

Modeling Thermal Remediation of Mixtures of Volatile and Nonvolatile Organic Compounds

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Summary. A three-dimensional finite difference model for three-phase (water-gas-nonaqueous phase liquid) flow and transport with energy transport and fully temperature dependent fluid properties and interphase partitioning has been developed and applied to examine the dynamics of removal of mixtures of volatile and nonvolatile organic compounds by steam flushing. The predictions show good agreement with laboratory experiments, and confirms the challenges in application of steam flushing to remediation of mixtures of volatile and nonvolatile organics.

1 INTRODUCTION

Hazardous organic chemicals often exist in the subsurface as mixtures of volatile, semivolatile, and nonvolatile compounds. Several laboratory, field, and modeling studies have shown the promise of thermal remediation methods, such as steam flushing, for the removal of volatile organics. As the volatility of the organic decreases the potential rates of removal decrease. Compounds such as DDT and a number of polyaromatic hydrocarbons which are solid at ambient temperature, are often dissolved in dense nonaqueous phase liquids (DNAPL), and comprise a fraction of the DNAPL that is essentially nonvolatile at typical steam flushing temperatures. Therefore, these nonvolatile compounds, can only be removed in any significant amount by hydraulic displacement of the DNAPL. Many nonvolatiles have melting points such that they are liquid at steam flushing temperatures, making hydraulic displacement feasible even after stripping of the volatiles. However, steam stripping of the volatiles decreases the DNAPL viscosity, reducing the potential hydraulic displacement rates. Downward movement of the melted nonvolatiles into capillary barriers can still be of concern, due to desaturation of the capillary barriers from water vaporization. The presence of the nonvolatile in the DNAPL also produces significant tailing in the removal of the volatiles, as their effective vapor pressures and volatilization rates decrease with preferential removal from the DNAPL. This effect results in the expenditure of larger amounts of energy for steam generation and longer times to reach remediation goals for the volatile organic than if the DNAPL was composed only of volatile organics. The fate of the remaining nonvolatile DNAPL must also be considered as removal of this fraction would be expected to be limited.

2 THEORY

2.1 Equations of Multiphase Flow and Transport

The model developed includes the three-phase (gas, water, organic) flow and transport of energy and an arbitrary number of species with equilibrium interphase mass transfer. Sleep and Sykes¹ gave the species molar balance equation describing the movement of species α in fluid phase β as:

$$\sum_{\beta=1}^3 \left\{ \frac{\partial}{\partial t} [\rho_{\beta} x_{\alpha\beta} (\phi S_{\beta} + K_{\alpha\beta,d} \rho_b)] + \nabla \cdot [\rho_{\beta} x_{\alpha\beta} \mathbf{q}_{\beta}] + \nabla \cdot [\phi S_{\beta} \mathbf{J}_{\alpha\beta}^D] - r_{\alpha\beta} - \Gamma_{\alpha\beta} \right\} = 0 \quad (1)$$

where ρ_{β} is molar phase density (n/L^3), $x_{\alpha\beta}$ is species α mole fraction in phase β , ϕ is porosity, S_{β} is phase saturation, $K_{\alpha\beta,d}$ is the linear sorption coefficient for species α in phase β and ρ_b is the bulk mass density of the soil phase (M/L^3). \mathbf{q}_{β} is the molar-averaged Darcy velocity vector for phase β (L/T), $\mathbf{J}_{\alpha\beta}^D$ is the dispersive molar flux vector for species α relative to the other molar-averaged velocity ($n/L^2 T$), $r_{\alpha\beta}$ represents interphase transfer of species α to or from phase β ($n/L^3 T$), and $\Gamma_{\alpha\beta}$ represents sources and sinks of species α to or from phase β ($n/L^3 T$).

The molar-averaged Darcy velocity is given by

$$\mathbf{q}_{\beta} = -\frac{\mathbf{k} k_{r\beta}}{\mu_{\beta}} (\nabla p_{\beta} + \gamma_{\beta} \mathbf{g} \nabla z) \quad (2)$$

where \mathbf{k} is the intrinsic permeability tensor (L^2), $k_{r\beta}$ is the relative permeability, μ_{β} is the phase viscosity (M/LT), p_{β} is the phase pressure ($M/L T^2$), γ_{β} is the mass density of phase β (M/L^3), \mathbf{g} is gravitational acceleration constant (L/T^2), and z is the elevation (L).

The dispersive molar flux is

$$\mathbf{J}_{\alpha\beta}^D = -\rho_{\beta} \mathbf{D}_{\alpha\beta} \cdot \nabla x_{\alpha\beta} \quad (3)$$

where $\mathbf{D}_{\alpha\beta}$ is the dispersion tensor (L^2/T), defined by Bear²].

Interphase partitioning of species can be described by Henry's law and Dalton's law if equilibrium conditions exist. The relationship between mole fractions of a species α in water ($x_{\alpha w}$), gas ($x_{\alpha g}$), and organic ($x_{\alpha o}$) phases is given by

$$x_{\alpha w} H = x_{\alpha g} p_g = x_{\alpha o} P_{\alpha}^v \quad (4)$$

where H is Henry's constant ($M/L T^2$), p_g is the gas phase pressure ($M/L T^2$), and P_{α}^v is the vapor pressure of species α ($M/L T^2$).

Energy transport is governed by (Carrigan and Nitao³):

$$\sum_{\beta=1}^3 \left\{ \frac{\partial}{\partial t} [\rho_{\beta} \phi S_{\beta} u_{\beta} + (1 - \phi) \gamma_b c T] + \nabla \cdot [h_{\beta} \rho_{\beta} q_{\beta}] \right. \\ \left. + \sum_{\alpha=1}^{n_c} [\nabla \cdot (h_{\alpha\beta} \phi S_{\beta} J_{\alpha\beta}^D) + h_{\alpha\beta} \Gamma_{\alpha\beta}] + \nabla \cdot (K_H \nabla T) \right\} = 0 \quad (5)$$

where u_{β} is the internal energy of each phase β (J/mol), γ_b is the soil bulk density, c is the soil heat capacity (J/C·kg), h_{β} is the specific enthalpy (J/mol) of phase β , $h_{\alpha\beta}$ is the specific enthalpy (J/mol) of species α in phase β , K_H is the thermal conductivity of the fluid-soil system (W/C·m), and T is temperature (C).

2.2 Numerical Implementation

Equations 1-5 are discretized using three-dimensional finite differences, and are implemented for an arbitrary number of organic and inorganic species. Water is assumed to be potentially present in the aqueous and gaseous phases, while organic compounds may be in any of the organic, aqueous, or gaseous phases. Air is assumed to partition between the gas and water phases according to Henry's Law.

The Newton-Raphson method is used to linearize the nonlinear equations. The method of primary variable substitution described by Sleep and Sykes¹ is used to deal with changes in phase due to appearance or disappearance of gas and organic phases in blocks. In addition to the primary variables listed in Sleep and Sykes¹ for isothermal multiphase flow and transport (water head, water saturation, organic saturation, species concentrations), temperature is a primary variable at all times. The procedure of Gudjberg et al.⁴ is used to prevent spurious water flow.

Temperature dependent vapor pressures and Henry's Law constants were calculated from temperature, T (K) using the Antoine equation:

$$\ln P_v = ANTA - \frac{ANTB}{ANTC + T} \quad (6)$$

The temperature and composition dependent viscosities of the DNAPL was described by:

$$\ln \mu_{\beta} = \sum_{\alpha=1}^{n_c} x_{\alpha\beta} \mu_{\alpha} \quad (7)$$

with the individual pure component viscosities, μ_{α} calculated as a function of temperature, T (C) from:

$$\ln \mu_{\alpha} = VISA \left(\frac{1}{T} - \frac{1}{VISB} \right) \quad (8)$$

Temperature dependence of capillary pressures was calculated using the correlations of She and Sleep⁵.



Figure 1: Laboratory scale tank simulated

3 MODEL CONDITIONS

The model was applied to simulation of steam flushing for removal of a mixture of monochlorobenzene (MCB) and DDT from a laboratory scale tank used by She and Sleep⁶ for studies of steam flushing for removal of perchloroethylene. The tank was 110.5 cm long by 57.5 cm high, by 10 cm thick, and filled with F75 silica sand and an 8 cm thick F110 silica sand capillary barrier (properties in Table 1), as shown in Figure 1. The tank was equipped with thermocouples, pressure transducers, and sampling ports. Wells (15 cm long) were installed at 7 cm from each end of the tank above the F110 capillary barrier

The tank was saturated with water, and all sides were closed, with all fluid entering and leaving the tank via the two wells. In the simulation, 150 mL of a DNAPL of 50 % by weight of MCB and DDT (properties given in Table 1) were injected into the sand tank just above the capillary barrier, halfway between the two wells over a period of 2 hours. During the injection both wells were open to allow water to flow out of the tank. The DNAPL was allowed to redistribute for 3 days before steam injection was initiated.

Steam flushing was initiated with an average injection rate of 3.47 kg/hour, with an approximate pressure of 65 kPa, and 40% quality (ratio of steam to liquid water). The injection rate varied somewhat over the steam flushing period as the steam front moved across

Fluid Properties			Soil Properties		
Property	MCB	DDT	Property	F75 Sand	F110 Sand
Boiling Point (C)	132	260	Horizontal Permeability (m ²)	1.5 x 10 ⁻¹¹	5.3 x 10 ⁻¹³
Melting Point(C)	-45	109	Vertical Permeability (m ²)	8.0 x 10 ⁻¹²	2.6 x 10 ⁻¹³
Solubility (mg/L)	500	0.03	Porosity	0.37	0.34
VISA*	477.76	1716.5	van Genuchten α (m ⁻¹)	1.86	1.33
VISB*	276.22	504.26	van Genuchten n	8.07	6.64
ANTA (P _v in mm Hg)	16.068	25.02	S _{wr} at 20 C	0.076	0.076
ANTB	3295.1	8033.5	S _{or} at 20 C	0.244	0.244
ANTC	-55.60	-96.0	Thermal Conductivity (W/m-K)	2.86	2.86
Spec. Gravity (20 C)	1.1	1.6	Heat Capacity (kJ/m ³ -K)	2515	2515
DNAPL-Water IFT (dyn/cm)	12				

Viscosity parameters determined from fitting to data of Davis⁷

Table 1: Fluid and soil properties

the tank, and with some minor adjustments of the steam pressures and inlet and outlet valves to maintain even steam flow. Heat loss from the side walls of the tank was modeled as a linear loss rate proportional to the temperature difference between the soil and the air in the laboratory (20 C), with a proportionality constant of 15 W/m²-K. Steam flushing was conducted for 4 hours. Effluent from the tank was passed through a condenser and collected in a Tedlar bag placed on a balance to determine the rate of effluent production.

4 RESULTS AND DISCUSSION

The spatial distributions of DNAPL after three days of redistribution is shown in Figure 2. The DNAPL is perched on the F110 sand layer, and has not spread out significantly, as it is mostly trapped by water and immobilized. At the initial temperature of 20 C the viscosity of the MCB-DDT DNAPL is 3.3 cP, which has also limited lateral movement of the DNAPL.

The predicted temperature profile is shown in Figure 3, while a comparison of the predicted temperatures with measured temperatures at two locations (T1 and T2, which were 13.5 cm from the top of the tank and 40 and 84 cm from the injection well, respectively) are shown in Figure 4. There is good agreement between the predicted and measured temperatures in the tank, with the differences attributed to fluctuations in the steam injection rate. The predicted temperature profile indicates that the steam propagated across the upper F75 sand zone, but the F110 sand layer was also heated due to transverse heat conduction. This heating resulted in vaporization of the water in this layer, particularly near the steam injection well at later times. DNAPL saturations in the tank after one hour of steam flushing

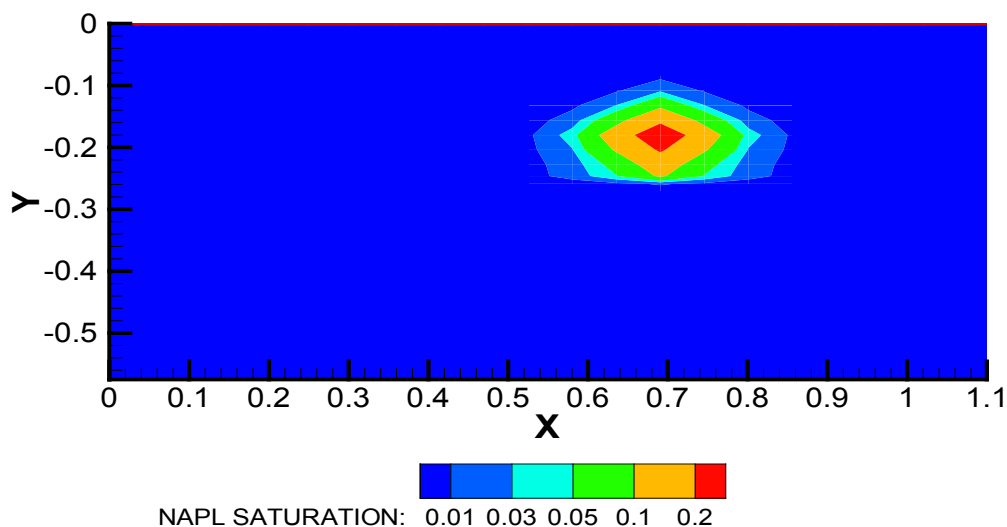


Figure 2: Initial DNAPL distribution before steam flushing

are shown in Figure 5. Following the injection of steam the DNAPL saturations in the original source zone were significantly reduced. However, DNAPL, which is almost pure DDT remained in the original DNAPL location shown in Figure 2. The concentration of MCB (results not shown) in both DNAPL and water were decreased near the steam injection zone, and increased downstream due to preferential removal from the DNAPL near the injection well and condensation at the steam front. Figure 6 shows the predicted changes in the moles of MCB and DDT in the tank with time. The rapid changes in MCB moles around 110 minutes correspond to the breakthrough of steam at the extraction well. At the end of 4 hours of steam flushing the model predicted that the MCB in the tank would be reduced to 3.8×10^{-4} moles (420 mg). Although this is a substantial reduction, the concentration of MCB in the cell

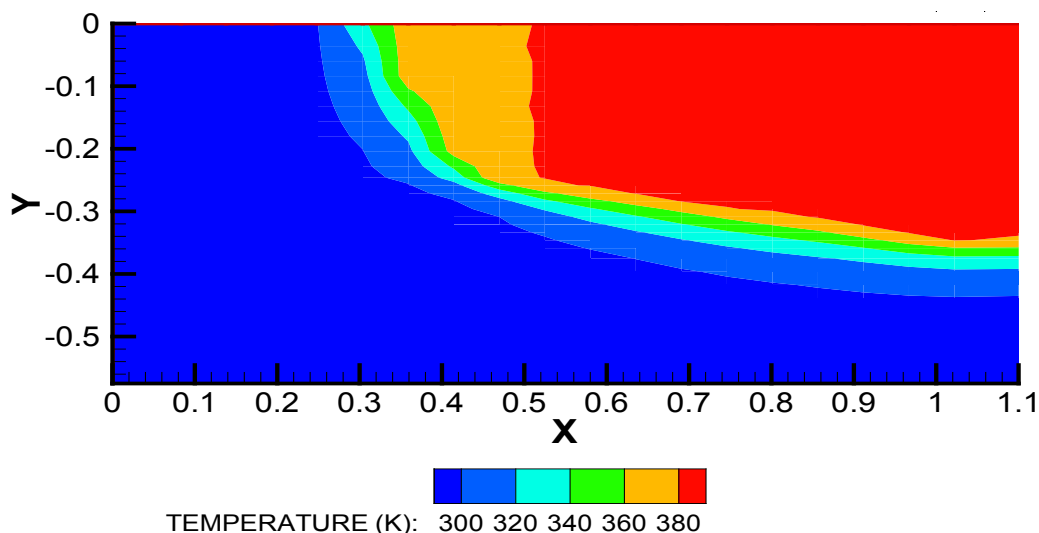


Figure 3: Temperatures (K) in the tank after one hour of steam flushing

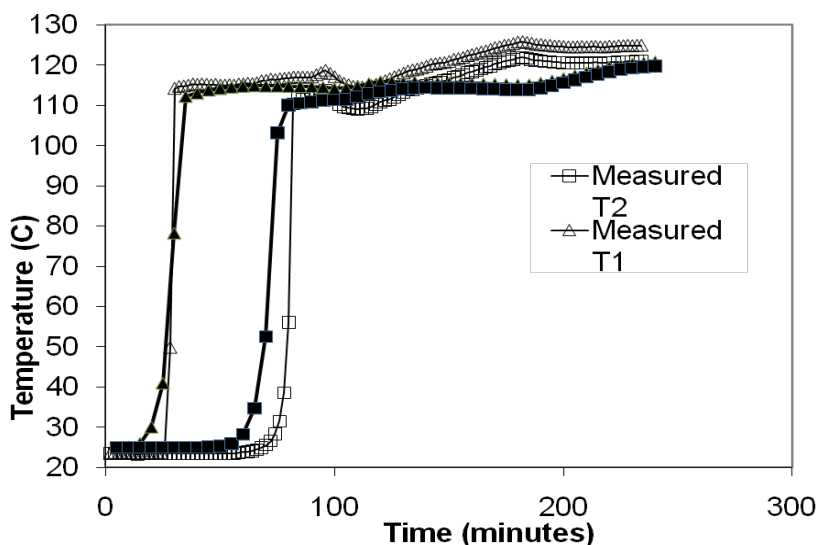


Figure 4: Comparison of measured and predicted temperatures after one hour of steam flushing

is still as high as 60 mg/L. At the rate of removal at the end of the 4 hours of steam flushing, an additional 6 hours of steam flushing would be required to remove all the MCB. This would correspond to a steam condensate volume 4.3 times the pore volume of the zone above the capillary barrier. The model, consistent with experimental observations, predicted that MCB and DDT moved below the F110 capillary barrier after it became desaturated due to vaporization of water. The unvolatilized DDT DNAPL moved downwards through the desaturated capillary barrier. However, once it moved to the bottom of the steam zone the DDT viscosity increased as the DDT cooled. The extent of viscosity reduction and solidification would depend on the amount of MCB remaining in the DNAPL, with viscosity at a given temperature increasing as the MCB fraction in the DNAPL was reduced.

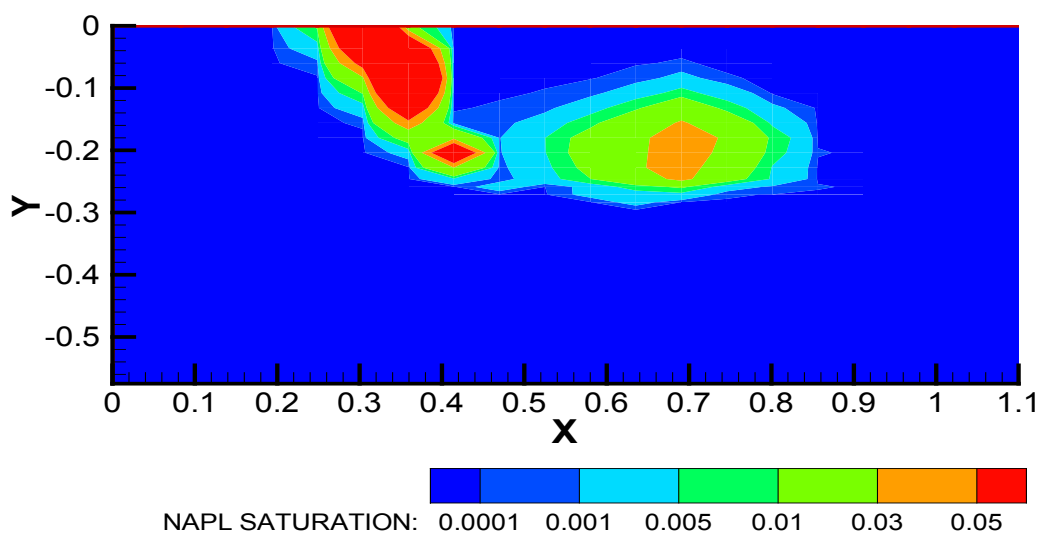


Figure 5: DNAPL saturation after one hour of steam flushing

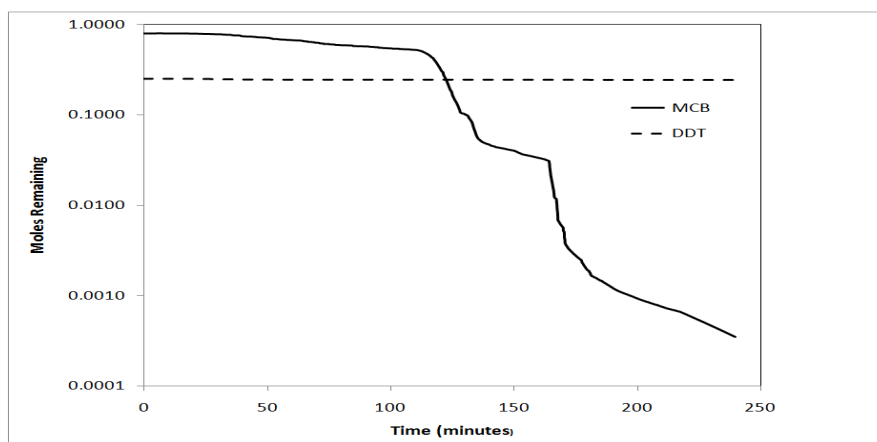


Figure 6: Changes in moles of MCB and DDT with time of steam flushing

5 CONCLUSIONS

Remediation of volatile organic compounds from DNAPL containing substantial amounts of low volatility organic compounds will be slow due to the declining effective vapor pressure of the volatile compound as the DNAPL becomes enriched in the nonvolatile organic. Downward mobilization of the remaining DNAPL may occur if capillary barriers restricting DNAPL movement become desaturated due to water vaporization.

REFERENCES

- [1] B. E. Sleep and J. F. Sykes, "Compositional simulation of groundwater contamination by organic compounds, 1. model development and verification", *Water Resour. Res.* 29(6):1697-1708 (1993).
- [2] J. Bear, *Dynamics of Fluids in Porous Media*. New York: Elsevier Publ. Co., (1972).
- [3] Carrigan, C.R. and J.J. Nitao. "Predictive and diagnostic simulation of in situ electrical heating in contaminated, low-permeability soils", *Env. Sci.Technol.*, 34(22): 4835-4841, (2000).
- [4] Gudjberg, J., Trötschler, O., Färber, A., Sonnenborg, T.O. and K.H. Jensen, "Unphysical behavior during numerical simulation of steam injection into water saturated soil", *J. Contam. Hydrol.* 75: 297-318, (2004).
- [5] H. Y. She and B. E. Sleep, "The effect of temperature on capillary pressure-saturation relationships for air-water and perchloroethylene-water systems", *Water Resour. Res.* 34(10):2587-2597 (1998).
- [6] She, H., and B. E. Sleep, "Removal of PCE from soil by steam flushing in a two-dimensional laboratory cell", *Ground Water Monitoring and Remediation*, 19(2), 70-77(1999).
- [7] Davis, E. L., *Final Addendum One-Dimensional Thermal Remediation Treatability Study Montrose Chemical Superfund Site Los Angeles County, California*, U.S. E.P.A. Region 9 website, accessed January 15, 2010, (2006).