Simulating natural attenuation and ethanol-induced benzene persistence in gasoline-contaminated aquifers

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Abstract A multicomponent reactive transport model (BIONAPL/3D) is used to simulate the effect of ethanol on the persistence of benzene in gasoline-contaminated aquifers. The model is used to compare the travel distance of benzene plumes dissolving from equivalent gasoline and 10% ethanol-gasoline (gasohol) sources. Under some conditions, the presence of ethanol increases the migration distance of the benzene plume by a factor of 3 relative to an ethanol-free spill. Benzene becomes more persistent in the presence of ethanol because ethanol preferentially consumes oxygen, which reduces the biodegradation rate of benzene. The impact is limited, however, because the non-retarded ethanol eventually advances beyond the retarded benzene plume, exposing benzene to higher background oxygen concentrations.

Key words biodegradation; BTEX; ethanol; gasohol; gasoline; modelling; reactive transport

INTRODUCTION

Concerns about groundwater contamination by MTBE-enhanced gasoline have led to its proposed phase-out in California (USA) (and elsewhere) and to its proposed replacement by ethanol as an alternate fuel oxygenate. Since aqueous ethanol is relatively non-toxic, concern about ethanol incorporation into gasoline is focused on potentially adverse impacts on the mobility and persistence of other toxic chemicals in gasoline (Powers et al., 2001).

Two main issues emerge: (a) ethanol at high concentration in water can enhance the solubility of mobile, toxic aromatic hydrocarbons (BTEX) from gasoline, and (b) ethanol may decrease the rate of BTEX biodegradation in groundwater mainly because ethanol may have preferential access to electron acceptors, particularly oxygen. In this paper, we address concern (b) by simulating the dissolution and reactive transport of multiple organic components from a gasoline and gasohol source.

NUMERICAL MODEL

In this study, we use BIONAPL/3D, a finite element numerical model that includes multi-component dissolution from a residual non-aqueous phase liquid (NAPL),
advective-dispersive transport within a porous medium, and electron acceptor-limited competitive biodegradation and microbial growth (Molson et al., 2002).

The model solves a reactive transport equation for each of the gasoline components, as well as for the electron acceptors and microbe populations. The governing equation for mass transport of several gasoline components can be written as:

$$\frac{\partial c^a}{\partial t} + \frac{\partial}{\partial x}(D^a \frac{\partial c^a}{\partial x}) = \nu \frac{\partial c^a}{\partial x} - \lambda^a c^a$$  

(1)

where $c^a$ is the aqueous phase organic concentration of component $a$ (mg l$^{-1}$), $R^a$ is the retardation, $D^a$ is the dispersion coefficient ($m^2 s^{-1}$), $v$ is the groundwater velocity ($m s^{-1}$), $x$ is the spatial dimension ($m$) and $t$ is time ($s$). The nonlinear biodegradation decay term $\lambda^a (s^{-1})$ follows a standard dual-Monod formulation, and an equivalent reactive transport equation is solved for each electron acceptor—in this case only oxygen (see Frind et al., 1989). An equilibrium mixing cell algorithm based on Raoult's law is used to simulate dissolution of the gasoline source (a kinetic form is also available).

In this application, we assume the source is immobile (at low saturation), and we neglect density, substrate inhibition and interfacial tension changes. Full details of the numerical approach can be found in Molson et al. (2001) and Frind et al. (1999).

CONCEPTUAL MODEL

The physical hydrogeologic parameters chosen for the simulations are similar to those of the Borden aquifer, assuming homogeneous, isotropic conditions (Fig. 1).

![Conceptual model](image)

Fig. 1 Conceptual model for the gasoline/gasohol simulations. The components are dissolving at their equilibrium solubility ($C_s$) from recharge ($q_0$) through the source.

The conceptual model assumes ethanol is degraded much faster than BTEX when both are present with oxygen, as shown by Corseuil et al. (1998) and (for methanol) by Hubbard et al. (1994). The hypothesis is that most of the oxygen will be utilized by
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ethanol degraders and not by BTEX degraders, thus slowing the biodegradation of benzene when ethanol is present in the groundwater. The model captures this aspect by assigning a rate of ethanol biodegradation five times higher than the benzene rate. Although ethanol itself may rapidly degrade, its anaerobic biodegradation products (organic acids, methane) will likely persist. Here, "ethanol" therefore represents the complete oxygen demand of the alcohol itself, as well as the oxygen-consuming byproducts. In addition to ethanol, we are considering a gasoline mixture including benzene, TEX, and a relatively less soluble remaining fraction.

Initial mole fractions for a standard PS-6 gasoline are used. The gasohol simulations assume the same fractions, but include 10% ethanol. The component concentrations ($C_s$) emanating from the residual source and entering the aquifer are provided in Fig. 2. All transport and degradation parameters are based on literature sources (Wiedemeier et al., 1999; Bekins et al., 1998).

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Fig. 2 Source concentrations ($C_s$) from the dissolving gasoline/gasohol mixtures.

SIMULATION RESULTS

A sample two-dimensional simulation using an ethanol-free gasoline source is provided in Fig. 3. Benzene dissolves from the source within 10 years and the 10 ppb drinking water limit reaches 220 m after 20 years. The benzene plume is completely degraded by 25 years. TEX continues to dissolve from the source because these compounds are more abundant and less soluble. A "shadow" of depressed oxygen concentrations precedes the benzene plume, since benzene and the other oxygen-consuming gasoline components move more slowly than the oxygen-depleted groundwater.

Figure 4 shows the TEX, benzene, ethanol and oxygen plumes from an otherwise equivalent gasohol source. The ethanol component is assumed to dissolve at the source within 1 pore volume (see Fig. 2), and migrates rapidly because it is non-retarded (for benzene, $R = 1.1$). Because ethanol preferentially consumes the oxygen, the benzene plume becomes more persistent and migrates further relative to the gasoline-source benzene plume (Fig. 3). The 10 ppb benzene concentration limit now reaches 380 m after 20 years. Oxygen continues to disperse behind the ethanol plume where it is depleted by the trailing benzene, TEX and remaining compounds. Once ethanol has advanced significantly ahead of the benzene plume, benzene can continue to degrade at more rapid rates, although still under oxygen-limiting conditions.
Fig. 3 Simulated 20-year plumes of TEX, benzene and oxygen from a gasoline source. Oxygen is only shown where it is depleted below the background concentration of 3.5 mg l\(^{-1}\). Note vertical exaggeration of 7x.

Fig. 4 Simulated 20-year plumes of TEX, benzene, ethanol and oxygen from a 10% ethanol-gasoline source. The benzene plume (and to a lesser extent the TEX plume) is now more persistent relative to Fig. 3.

CONCLUSIONS

In all the scenarios considered, the extension of the benzene plume is greater when gasohol is spilled as opposed to ethanol-free gasoline. The greatest extensions, up to 150% after 40 years, occur when background oxygen levels are low, and when the benzene migration rate is close to the rate of groundwater flow (i.e. under low retardation). Under low oxygen conditions, both benzene and ethanol remain more persistent and are therefore competing for the available oxygen over a longer time. Similarly, when benzene retardation is low, benzene remains within the oxygen-
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Consuming ethanol plume for a longer period. Aquifers rich in organic matter are therefore likely to be more protected with respect to ethanol-induced benzene persistence.

Longer-term spill scenarios could produce even greater impacts on the extent of the benzene plumes. The model includes many assumptions, and documented field data at real gasohol spill sites are required to confirm the simulated behaviour.

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REFERENCES


