NUMERICAL SIMULATIONS OF MULTICOMPONENT EVAPORATION AND GAS-PHASE TRANSPORT USING M^2NOTS

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Abstract

The multiphase, multicomponent, non-isothermal simulator M^2NOTS was tested against several one-dimensional experiments. The experiments represented a through-flow limiting condition of soil venting in which air flows through the contaminated region. Predictions using M^2NOTS of changing in situ compositions and effluent concentrations for toluene and o-xylene mixtures were compared to the observed results. Results showed that M^2NOTS was able to capture the salient trends and features of multicomponent through-flow venting processes.

Introduction

Soil vapor extraction is a technique that has been used widely in the remediation of subsurface sites contaminated with volatile organic compounds or NAPLs (non-aqueous phase liquids). In this process, liquid contaminants are volatilized and entrained into an advective air stream induced by a system of pumps and underground wells. The effectiveness of this method depends on how readily the contaminant vapors can be entrained into the advective flow.

Previous studies have provided experimental and theoretical evidence of significantly different contaminant removal rates for two limiting conditions of soil vapor extraction (Ho et al., 1994; Ho and Udell, 1993; Ho and Udell, 1992; Johnson et al., 1990). In the ideal through-flow case, air flows through the contaminated regions, causing higher volatility components to be removed preferentially. However, in diffusion-limited cases where the air stream bypasses the contaminated region, preferential recovery of the higher volatility components is not attained. As a preliminary assessment, the through-flow condition has been examined in this study.

The numerical code M^2NOTS (Multiphase Multicomponent Nonisothermal Organics Transport Simulator) developed by Adenekan (1992) was used to simulate laboratory experiments of multicomponent through-flow soil vapor extraction. Comparisons between the results of the numerical code and the experiments were made to verify the gas-NAPL formulation in M^2NOTS and to assess the performance of M^2NOTS in modeling multicomponent evaporation and gas-phase transport.

Experimental Approach

The one-dimensional experiments that were numerically simulated in this paper represented through-flow soil venting of liquid contaminant mixtures. Complete details of the experiments can be found in Ho and Udell (1993). Air at ambient conditions was blown from a compressor through activated carbon, a flowmeter, and then through a sand-filled glass tube (~2 cm diameter). The tube contained dry, machine sifted, 48-65 mesh Monterey sand (average particle diameter = 0.25 mm). The air then passed through a gas sampling bulb before being exhausted into a fume hood.

Prior to each experimental run, a mixture containing equal volumes of toluene and o-xylene was emplaced into the sand with a pipette at a rate of 1–2 ml/minute from the top end of the tube. The properties of toluene and o-xylene at 20 °C are given in Table 1 (Vargaftik, 1975). Approximately 3.6 ml of total liquid were emplaced in the sand. The tube was sealed and the liquid was allowed to drain under the forces of gravity and capillarity until visible movement ceased (~ 2 days). The airflow was then initiated through the apparatus.

The in situ liquid mole fractions were obtained by shutting the airflow off at a specified time. Then, the entire tube was sealed and placed into an ice bath to lower the vapor pressures of the liquid compounds remaining in the sand. Sections of the sand at various axial locations within the tube were then scooped out of the tube and placed into separate vials, which were analyzed by gas chromatography for liquid mole fractions. The liquid saturation of each sample was also determined by weighing the sample to determine the mass of liquid and sand present. Effluent gas concentrations were also recorded by using gas chromatography to analyze samples taken from the gas sampling bulb.

Table 1. Properties of toluene and o-xylene at 20 °C.

	Toluene	o-Xylene
molecular weight [kg/kgmol]	92.14	106.17
density [kg/m^3]	865	876
saturated vapor pressure [Pa]	2910	660
saturated vapor concentration [kg/m^3]	0.11	0.0288
binary diffusion coefficient of vapor in air [m^2/sec] (Fuller, Shettler, & Giddings, 1965)	7.9 x 10^{-6}	7.3 x 10^{-6}

Numerical Approach

The numerical code M^{2}NOTS was used to simulate the venting experiments described in the previous section under isothermal conditions. M^{2}NOTS is an extension of TOUGH2, which was developed by Pruess (1991) as a multiphase, multidimensional, nonisothermal code that simulates the transport of air, water, and heat in porous media. The unique feature of M^{2}NOTS is the additional capability to model the transport of any number of contaminant components in porous media. M^{2}NOTS contains balance laws for each component (air, water, heat, and N-contaminant components) in three phases: gas, aqueous, and NAPL. Each component can partition into all of the fluid phases that are present. In addition, each fluid phase can completely disappear or evolve in any part of the modeled domain. Complete mathematical details on the formulation of M^{2}NOTS can be found in Adenekan et al. (1993).

Major assumptions inherent in M^{2}NOTS include the assumption of local chemical and thermal equilibrium, the use of Darcy's law for all phase velocities, and the ideality of the NAPL and gas mixtures. Although these assumptions may be justified in many problems, the purpose of this study was to test the formulation and assumptions in M^{2}NOTS for a gas-NAPL system in which well-controlled experimental data could be obtained. One caveat of the gas-NAPL formulation that was identified even before the numerical simulations could be performed was the need for a fixed Henry's constant that relates the partial pressure of water vapor to the mole fraction of water in the NAPL phase. The original constant used in the code (4x10^7 Pa) yielded vapor mole fractions that were greater than one, which prevented the code from running properly. A smaller value of 1x10^5 Pa, which was used in this study, produced reasonable vapor mole fractions and solutions in the gas-NAPL system.

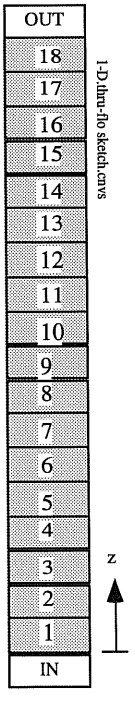
The M^{2}NOTS numerical model that was used to simulate the through-flow experiment is shown in Figure 1. In Figure 1, the numbered elements represent the sand where the liquid contaminants were emplaced. The "IN" and "OUT" elements are boundary elements that do not participate in the balance laws. The pressure of these elements was fixed to yield an inlet air flow rate of 1x10^{-5} m^3/sec that was observed for all the experiments. Element 18 was used to obtain effluent gas concentrations. The chemical parameters that were used in M^{2}NOTS were obtained from Reid et al. (1987). The initial and ambient (outlet) pressures were assumed to be 1.01x10^5 Pa for all cases.

The parameters that were used to calculate the gas-NAPL capillary pressures and relative permeabilities were based on values used in Adenekan (1992) for a generic sand (see Table 2). Although the Stone II model (1973) is used to calculate three-phase relative permeability to oil in M^{2}NOTS, the exponential equations of Corey (1954) are used to calculate two-phase relative permeabilities that were used in this study as follows:

$$k_{rog} = k_{rocw}\left[\frac{1 - S_{org} - S_g}{1 - S_{wir} - S_{org}}\right]^{n_{og}} \quad (1)$$

$$k_{rg} = k_{rgro}\left[\frac{S_g - S_{gr}}{1 - S_{wir} - S_{org} - S_{gr}}\right]^{n_g} \quad (2)$$

where k_{rog} is the relative permeability of oil, k_{rg} is the



Element	z (cm)	Δ z (cm)	Volume (m^3)
1	0.5	1.0	3.4e-6
2	1.5	1.0	3.4e-6
3	2.5	1.0	3.4e-6
4	3.5	1.0	3.4e-6
5	4.5	1.0	3.4e-6
6	5.5	1.0	3.4e-6
7	6.5	1.0	3.4e-6
8	7.5	1.0	3.4e-6
9	8.5	1.0	3.4e-6
10	9.5	1.0	3.4e-6
11	10.5	1.0	3.4e-6
12	11.5	1.0	3.4e-6
13	12.5	1.0	3.4e-6
14	13.5	1.0	3.4e-6
15	14.5	1.0	3.4e-6
16	15.5	1.0	3.4e-6
17	16.5	1.0	3.4e-6
18	17.5	1.0	3.4e-6
In	—	—	0.0
Out	—	—	0.0

area of sand elements = 3.4e-4 m^2

Figure 1. Numerical model used in MNOTS.

relative permeability of gas, S_g is the gas saturation, and the other parameters are given in Table 2. The expressions of Parker et al. (1987) are used to calculate capillary pressures. For the gas-NAPL system studied here, the following equation was used to relate gas- and NAPL-phase pressures:

$$P_{cgo} = \frac{\rho_w g}{\alpha_{go}} \left\{ \left(\frac{S_w + S_o - S_m}{1 - S_m} \right)^{-1/m} - 1 \right\}^{1/n} \quad (3)$$

where P_{cgo} is the gas-NAPL capillary pressure (gas pressure minus the oil pressure), $\rho_w g$ is the specific gravity of water, S_w is the water saturation, S_o, is the oil saturation, and the other parameters are given in Table 2. Although the selection of the parameter values used in Equations (1)–(3) were fairly arbitrary, the mobility of the NAPL phase was expected to be small compared to the gas-phase transport. However, future assessment of these parameters may need to be considered.

Table 2. Sand parameters used in M^{2}NOTS.

Permeability (measured) [m^2]	8.4×10^{-11}
Porosity (measured)	see Table 2
Residual NAPL saturation, S_{org}	0.08
Irreducible water saturation, S_{wir}	0.1
k_{rocw}	1.0
k_{rgro}	1.0
n_{og}	1.8
n_g	1.2
S_m	0.1
α_{go} [1/m]	40
n	2

Results and Discussion

Figure 2 shows the experimentally determined liquid mole fraction distributions for toluene and o-xylene along with the liquid saturations after 15, 29, and 45 minutes (Runs 1, 2, and 3) of through-flow venting. The numerical predictions using M^{2}NOTS are also shown in Figure 2. The mole fractions and saturations are plotted as a function of position along the tube (note the orientation of the z-coordinate in Figure 1. An initial discussion of the experimental results will be followed by a comparison with the numerical predictions.

The initial liquid mole fractions of the emplaced mixture of toluene and o-xylene were 0.53 and 0.47, respectively. However, since toluene was more volatile, greater quantities of toluene were evaporated and entrained in the advective gas flow near the entrance (z=0 cm) where clean air initially swept through the contaminated region. This process continued until the experiment was stopped at 15 minutes (Run 1), at which time most of the toluene between z=0 cm and z=5 cm had already been removed. Between z=9 cm and z=18 cm, the remaining contaminant in situ contained toluene and o-xylene at the initial composition.

In Run 2 the liquid mole fractions were determined after 29 minutes of through-flow venting. At this time, Figure 2 shows that a nearly complete recovery of toluene existed upstream of z=12 cm. However, o-xylene still existed in-between z=5 cm and z=12 cm. This distribution indicates that the volatilization of the toluene and o-xylene behaved similarly to the propagation of separate evaporation fronts at different velocities (see Ho et al. (1994) for a detailed analysis of the propagation of evaporation fronts). At 29 minutes the o-xylene evaporation front was near z=5 cm while the toluene evaporation front was near 12 cm. Upstream of the o-xylene evaporation front nearly all of the contaminant had been recovered.

Run 3 was used to determine the liquid mole fraction distribution throughout the contaminated region at 45 minutes. At this time, the toluene mole fraction is shown in Figure 2 to be nearly zero everywhere, indicating that the evaporation front had propagated completely through the sand. However, significant amounts of o-xylene still remained downstream of the location of the o-xylene evaporation front at z=7 cm.

The results of M^{2}NOTS shown in Figure 2 are seen to behave very similarly to the experimental results. Although the liquid mole fraction distributions and liquid saturations appear to lag the experimental results, M^{2}NOTS seems to replicate the preferential evaporation of the toluene. The larger spread in the liquid mole fractions may be a result of the relatively coarse mesh used in the simulations. Nevertheless, the predictions shown in Figure 2 still give the appearance of evaporation fronts of toluene and o-xylene propagating downstream with time.

Figure 3 shows the results of Run 4 in which the effluent gas concentration of toluene and o-xylene were obtained from the through-flow venting experiment. These results are consistent with the results of the in situ mole fractions shown in Figure 2. Just after 30 minutes of venting, the toluene gas concentration drops to zero since the toluene was completely removed from the system (the toluene evaporation front had propagated through the entire system). As a result, the o-xylene liquid mole fraction jumped to one and the o-xylene effluent gas concentrations increased as shown in Figure 3. Finally, at 100 minutes, all of the o-xylene was removed from the system and the gas concentrations went to zero. The predictions of M^{2}NOTS are seen to correspond very closely to the experimentally observed results in Figure 3. This implies that for the flow rates used in the experimental study, the assumption of local chemical equilibrium was sufficient to describe the system.

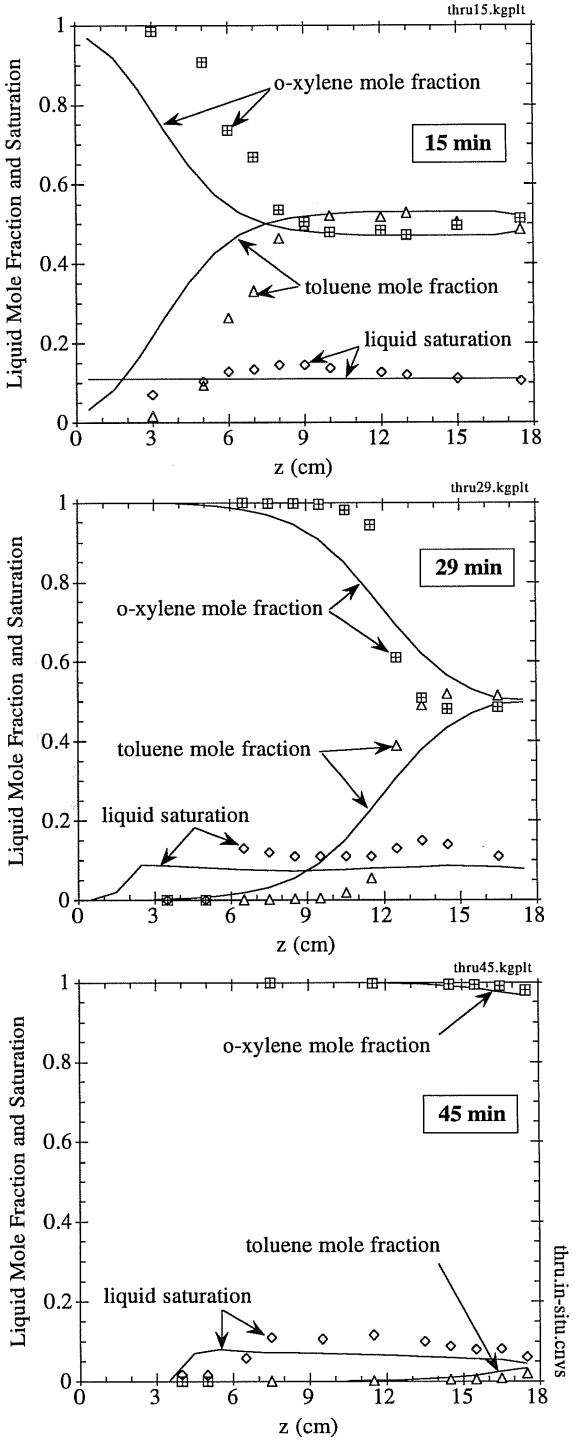


Figure 2. Liquid saturations and mole fractions of toluene and o-xylene after 15, 29, and 45 minutes of through-flow venting (Runs 1, 2, and 3). The solid lines are numerical predictions from M^{2}NOTS and the symbols are experimental results.

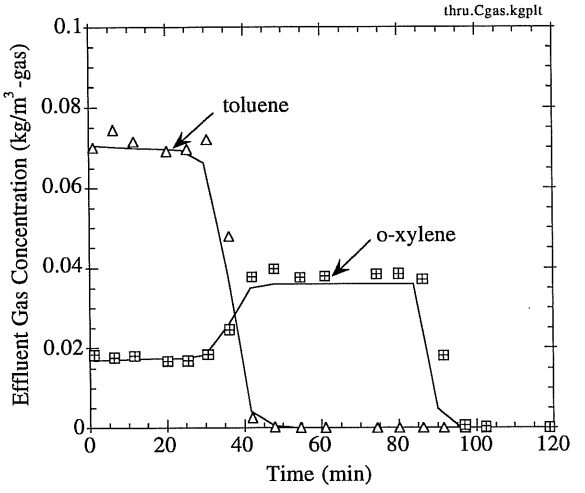


Figure 3. Effluent gas concentrations for toluene and o-xylene during through-flow venting (Run 4). The solid lines are numerical predictions from M^{2}NOTS and the symbols are experimental results.

Conclusions

The results of one-dimensional experiments simulating through-flow venting conditions were compared with numerical simulations using M^{2}NOTS. Based on these comparisons, several conclusions can be drawn:

- M^{2}NOTS was capable of simulating the selective evaporation of toluene during through-flow venting. Propagating evaporation fronts, corresponding to the location of volatilization of each compound, were observed in the simulations and in the experiments.
- Only the gas-NAPL formulation of M^{2}NOTS was tested in this study. Other phase combinations may need to be systematically tested against experiments or field studies to ensure robustness.
- Parameters controlling the mobility of the liquid phase (relative permeability and capillary pressure parameters) were uncertain and may need to be more rigorously assessed in problems where the liquid phase is mobile.
- Specified Henry's Constants in M^{2}NOTS may need to be altered to yield physically realistic results for specific multiphase problems.

Acknowledgments

This study was performed with financial support from the SNL LDRD project titled "Physical Simulation of Nonisothermal Multiphase Flow in Porous Media". Discussions with Mario Martinez, Ade Adenekan, and Steve Webb were greatly appreciated during the course of this study.

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