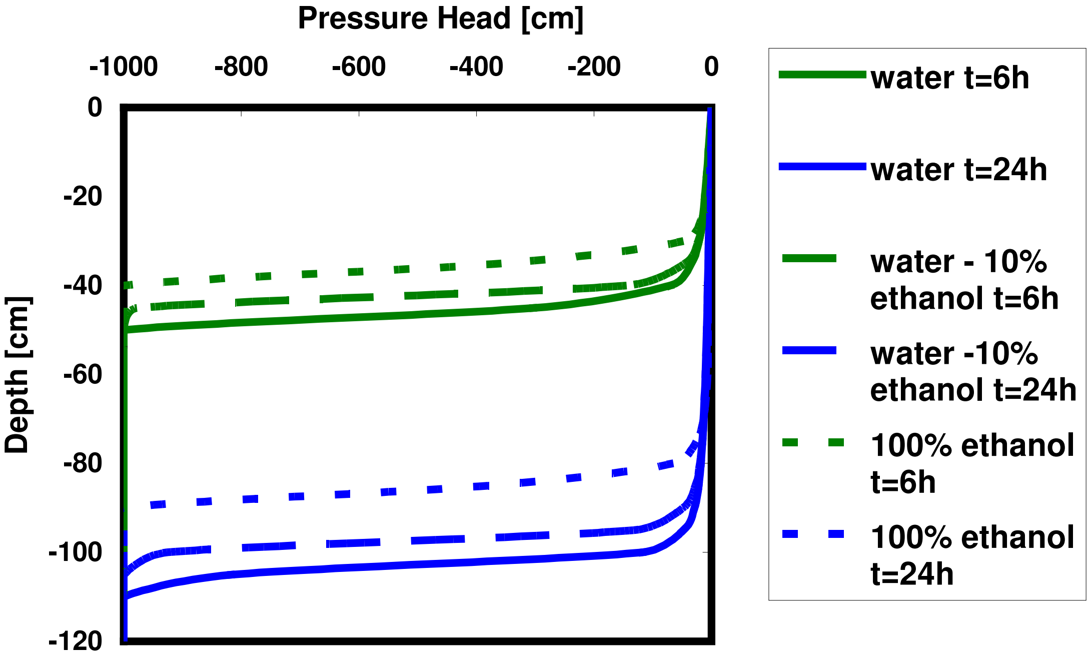

Figure 3.4. Pressure head profiles for scenario 1.

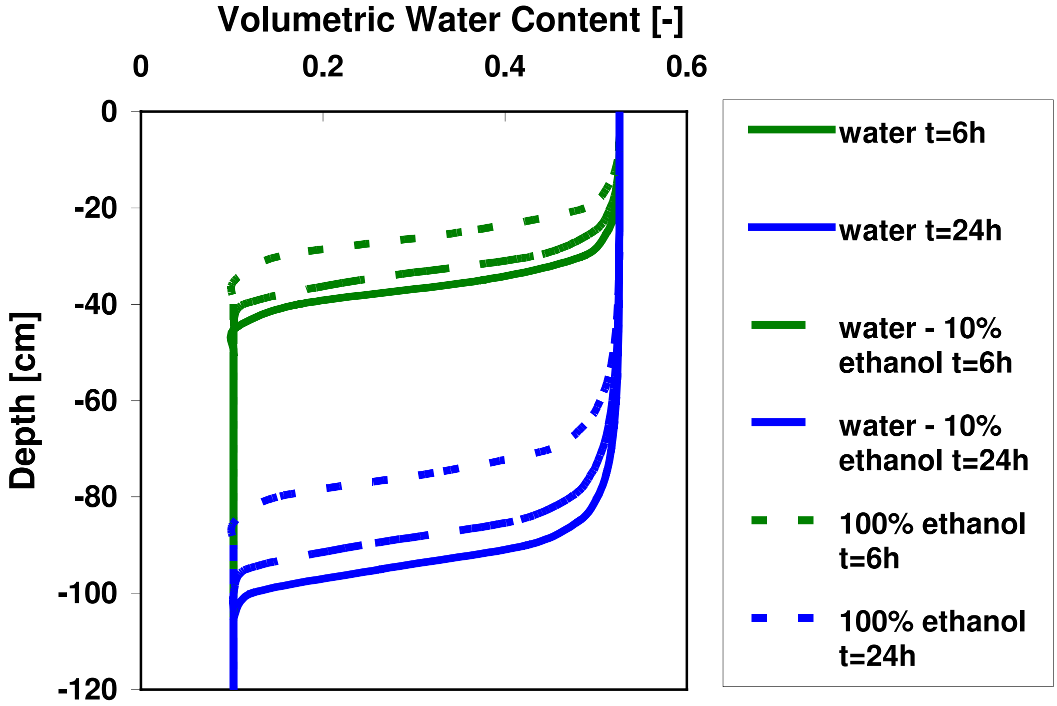

Figure 3.5. Volumetric water content profiles for scenario 1.

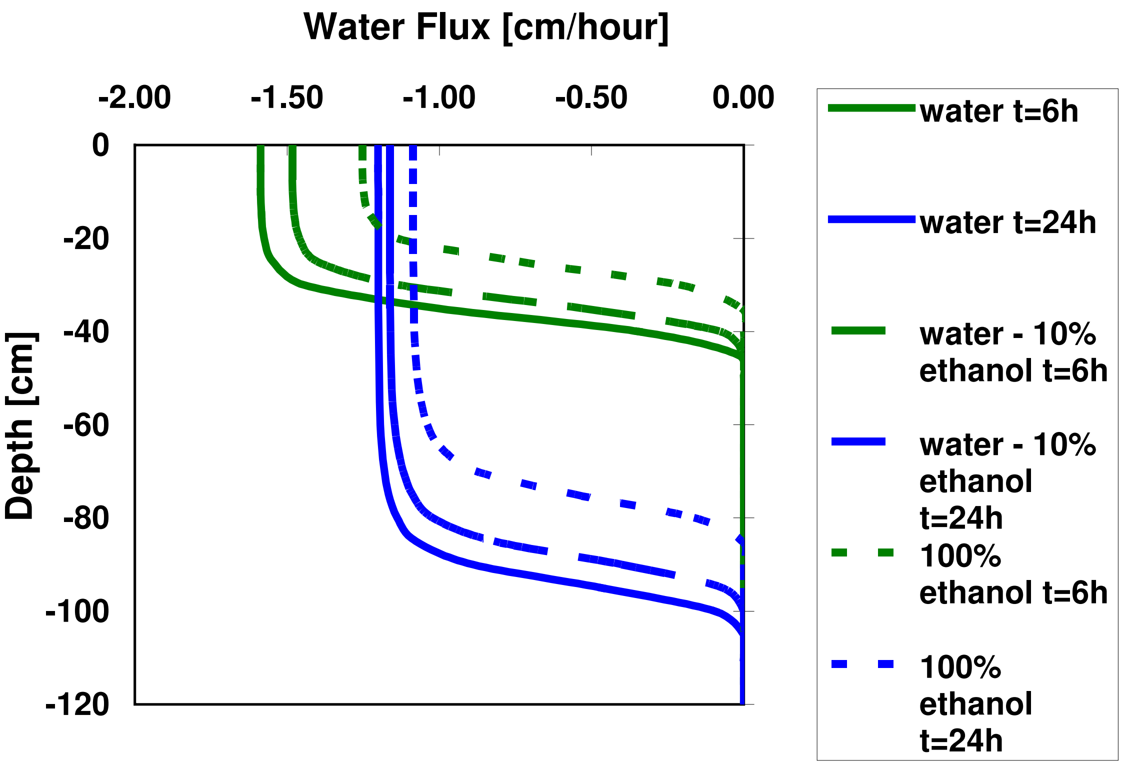

Figure 3.6. Water flux profiles for scenario 1.

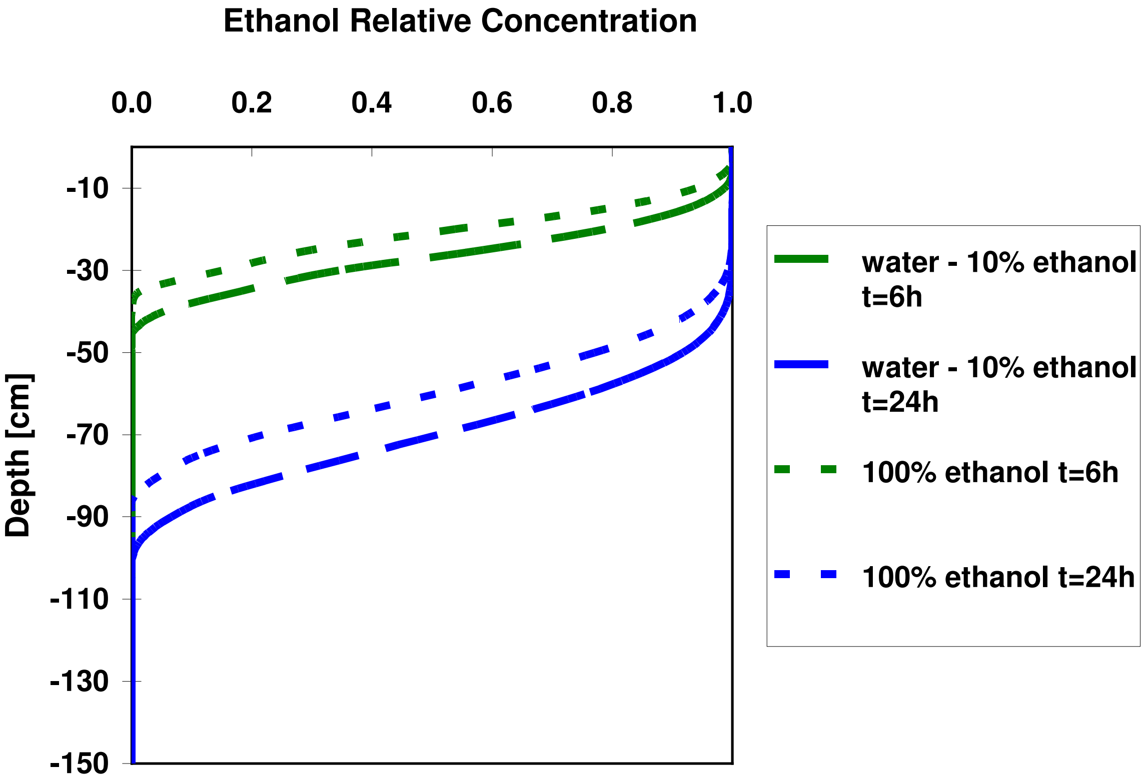

Figure 3.7. Relative ethanol concentration profiles for scenario 1.

Scenario 2: Benzene Transport during Ponding of a Soil with 10% Ethanol

In this scenario we investigated the impact of ethanol on the transport of a contaminant, which we assume to be benzene. As mentioned in section 1.2, benzene is a common diesel compound, carcinogenic, persistent, and widely studied. We simulated water flow and benzene transport into a soil, with water initially at 1000 cm suction and with 0% or 10% ethanol, due to ponding with water containing also 0% or 10% ethanol and benzene. The soil is the same as for scenario 1, the value for α is effectively changed to 0.042 1/cm in the case of the omnipresent 10% ethanol concentration. Since the ethanol concentration of resident and inflowing water is the same, there is no need to model ethanol transport. Instead, the transport problem involves benzene. We assume a constant benzene concentration at the top, zero gradient at the bottom, and no retardation or degradation in the soil. For 0% ethanol, we assumed that the surface concentration for benzene was equal to its aqueous solubility of 1.78 g/L. For 10% ethanol, the aqueous solubility of benzene will approximately be 2.39 g/L (cf. Heermann and Powers, 1998). The resulting concentration profiles after 6 and 24 hours of ponding are depicted in Fig. 3.8. From the figure it is clear that the presence of ethanol in the soil column will cause an increase of the concentration of benzene in the aqueous phase, while it will slow down its infiltration.

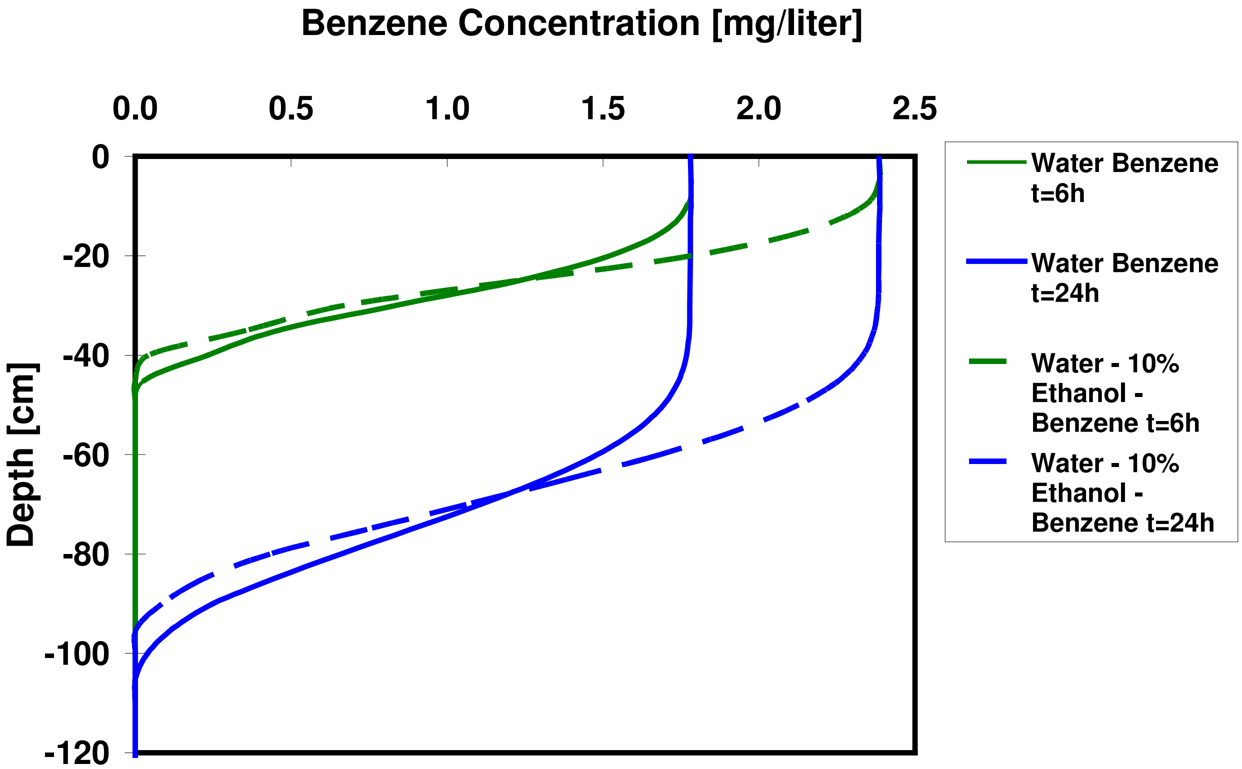

Figure 3.8. Benzene profiles for ponding with water with 0% and 10% ethanol for scenario 2.

3.4.3. Prescribed Infiltration

Water is applied at a rate of 1 cm/hr during the first hour, followed by a minimal flux of 10^{-4} cm/hr. The soil is a sandy loam whose retention parameters and saturated conductivity are given in Table 3.2. The soil dispersivity is equal to 1 cm. All other conditions are the same as for the previous ponding scenarios. The retention and the hydraulic conductivity functions for aqueous solutions with 0%, 10%, and 100% volume fractions of ethanol are given in Figs. 3.9 and 3.10. Notice the retention and conductivity functions change more abruptly than for the silt loam soil, the soil does not transmit appreciable amounts of water for *h* <-50cm for pristine water and this limit is reached even sooner if ethanol is present.

Table 3.2. Soil Parameters for the Sandy Loam used for Prescribed Flux Simulations

θ_r [-]	θ_s [-]	α [cm^{-1}]	n [-]	K_s [cm/hr]
0.053	0.3747	0.0353	3.1798	26.79

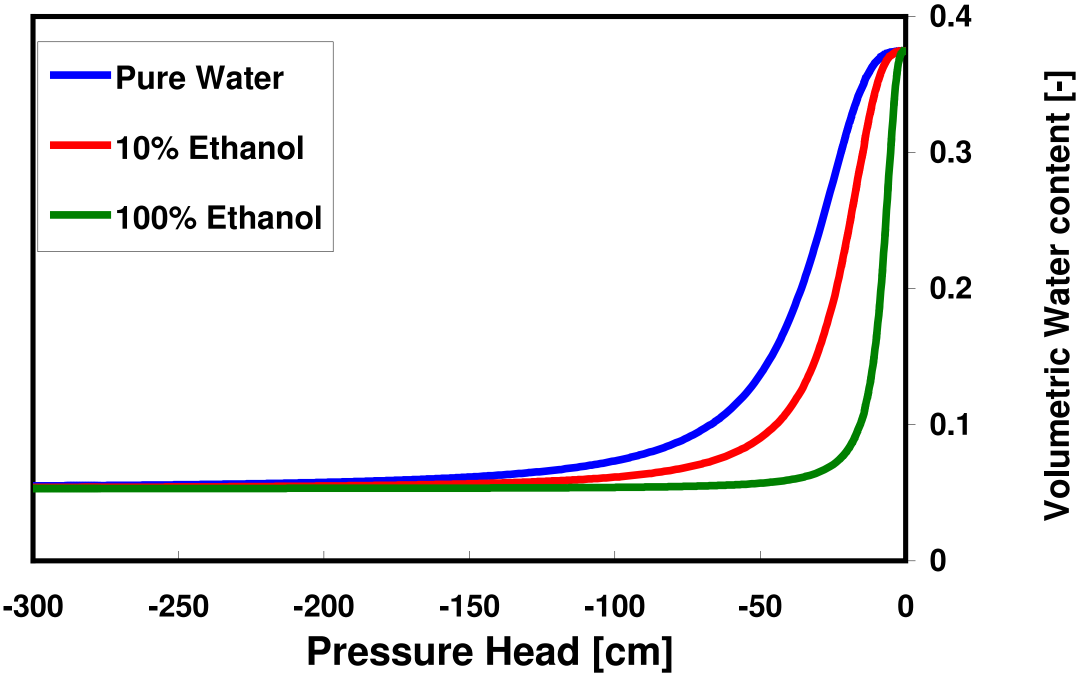

Figure 3.9. Retention curves for silt loam soil in equilibrium with 0%, 10%, and 100% ethanol solutions.

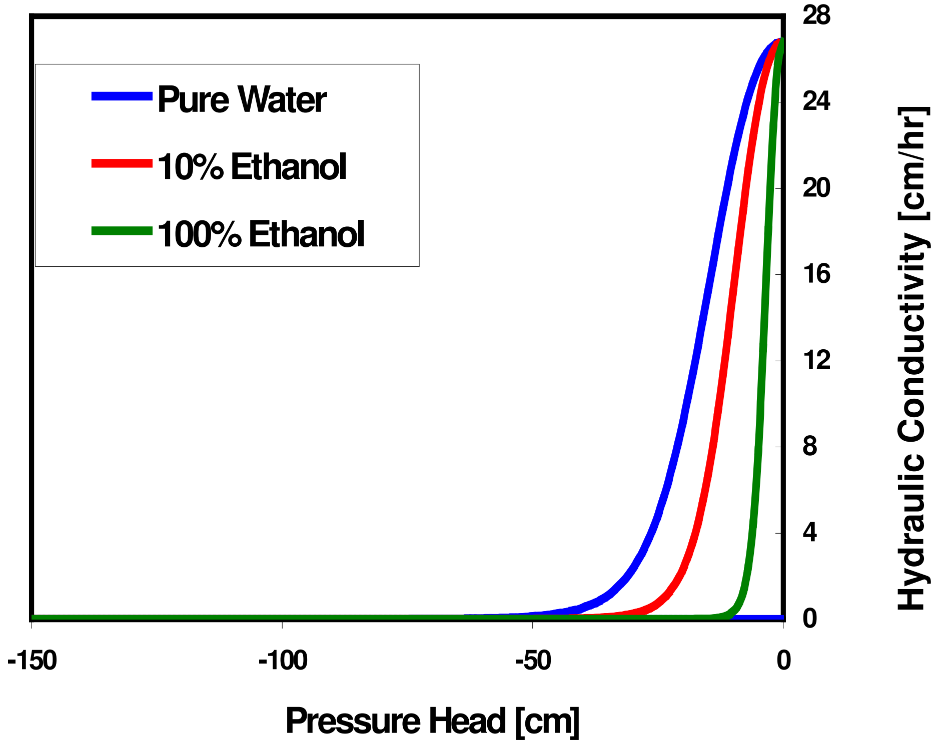

Figure 3.10. Hydraulic conductivity curves for silt loam soil in equilibrium with 0%, 10%, and 100% ethanol solutions.

Scenario 3: Prescribed Infiltration Flux into an Ethanol-free Soil

As was the case for the silt loam scenario 1, we need to simultaneously model unsaturated water flow and ethanol transport. Water flow depends on the ethanol concentration due to the changes in interfacial tension whereas transport is governed by the pore-water velocity. We will only show results where the infiltrating water has 0% or 10% ethanol. The pressure head, water content, and ethanol profiles are given in Figs. 3.11-3.13 for t= 1, 6, and 24 hours after the start of infiltration. Note that the infiltration is 1 cm/h for the first hour and then becomes negligible.

When ethanol is not present water is retained more strongly in the soil and therefore the water content for pure water is larger than the water content for the ethanol solution in the upper portion of the soil. The presence of ethanol will lower the surface tension of the aqueous solution; less water will be retained and more will be available to move downward. This explains why in the upper portion of the soil the water content is lower and in the lower portion of the soil profile it will be higher for infiltration with water containing 10% compared to 0% ethanol (Fig. 3.12). This can be illustrated more clearly with normalized variables.

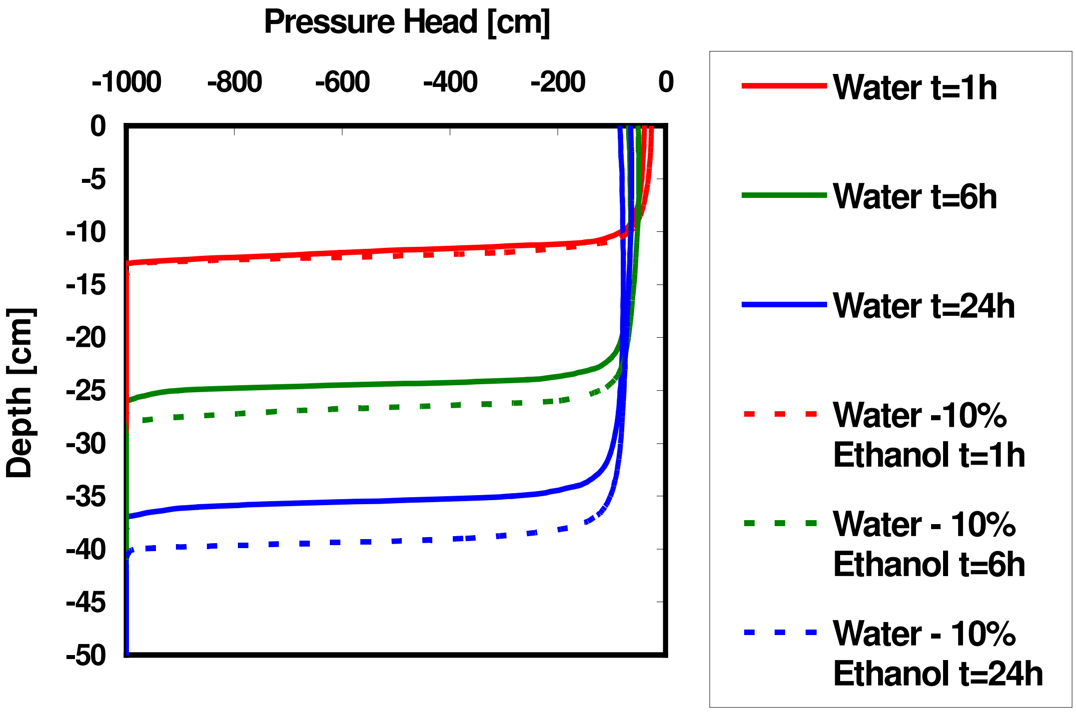

Figure 3.11. Pressure head profiles for scenario 3.

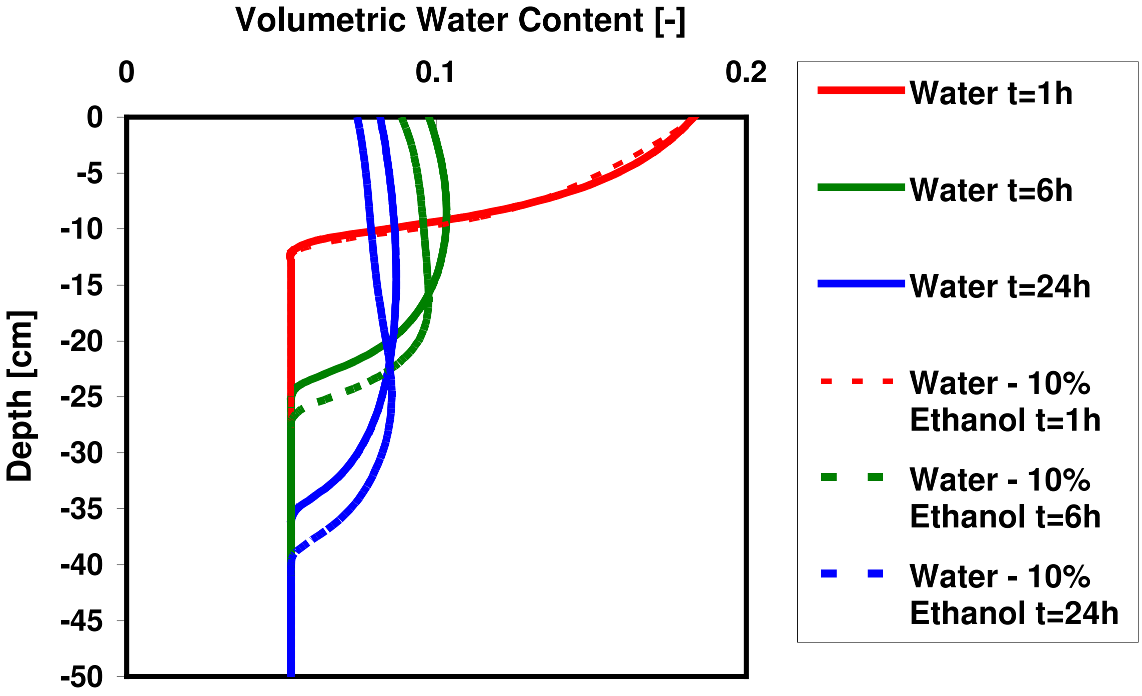

Figure 3.12. Volumetric water content profiles for scenario 3.

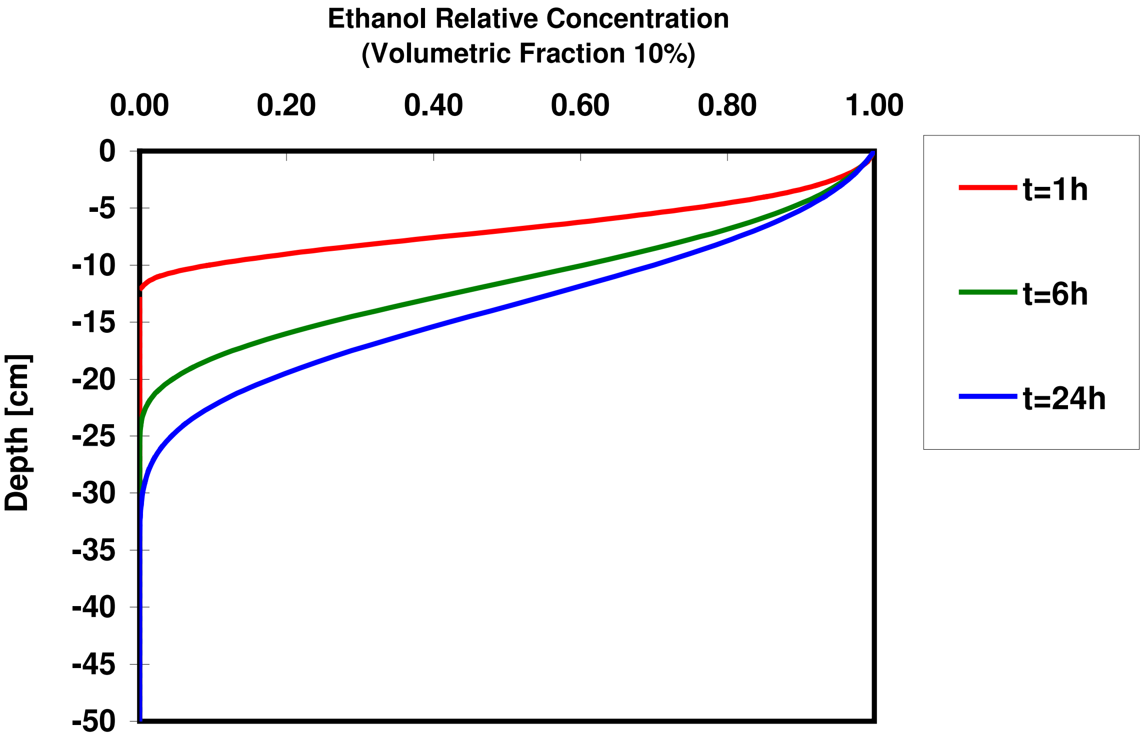

Figure 3.13. Relative ethanol concentration profiles for scenario 3.

The normalized pressure head is defined as follows:

$$h_{norm} = \frac{(h - h_{initial})}{(h_{\max} - h_{initial})} \tag{3.8}$$

where h_{max} is the maximum value of the pressure head at the time considered in the analysis and $h_{initial}$ is the pressure head at the beginning of the simulations (t = 0). The normalized volumetric water content is given by:

$$\theta_{norm} = \frac{(\theta - \theta_{initial})}{(\theta_{\max} - \theta_{initial})} \tag{3.9}$$

where θ_{max} is the volumetric water content at the specified time and $\theta_{initial}$ is the soil water content at the beginning of the simulations (t = 0).). Figure 3.14 shows the normalized profiles for pressure head, water content and concentration after 24 hours. Especially the water content profile clearly shows less retention and farther penetration as a result of applying water with ethanol to the surface.

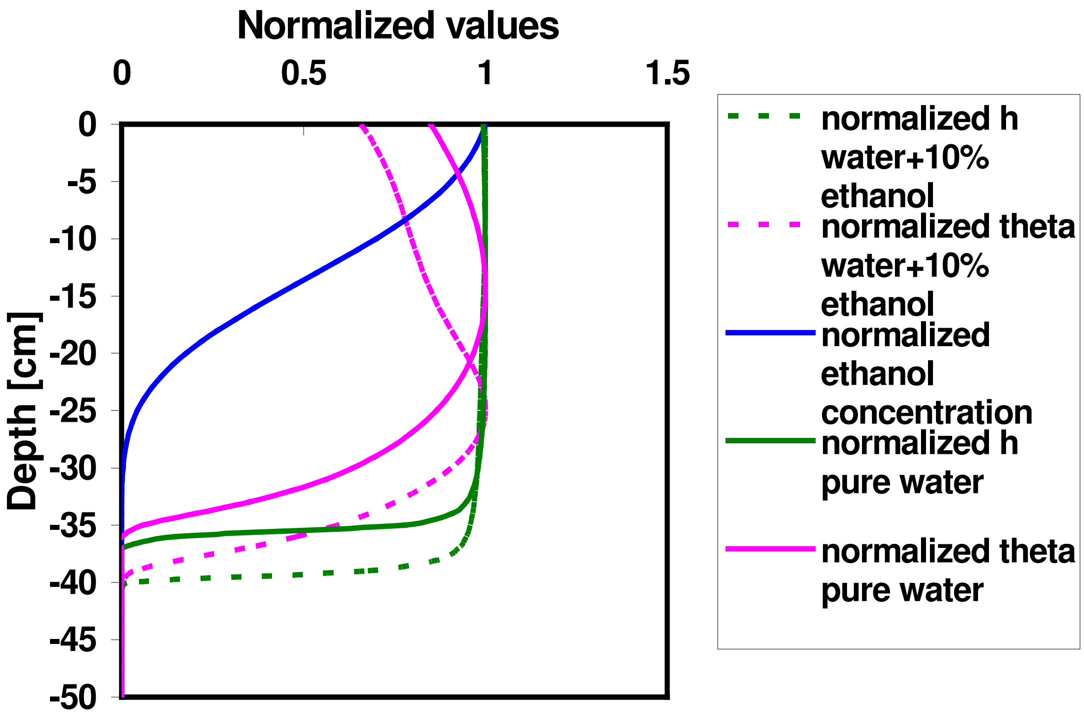

Figure 3.14. Normalized pressure head, water content, and ethanol concentration for scenario 3.

Scenario 4: Benzene Transport due to a Prescribed Infiltration Flux into a Soil with 10% Ethanol 2

The ethanol concentrations of infiltrating and initial water are the same (either 0 or 10%). We want to investigate how ethanol affects the transport of benzene as a result of the prescribed flux at the surface of this fairly coarse soil (cf. Table 3.2). All conditions are the same as for scenario 3. For the transport problem we assume a surface condition determined by the aqueous solubility of benzene (i.e., 1.78 and 2.39 g/L for 0 and 10% ethanol, respectively).

The ethanol-benzene solution is infiltrating in a soil where, as in scenario 2, the hydraulic properties have already been altered due to the resident ethanol. The soil is drier and less permeable than for the benchmark case of 0% ethanol. Coupled with the higher aqueous solubility of benzene, this translates into higher benzene concentrations near the surface and somewhat lower concentrations near the wetting front. It should be emphasized that these findings are for a single, relatively short wetting cycle. During prolonged wetting and drying cycles, the hydraulic regime may be quite different.

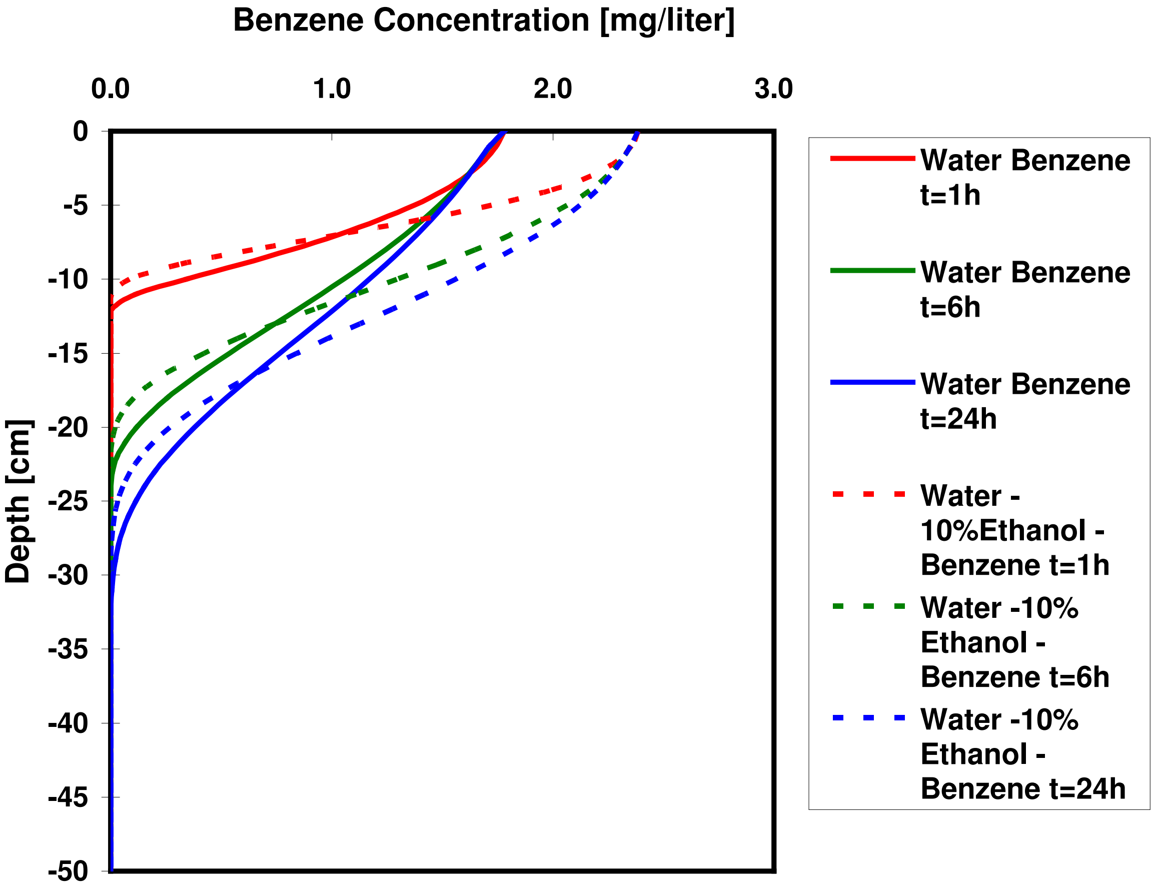

Figure 3.15. Benzene concentration profile for scenario 4.

4 AQUIFER

4.1. Introduction

Although ethanol degrades relatively rapidly under aerobic conditions, it may end up in aquifers (saturated zone of porous media) and exacerbate contamination by fuel components and other persistent contaminants. Pollution from storage tanks with ethanol or ethanol-blended fuel, which is often not readily detected, may result in gradual and extensive contamination of the subsurface environment. There also a few well-documented examples of more extensive release of pure ethanol, which may occur during production, transportation, or storage (Rice and Cannon, 1999). The presence of ethanol in aquifers may affect the development of contaminant plumes by enhancing the aqueous dissolution of organic contaminants and by reducing their degradation. The organic could be one of the many that constitute fuel mixtures, or it could be a persistent NAPL contaminant already present in the subsurface prior to the ethanol release.

We will illustrate the impact of ethanol on plume development for two contaminant scenarios that are solved analytically. The use of an analytical solution requires that the transport problem is linear with "simple" mathematical conditions and parameters. The simplifications are often reasonable since we typically do not have the detailed knowledge of soil and solute parameters as function of time or space that would necessitate a numerical solution. In the following we will show the utility of analytical solutions for a scenario where fuel leaks from a source perpendicular to the aquifer flow and for mass transfer from a pool of persistent organic contaminants parallel to the main direction of groundwater flow (i.e., at the bottom of the aquifer). Co-solubilization due to ethanol is accounted for by using an appropriate boundary condition while the impact of ethanol on degradation may also be quantified.

4.2. Dissolution and Degradation for Perpendicular Contaminant Source

4.2.1. Analytical Model

We consider plume development in a two-dimensional vertical plane of the subsurface. The two-dimensional advection-dispersion equation (ADE) for transport of a solute – either ethanol or an organic contaminant –subject to first-order degradation in a uniform porous medium is given by

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} + D_y \frac{\partial^2 C}{\partial y^2} - \lambda C \quad 0 < x < \infty \,, -\infty < y < \infty \tag{4.1}$$

where t is time [T], x and y are the longitudinal and transversal directions [L], C is the aqueous concentration of the NAPL [ML^{-3}], V is the pore-water velocity in the x-direction [LT^{-1}], λ is a first-order degradation coefficient (T^{-1}), and D_x and D_y are the longitudinal and transversal dispersion coefficients, respectively [L^{2}T^{-1}]. The solution may be used to generate breakthrough curves and one- or two-dimensional profiles of ethanol or organic contaminants. The solute is subject to transport due to ground water flow (advection) and dispersion parallel and perpendicular to the flow direction. We will ignore adsorption of the solute by the soil although linear retardation could be readily accounted for. Ethanol is not adsorbed while other hydrocarbons will be sorbed if the aquifer has an appreciable amount of organic matter. It is assumed that the organic contaminant dissolves into the aqueous phase from a rectangular area perpendicular to the flow, the inlet region, starting at time t=0. The boundary and initial conditions are given by:

$$C(x, y, 0) = 0 \quad , \quad 0 < x < \infty \, , \quad -\infty < y < \infty$$

$$C(0, y, t) = \begin{cases} C_o & -a < y < a \\ 0 & \text{otherwise} \end{cases} \quad , \quad \frac{\partial C}{\partial x}(\infty, y, t) = 0 \quad , \quad t > 0 \tag{4.2}$$

$$\frac{\partial C}{\partial y}(x, \pm\infty, t) = 0 \quad , \quad t > 0 \tag{4.3}$$

The solution of the problem is given by (Leij et al., 1991):

$$C(x, y, t) = \frac{C_o}{2} \int_0^t \frac{x}{\sqrt{4\pi D_x \tau^3}} \exp\left(-\lambda\tau - \frac{(x - v\tau)^2}{4 D_x \tau} \right) \left[\operatorname{erfc}\left(\frac{y - a}{\sqrt{4 D_y \tau}} \right) - \operatorname{erfc}\left(\frac{y + a}{\sqrt{4 D_y \tau}} \right) \right] d\tau \tag{4.4}$$

Transport and flow parameters are adapted from the well-documented study of transport in a sand aquifer at the Borden site (Mackay et al., 1986; Freyberg, 1986). A chloride plume moved for approximately 87 m during 647 days, with longitudinal and transverse dispersivities of 0.36 and 0.039 m, respectively. Based on these data, we set V=0.134 m/d, D_x =0.048 m^2/d and D_y =0.0052 m^2/d. We will simulate the movement of benzene, a carcinogenic that is an ubiquitous compound in fuel, by determining concentration contours 500 days after starting the release of the solute. The solution domain is given by 0< x<100m and -20m< y<20m; the benzene source is centered at x = y =0 and has a length of 1m (i.e., a=0.5m). First we consider the impact of ethanol on dissolution and then we will compare benzene contours with and without degradation.

4.2.2. Dissolution

It is well known that the aqueous solubility of polar organic compounds is enhanced in the presence of ethanol (Powers and Heermann, 1999). He (2002) reported enhancement values for benzene, toluene, xylene (i.e, BTX), 1,2,4-trimethylbenzene (TMB), and n-octane for dissolution from the organic phase of a mixture of the aforementioned compounds, into the aqueous phase in the presence of ethanol. Enhancement factors were determined for a wide range of ethanol concentrations. Benzene experiences the least cosolubilization in the presence of ethanol. The enhancement of its solubility in pure water was 1.65 for 150 g ethanol/L and 23.73 for 470 g ethanol/L. Assuming an aqueous solubility of benzene C_s= 1.78 g/L for pure water, this corresponds to C_s= 2.94 and 42.2 g/L for 15% and 47% ethanol mixtures.

Figure 1 shows the solute contours that were obtained if we used C_o =C_s=1.78, 2.94 and 42.2 g/L. In other studies, lower values have been selected for C_o (Powers and Heermann, 1999). The solute plume after 100 d is somewhat larger for the solubility of 2.94 than for the “conventional” C_s=1.78 g/L. If a substantial amount of ethanol is present at the source the benzene plume would be more extensive, especially the enlargement of the area of the highest concentration (>1 g/L) is evident.

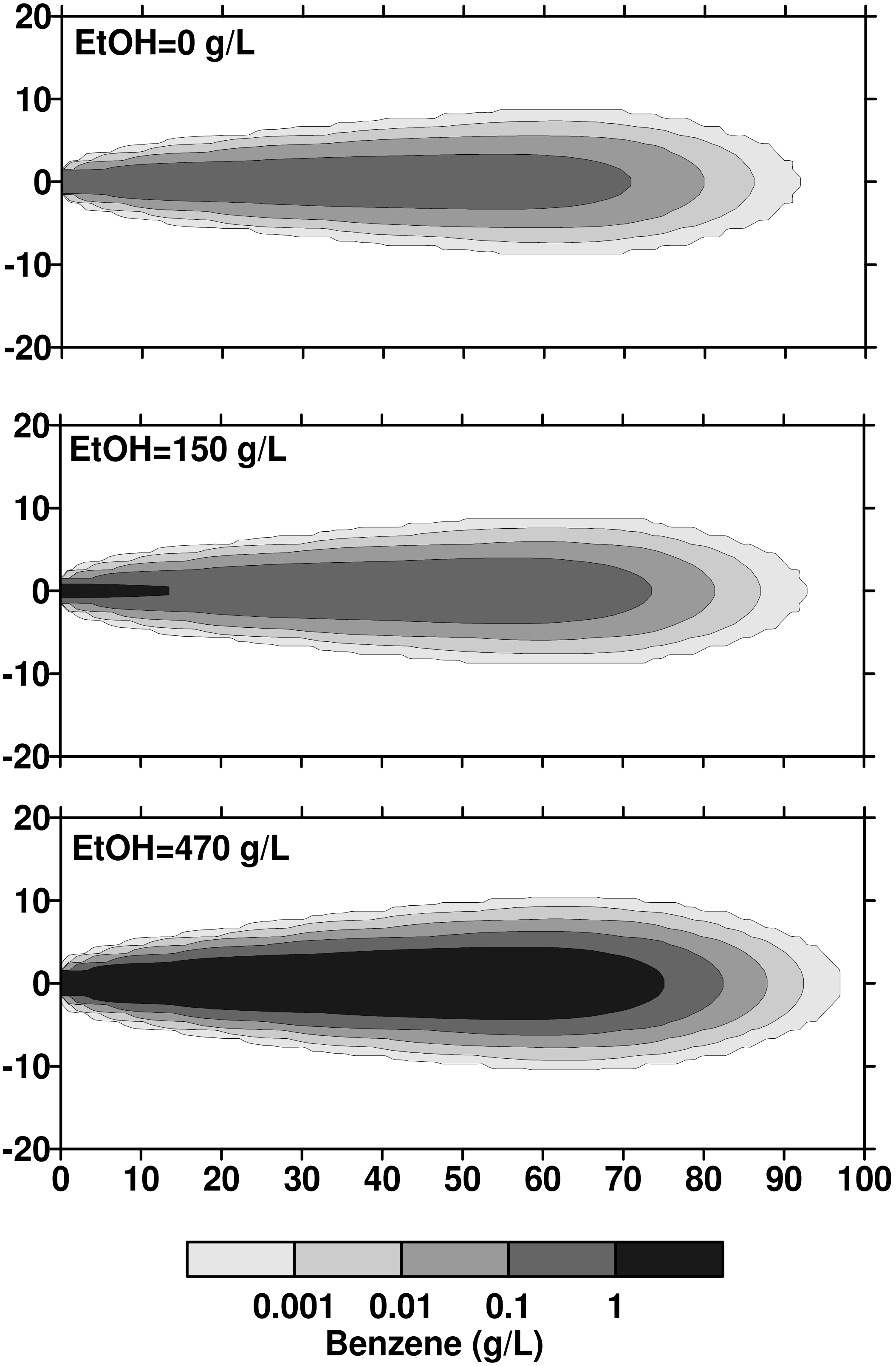

Figure 4.1. Benzene contours after 500 days during groundwater flow with V=0.134 m/d, D_x =0.048 m^2/d and D_y =0.0052 m^2/d resulting from release at a line source (x=0, -0.5<y<0.5m) with strength C_o =1.78, 2.94 and 42.2 g/L corresponding to the aqueous solubility C_s for water-ethanol mixtures with 0, 150, and 470 g ethanol/L.

4.2.3. Degradation

The previously presented analytical solution may be used to quantify the effect of first-order degradation on plume development. Both ethanol and benzene will be subject to biodegradation. Under field conditions, a conservative estimate of λ=0.014 1/d has been proposed to describe first-order degradation of ethanol (Powers and Heermann, 1999). The value is likely greater, a ten-fold increase may be expected for laboratory settings. Figure 4.2 shows the distribution of ethanol resulting from a source concentration of 150 g/L after 500 days for the same flow parameters used to generate the benzene contours in Figure 4.1. The relatively rapid decrease in ethanol with travel distance *x*, which corresponds to opportunity for degradation, can be readily inferred from Fig. 4.2.

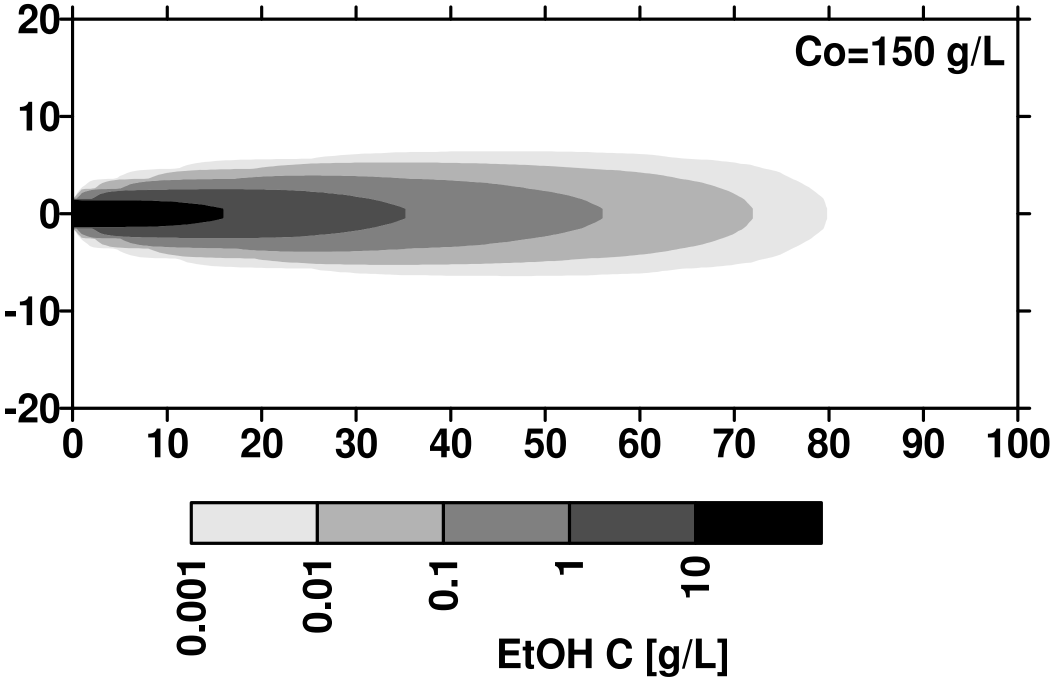

Figure 4.2. Ethanol contours after 500 days during groundwater flow with V=0.134 m/d, D_x =0.048 m^2/d, D_y =0.0052 m^2/d, and λ=0.014 1/d resulting from release at a line source (x=0, -0.5<y<0.5m) with strength C_o =150 g/L.

The degradation and decay of organic contaminants such as benzene is of considerable interest. As was reviewed in section 2.4, the presence of ethanol may hamper bioremediation and attenuation of more persistent and/or toxic contaminants in the subsurface environment. In the study of the fate and transport of benzene reported by Malcolm Pirnie, Inc. (1998), a value of $\lambda=0.0062$ 1/d was used while benzene degradation was inhibited above ethanol concentrations of 3 mg/L.

Figure 4.3 shows benzene contours for dissolution in ethanol-free water without (Fig. 4.3a, also shown in Fig. 4.1) and with (Fig. 4.3b) degradation. A comparison between the two figures shows that the degradation noticeably reduces the benzene concentration. Figure 4.3c depicts the benzene concentration for the higher solubility due to the 150 g/L ethanol concentration at the inlet without any degradation. The dashed line in the figure corresponds to an ethanol concentration of 3 mg/L. There is presumably no degradation of benzene for ethanol concentrations above this threshold. This figure clearly illustrates the double impact of ethanol, greater solubilization and reduced degradation of organic contaminants. The elevated benzene levels due to co-solubilization would potentially have benefited from biodegradation. However, in a large region of the benzene plume the ethanol level is too high to permit degradation. Several researchers have therefore speculated that the greatest negative impact of ethanol is the reduced degradation rather than the enhanced solubility of organic contaminants (Corseuil and Kulkamp, 2003; He, 2002).

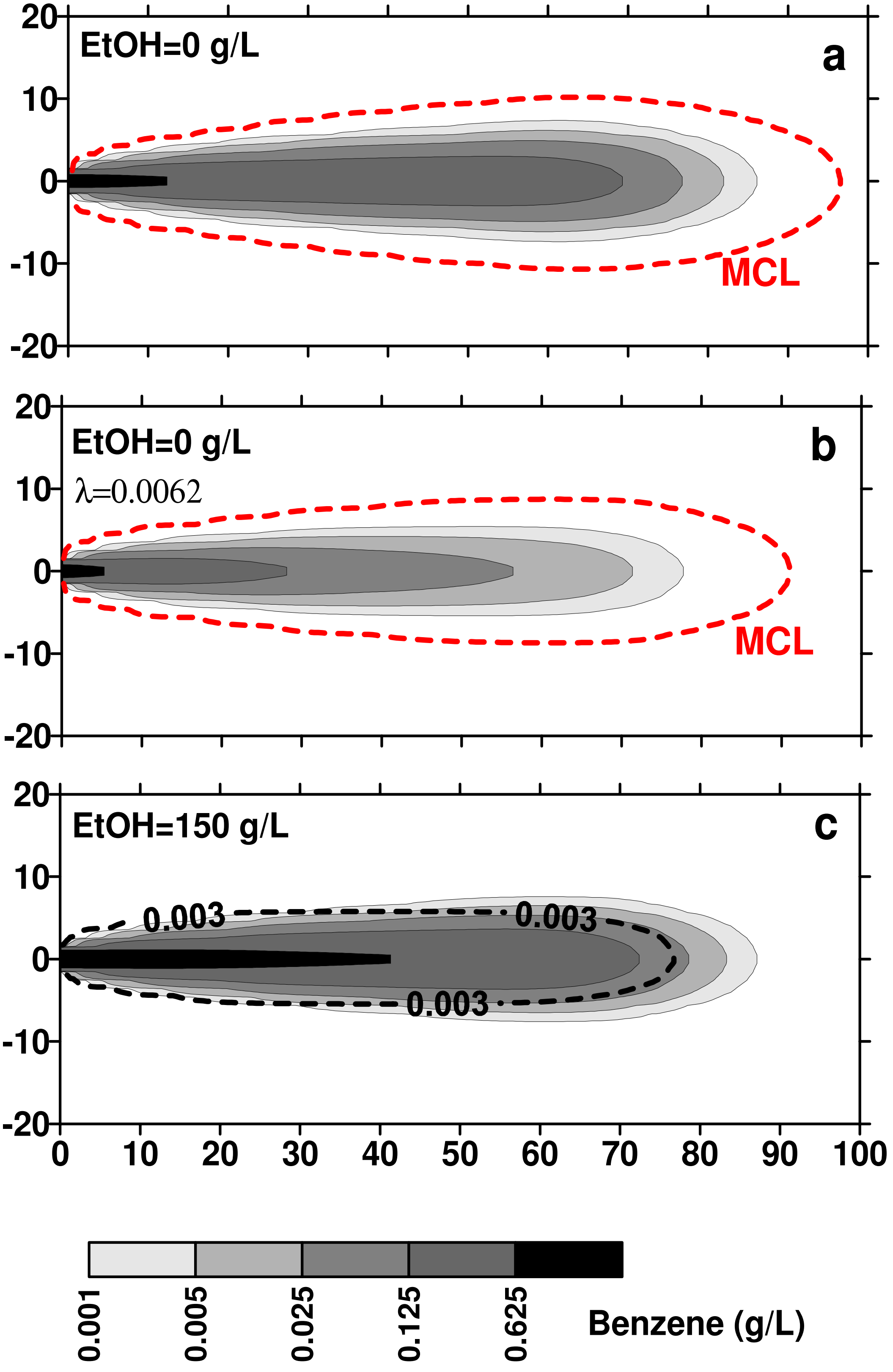

Figure 4.3. Benzene contours after 500 days during groundwater flow with V=0.134 m/d, D_x =0.048 m^2/d and D_y =0.0052 m^2/d resulting from release at a line source (x=0, -0.5<y<0.5m): a) C_o =1.78 g/L and λ_{benzene}=0 1/d (dashed line denotes maximum contaminant level of 5μg/L), b) C_o =1.78 g/L and λ_{benzene}=0.0062 1/d , and c) C_o =2.94 and λ_{benzene}=0 1/d (dashed line denotes 3 mg/L ethanol contour computed with C_o =150 g/L and λ_{ethanol}=0.014 1/d).

4.3. Mass Transfer from a Parallel Contaminant Source

There is concern that accidental release of ethanol at sites where contaminants are present in a separate nonaqueous phase, may lead to enhanced contaminant transfer into the aqueous phase. As an example, consider chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE). These are dense nonaqueous phase liquids (DNAPLs) that may reside as a pool at the bottom of an aquifer above a low-permeability layer. Mass transfer from the contaminant pool into the aqueous phase will often result in the formation of a contaminant plume in the aquifer. Contaminant transport in the aquifer may again be described by the ADE. We consider a scenario where the aqueous phase has a time-dependent ethanol concentration which results in time-dependent mass transfer from the DNAPL-pool. If we neglect degradation and retardation – although this is not necessary, the two-dimensional mathematical problem for the contaminant may be written as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} + D_y \frac{\partial^2 C}{\partial y^2} \quad -\infty < x < \infty\,,\, 0 < y < \infty \tag{4.5}$$

subject to:

$$C(x,y,0) = 0 \quad , \quad -\infty < x < \infty\,, \quad 0 < y < \infty \tag{4.6}$$

$$\frac{\partial C}{\partial x}(\pm\infty, y, t) = 0 \quad , \quad 0 < y < \infty\,, t > 0 \tag{4.7}$$

$$\frac{\partial C}{\partial y}(x,0^+,t) = \begin{cases} -\Gamma(t) & -x_1 < x < x_2 \\ 0 & \text{otherwise} \end{cases} \quad , \quad \frac{\partial C}{\partial y}(x,\infty,t) = 0 \quad , \quad -\infty < x < \infty\,, t > 0 \tag{4.8}$$

where Γ(*t*) denotes a time-dependent transverse solute gradient at the interface of the organic phase of the pool and the aqueous phase of the porous medium. This condition is rooted in boundary layer theory involving heat or mass transfer during the development of a laminar velocity profile for fluid flow above a flat plate (Schlichting, 1979; Chrysikopoulos et al., 1994). We will use a gradient that is averaged along the (linear) pool in the flow direction. This gradient may be used to quantify a dissolution flux that will vary with time depending on the ethanol concentration in the aquifer. The solution of the problem, which may be derived with Green's functions (cf. Leij et al., 2000), is given by:

$$C(x,y,t) = \int_0^t \frac{\Gamma(t-\tau)}{\sqrt{4\pi\tau / D_y}} \exp\left(-\frac{y^2}{4D_y\tau}\right)\left[\operatorname{erfc}\left(\frac{x - x_2 - V\tau}{\sqrt{4D_x\tau}}\right) - \operatorname{erfc}\left(\frac{x - x_1 - V\tau}{\sqrt{4D_x\tau}}\right)\right] d\tau \tag{4.9}$$

The same transport and flow parameters will be used as before. For illustrative purposes, the solute will be assumed to be TCE. The aqueous solubility C_s=1.10 g/L for TCE (Schwille, 1988). Figure 4.4 illustrates the TCE contours due to mass transfer from a pool located between *x*=5 and 10m at the bottom of the domain (*y*=0) after 100 and 500 days. The gradient Γ is either constant or exhibits an exponential decrease, both the constant and the exponential rate parameter are selected arbitrarily but may be readily modified to account co-solubilization due to ethanol. Figures 4.4a and b illustrate the evolution of the contours without ethanol, the steady-state distribution is shown for *t*=500d. Figures 4.4c and d depict the impact of a dissolution flux (gradient) that decreases with time. Especially at *t*=500d there is a strong contrast in TCE concentration near the pool (Fig. 4.4b versus 4.4d).

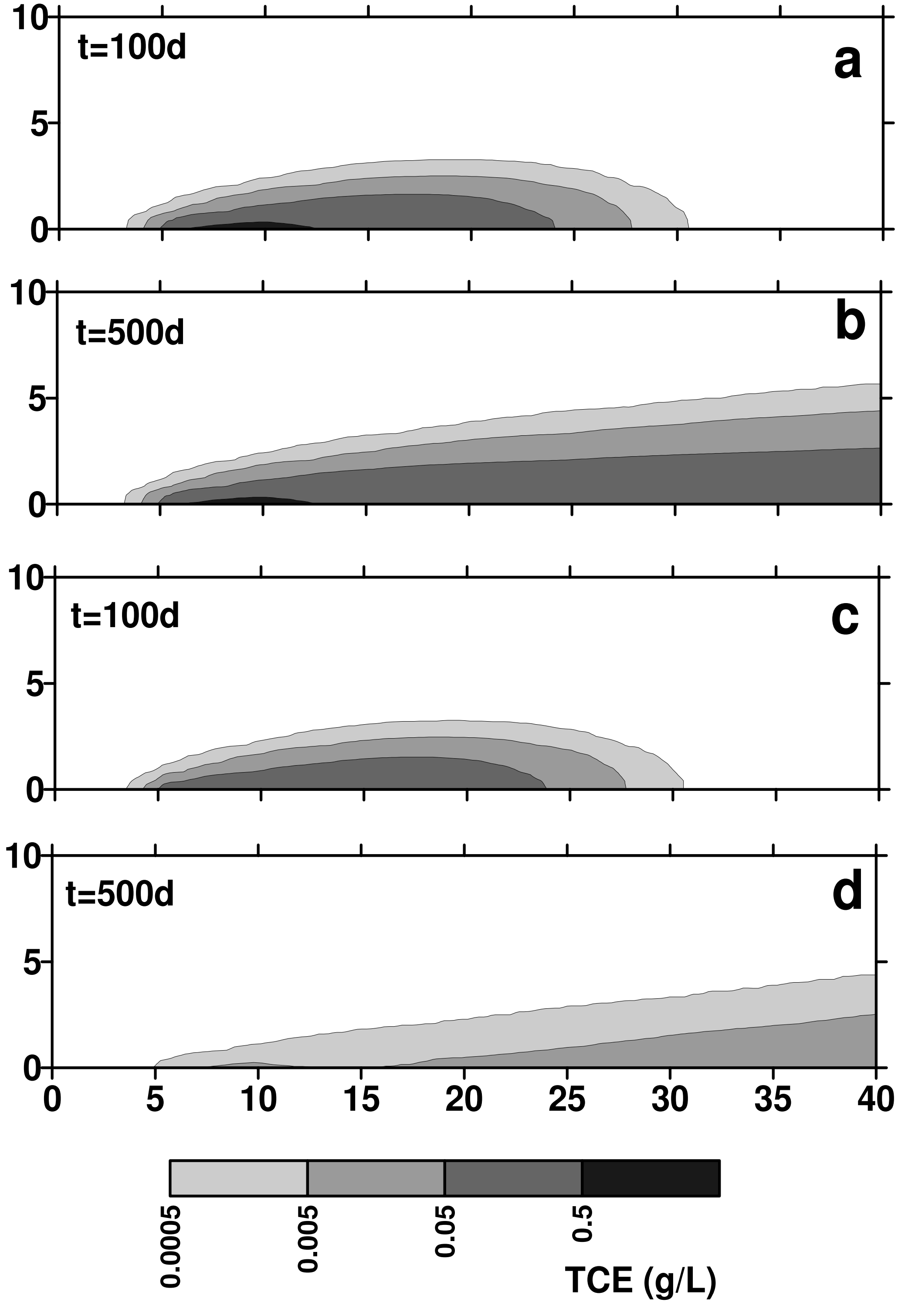

Figure 4.4. TCE contours 100 or 500 days after the start of dissolution from a linear pool ($5<x<10$m, $y=0$) during groundwater flow with $V=0.134$ m/d, $D_x = 0.048$ m^2/d and $D_y = 0.0052$ m^2/d with a constant or time-dependent gradient Γ [g L^{-1} cm^{-1}]: a) $\Gamma = 2$ after 100d, b) $\Gamma = 2$ after 500d, c) $\Gamma = 2 \exp(-0.01\ t)$ after 100d, and d) $\Gamma = 2 \exp(-0.01\ t)$ after 500d.

5. CONCLUSIONS AND IMPLEMENTATION

The purpose of the present study was to quantify the impact of the release of a potential new diesel fuel on the movement and fate of contaminants in the aqueous phase of the vadose and saturated zone of the subsurface.

Existing software has been modified to model subsurface flow in the vadose zone, the model accounts for the effect of surfactants (ethanol and other fuel additives) on flow properties, and the dissolution of diesel components (benzene in this case)

Two scenarios were simulated: ponded infiltration in an ethanol-free soil of water with 10% ethanol content and pure ethanol and infiltration with prescribed flux of water with 10% ethanol content and pure ethanol in an ethanol-free soil. Both scenarios were compared with the reference case when there is no ethanol to lower the surface tension.

The results for the first scenario showed that ethanol reduces infiltration. The soil moisture front travels more slowly when ethanol is present, because the porous medium "sorbs" less water due to the reduced surface tension. For infiltration with a prescribed flux, water and dissolved substances will penetrate farther because less water is retained per volume of porous medium.

For both scenarios we simulated water flow and benzene transport into the soil, in which the aqueous phase contained 0% or 10% ethanol. The infiltrating water contained also 0% or 10% ethanol and benzene. Higher benzene concentrations were observed in both scenarios when ethanol was present. The ethanol-benzene solution was infiltrating in a soil where the hydraulic properties were altered due to the resident ethanol. The soil was drier and less permeable than for the benchmark case of 0% ethanol. Coupled with the enhanced solubility, this resulted in higher benzene concentrations near the surface and somewhat lower concentrations near the wetting front.

The impact of ethanol on dissolution and degradation of fuel compounds and pre-existing organic contaminants in the groundwater was analyzed using a model based on analytical solutions. The analysis confirms the findings reported in the literature. Ethanol enhances the solubility of other contaminants and hampers their biodegradation rates. As a consequence the contaminants are more persistent in groundwater and the extent of the contamination is more significant than when ethanol is not present.

The results of this study provide a preliminary analysis of the impact of ethanol-blended diesel (and fuels in general) on the subsurface water. It must be pointed out that the models used to simulate the scenarios in both vadose and saturated zone are based on simplifying assumptions. A main assumption in the simulation of benzene transport in the unsaturated zone was that the ethanol concentration is uniform with time and position. The impact of ethanol on benzene degradation was not accounted for. Finally, no experimental data were available to predict the impact of ethanol on surface tension and viscosity on the soil hydraulic properties. These simplifying assumptions were justified because of the scope of the present project involving sensitivity analyses for both the unsaturated (vadose) and unsaturated (aquifer) zone. However, they should be scrutinized if we want to correctly gage the impact of ethanol.

In the future, work should focus on the vadose zone and its main objective should be the improvement of the simulation of flow and transport to better assess the impact of ethanol. The following tasks are envisioned:

(i) Determine the water retention curve and saturated hydraulic conductivity in the laboratory for typical California soils for pristine and gasoline-contaminated water. Measure viscosity and surface tension for aqueous solutions equilibrated with different amounts of regular and ethanol blended gasoline. Examine the transient nature of soil hydraulic properties.

(ii) Analyze the biodegradation of ethanol and other contaminants under different redox and nutrient conditions. Formulate a mathematical model for contaminant degradation as a function of ethanol level.

(iii) Develop a numerical code to model the flow of water and the transport of ethanol and gasoline components (benzene) in the vadose zone. The model will employ a staggered solution where the first step involves an iterative simulation of ethanol transport and unsaturated water flow, and the second step involves the simulation of (organic) contaminant transport.

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