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Modeling LNAPL Transport in the Vadose Zone[1]

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Abstract

Groundwater contamination is an ever growing problem. In particular, problems associated with light non-aqueous phase liquids (LNAPLs) such as gasoline, diesel fuel, and jet fuels are becoming more common. This paper presents the development and application of an analytical model for predicting LNAPL concentrations at the water table.

Based on the volume of the spill, the model has two parts: a pancake model for predicting the behavior of the LNAPL if the spill volume is large enough to reach the water table; and an advection/dispersion model that assumes that the LNAPL does not reach the water table as a slug, but creates a contaminated soil layer from which soluble LNAPL components can be mobilized and transported vertically downward while undergoing advection, dispersion, sorption, volatilization, and biodegradation.

Maximum and current concentrations are calculated at the water table for the pancake model using a solubility-limited approach, and an analytical expression derived using Laplace transforms for the advection/dispersion model.

The behavior and sensitivity of the model is evaluated for a hypothetical site using an LNAPL having ten components that represent a cross section of organic compounds commonly found in spills including BTEX, branch alkanes, and polynuclear aromatic hydrocarbons. Results of the study indicate that the most important LNAPL group is the BTEX compounds, and that, of these, benzene would have the largest maximum concentration at the water table because of its relatively long biodegradation half-life. Other parameters of importance include total precipitation, depth to the water table, and the fraction of organic carbon in the soil.

Introduction

Following a spill, LNAPLs follow a path that starts

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with infiltration into the unsaturated zone. The LNAPL's fate depends on dissolution, sorption, dispersion, volatilization, and biodegradation (Lyman et al. 1992).

If the volume of LNAPL is small, it may not reach the water table. Instead, a contaminated layer is formed in the vadose zone. The concentration of LNAPL in this layer is equal to the residual oil-filled porosity of the soil. With time, the soluble components are dissolved by infiltrating precipitation and are transported to the water table by mobile pore water. While in transport, the components may degrade and be retarded. If there is sufficient volume to reach the water table, an LNAPL pancake forms on the water table. In time, the soluble components mix with groundwater leaving behind the less soluble components (weathering).

Many models have been proposed to estimate LNAPL concentrations in unsaturated groundwater systems (Abriola 1989). These models include sharp interface models, models that include capillarity, and models that consider interphase mass transfer. This study adopts the simplest of these, the sharp-interface model (El-Kadi 1992).

Pancake Model

After entering the soil, the LNAPL moves downwards. Sorption is negligible because the soil is water-wetted (Reible et al. 1990). If sufficient volume is available, the LNAPL can reach the water table. If the penetration distance, H, given by the relation:

$$H = \frac{VOL}{\pi \, R_0^2 \, \phi_{r0}} \tag{1}$$

(where VOL is the spill volume, R_0 is its radius, and ϕ_{r0} is the residual oil fraction of the soil), is greater than the depth of the water table, an LNAPL pancake will form. Soluble components will dissolve and move into the saturated zone (Fried et al. 1979), leaving behind a weathered organic. Dissolution is assumed to be instantaneous. The dissolved concentration is equal to the product of the component's mole fraction, M_i, and solubility (Geller and Hunt 1993).

Advection/Dispersion Model

If the spill volume is insufficient to reach the water table, a contaminated layer having a thickness H is formed. With time, the soluble components are dissolved by infiltrating water and transported to the water table. While in transport, the components may undergo dispersion, volatilization, sorption, and biodegradation. I.e.,

$$\frac{\partial C}{\partial t} = \frac{D}{R}\frac{\partial^2 C}{\partial z^2} - \frac{V}{R}\frac{\partial C}{\partial z} - \lambda C \tag{2}$$

where C is concentration, D is the dispersion coefficient, t is time, V is the volumetric water flux, and z is depth (Jury et al. 1983; Jury et al 1990).

R in Equation 2 is retardation given by:

$$R = \rho_b K_d + \Phi_w + aK_h \tag{3}$$

where a is the air-filled porosity, K_h is Henry's constant, K_d is the distribution coefficient, ρ_b is bulk density, and Φ_w is the water-filled porosity (Hern and Melancon 1987). Biological degradation is represented by a first-order rate constant, λ (ln(2)/half-life).

Equation 2 is subject to the following constraints: as z goes to infinity, the concentration goes to zero; the vadose zone is initially clean; and the contaminated layer acts like a unit step function source in time (Hildebrand 1976). The initial concentration at z=0 is given as the product of the component's mole fraction and solubility. The duration of the source is given by:

$$\Delta t = \frac{VOL\ \rho\ X_j}{I_w\ \pi\ R_0^2\ \phi_{ro}\ SOL} \tag{4}$$

where I_w is the infiltration rate, SOL is solubility, X_j is mass fraction, and ρ is the density of the LNAPL.

Equation 2 is solved with Laplace transforms to give:

$$\frac{C}{C_0} = \frac{e^{\frac{VZ}{2D}}}{2}\ (e^{-\sqrt{\frac{Z^2}{D}(\frac{V^2}{4D} + \lambda)}}\ erfc(\frac{1}{2}\sqrt{\frac{RZ^2}{Dt}} - \sqrt{(\frac{V^2}{4DR} + \frac{\lambda}{R})\, t}\ ) \tag{5}$$

$$+\ e^{\sqrt{\frac{Z^2}{D}(\frac{V^2}{4D} + \lambda)}}\ erfc(\frac{1}{2}\sqrt{\frac{RZ^2}{Dt}} + \sqrt{(\frac{V^2}{4DR} + \frac{\lambda}{R})\, t}\ )\ )$$

$$-\ \frac{e^{\frac{VZ}{2D}}}{2}\ H(t - \Delta t)\ \ (e^{-\sqrt{\frac{Z^2}{D}(\frac{V^2}{4D} + \lambda)}}\ X$$

$$erfc(\frac{1}{2}\sqrt{\frac{RZ^2}{D(t - \Delta t)}} - \sqrt{(\frac{V^2}{4DR} + \frac{\lambda}{R})\,(t - \Delta t)}\ )$$

$$+\ e^{\sqrt{\frac{Z^2}{D}(\frac{V^2}{4D} + \lambda)}} erfc(\frac{1}{2}\sqrt{\frac{RZ^2}{D(t - \Delta t)}} + \sqrt{(\frac{V^2}{4DR} + \frac{\lambda}{R})\,(t - \Delta t)}\ )$$

where H is the Heaviside function and erfc is the complementary error function (Hildebrand 1976).

Case and Sensitivity Studies

For the case study, an LNAPL having ten components was simulated. The components include BTEX (benzene, toluene, ethylbenzene, and m-xylene); branch alkanes (n-octane and n-hexane); polynuclear aromatic hydrocarbons (1-ethylnapthalene and acenapthylene); and other hydrocarbons (cyclohexane and biphenyl). Calculations were done to determine maximum and current concentrations at the water table. Physical parameters of BTEX and the unsaturated zone are given in Tables 1 and 2, respectively.

Table 1. Physical Parameters for the BTEX Components in the Synthetic LNAPL

Component	Benzene	Toluene	Ethylbenzene	m-Xylene
X_j	0.03	0.05	0.02	0.07
M_i	0.0359	0.0507	0.0176	0.616
SOL_i (ml/g)	0.00178	0.000537	0.000176	0.000162
K_d (ml/g)	0.62	1.1	2.0	2.1
λ (1/d)	0.000949	0.2475	0.003039	0.02475
K_h	0.2199	0.2735	0.2698	0.2861
D (ft^2/d)	0.00744	0.006645	0.006320	0.006324

Table 2. Unsaturated Zone Parameters for Study

Parameter	Value	Range
Rainfall (in/y)	38.39	20 to 90
Water table depth (ft)	25	4 to 180
Total porosity	0.3	not varied
Air-filled porosity	0.05	not varied
Residual oil-filled porosity	0.1	not varied
Water-filled porosity	0.15	not varied
Maximum oil saturation	0.8	not varied
Radius of spill (ft)	25	not varied
Hydraulic conductivity (cm/s)	1.0×10^{-5}	1.0×10^{-7} to 1.0×10^{-3}

Figure 1 shows the maximum concentration at the water table as a function of spill volume for BTEX for a spill that occurred 1,000 days ago. The model switches from the advection/dispersion branch to the pancake branch at a volume of about 5,000 ft^3. For volumes less than 5,000 ft^3, benzene has the largest maximum concentration. This behavior occurs because benzene has the longest biodegradation half-life.

If the time since the spill is less than the time to reach the maximum concentration, the concentrations will be less than the maxima. For example, if the time is decreased to 100 days, the concentrations are all less than the maxima, and the concentrations at the water table are equal to 0.0 for volumes greater than 5,000 ft^3 (Figure 2). While the volume of LNAPL spilled is sufficient to reach the water table, insufficient time has passed for it to reach the capillary fringe.

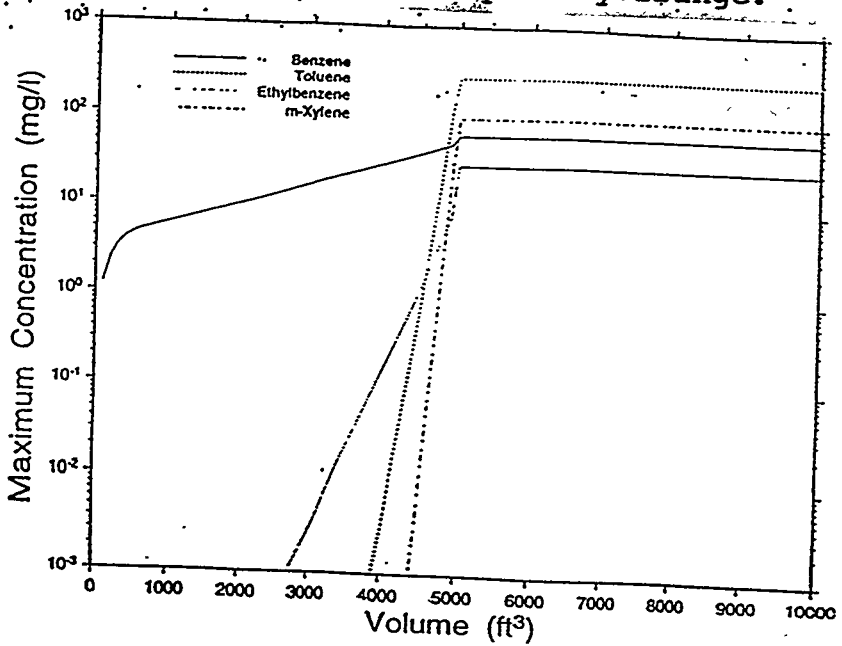

Figure 1. Maximum BTEX concentration at the water table as a function of spill volume

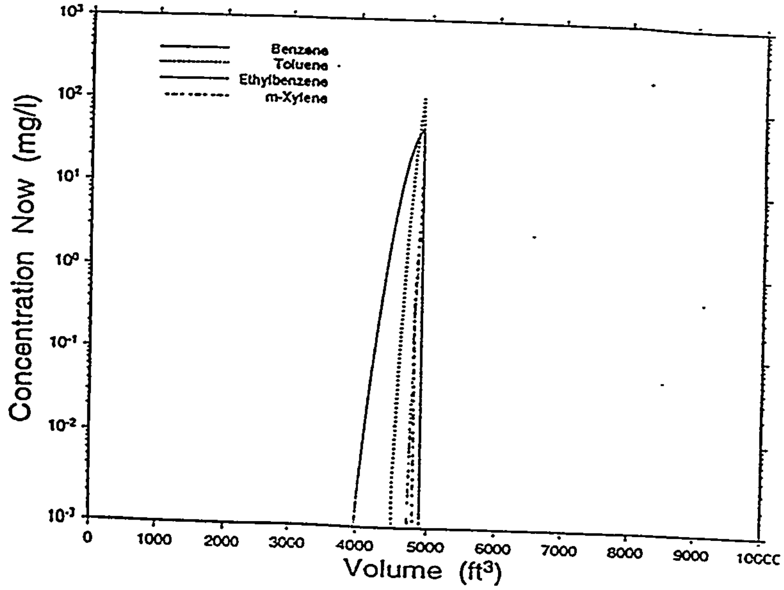

Figure 2. BTEX concentration after 100 days

A sensitivity study (Table 2) was also performed using benzene, the component that had the greatest maximum concentration at the water table. This study indicated the importance of total precipitation, depth of the water table, biodegradation half-life, and the fraction of organic carbon present. Large maximum concentrations were produced by more precipitation, shallow water tables, long biodegradation half-lifes, and small fractions of organic carbon.

SUMMARY

This paper presented the development of an analytical model for predicting concentrations of LNAPL components at the water table. Based on the volume of the spill, the model has two parts: a pancake model, and an advection/dispersion model. Following development of the model, the results of a case and sensitivity study were discussed for a ten-component LNAPL. These studies indicated the behavior of the model and the importance of total precipitation, depth of the water table, biodegradation half-life of the LNAPL component, and the fraction of organic carbon present in the soil.

Because of its simplicity, the model is recommended for quick, scoping calculations.

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