Example Problem 7
DNAPL vapor behavior in unsaturated porous media

Abstract: *Density effects may be important when contaminant vapors are moved through the subsurface. Volatile organic compounds with a relatively high molecular weight such at trichloroethene (TCE) and carbon tetrachloride may cause density differences to occur in the gas phase. An example is presented that allows the user to investigate when density effects may be important. The user is also asked to develop a soil vapor extraction system that accelerates the removal of a residual NAPL source. The object of this problem is to introduce the user to transport of organic components in the gaseous phase. The Water-Oil-Air mode (STOMP-WOA) is used for this application.*

7.1 Problem Description

Volatile organic compounds (VOCs) such as solvents and hydrocarbon fuels are commonly found in the subsurface at many sites. Typically, industrial VOCs have entered the subsurface as nonaqueous-phase liquids (NAPLs) via chemical spills, leaks in storage or transmission structures, and direct disposal to waste sites. VOCs have characteristically a high vapor pressure at normal temperatures and pressures near the earth's surface; therefore, a substantial mass of VOCs will likely be present in the gaseous phase of the subsurface.

Once in the subsurface, VOCs can exist as a separate phase (i.e., a NAPL), as a component of the gaseous phase, and as a component of the aqueous phase. VOCs may also be adsorbed on solid material, either organic or inorganic. The movement of VOCs in the subsurface can occur by advective, diffusive, and dispersive fluxes of the separate fluid phases. Therefore, to model VOC transport in the gaseous phase, advection, diffusion, and dispersion processes need to be considered. In many fluid flow and transport models, however, gas-phase pressures are assumed to be atmospheric and diffusion the only mechanism with which chemicals in the gaseous phase migrate.

Gas-phase advection is controlled by the network of pores that contain gas, the viscosity of the gaseous phase, and a spatial difference in the gas-phase total potential, which is commonly defined as the sum of the gas-pressure potential and the gravitational potential. Very small gradients in the gas-phase total potential can yield significant advective fluxes because the resistance to gas flow is small (i.e., negligible gas-phase viscosities), and the gaseous phase is contained in the largest pores of liquid-unsaturated porous media. Several investigators have examined density-driven flow of gas caused by VOC contamination and concluded that VOC molecular mass and porous medium permeability are important factors in determining whether density-driven advection is an important transport mechanism.

The problem *input* file is given in section 7.3. The domain is 30 m long in the x-direction and 10 m high in the z-direction. The porous medium is uniform and the water table is located at the bottom of the domain. There is no gradient in the aqueous phase. A zone with residual NAPL saturation of 0.2 is located in a 1 m^3 zone near the west boundary. The DNAPL has a vapor pressure of 12,000 Pa and a molecular weight of 153.82 g/mol. Compared to STOMP4 simulations (Water-Oil), the only additional Card to be specified is the Gas Relative Permeability Card. The total simulation time is 100 days. Plot files are created at 4 additional times. Vapors develop from the NAPL and are transported through the domain via advection and diffusion.

7.2 Exercises

1. Given the vapor pressure and Henry's constant, compute the aqueous phase mole fraction of the NAPL.
2. Explain the choice of the values for the gas initial pressure at node (1,1,1) (101319.15 Pa) and the vertical gradient (-11.71 Pa/m).
3. Based on the *input* file, explain why the NAPL is forced to be residual.
4. Run the simulation. Plot the gas concentration at t =100 days.
5. Make changes in the *input* file to remove density-driven advection in the gaseous phase. Plot the gas concentration at t =100 days and compare with results of previous exercises.
6. Density effects are assumed to be strong functions of the porous medium permeability. Lower the permeability by a factor 10 and by a factor 100 and plot the results at t = 100 days.
7. Install a vapor extraction system in node (10,1,1). Allow the pumping to start at t = 25 days. Extract with a constant rate from t = 25 to t =100 days. Choose various rates and observe the effect on the remaining NAPL in the source zone and the final gas concentrations at t = 100 days.
8. Do the same at node (5,1,1). Comment on the differences with what was observed in Exercise 8.

7.3 Input File

```
#-------------------------------------------------------
~Simulation Title Card
#-------------------------------------------------------
1,
STOMP Tutorial Problem 7,
Mart Oostrom/Mark White,
PNNL,
June 03,
15:00,
2,
Simulation of 2D vapor density problem,
Carbon tetrachloride vapor behavior,

#-------------------------------------------------------
~Solution Control Card
#-------------------------------------------------------
Normal,
Water-Oil-Air,
1,
0,s,100,d,10,s,10,d,1.25,8,1.e-6,
10000,
Variable,
Constant,0.9e-6,m^2/s,0.9e-6,m^2/s,
0,

#-------------------------------------------------------
~Grid Card
#-------------------------------------------------------
Cartesian,
20,1,10,
0,m,10@1,m,10@2,m,
0,m,1,m,
0,m,10@1,m,

#-------------------------------------------------------
~Rock/Soil Zonation Card
#-------------------------------------------------------
1,
Sand,1,20,1,1,1,10,

#-------------------------------------------------------
~Mechanical Properties Card
#-------------------------------------------------------
Sand,2650,kg/m^3,0.4,0.4,,,Millington and Quirk,

#-------------------------------------------------------
~Hydraulic Properties Card
#-------------------------------------------------------
Sand,100.0,hc m/day,,,100.0,hc m/day,


#-------------------------------------------------------
~Saturation Function Card
#-------------------------------------------------------
72.0,dynes/cm,,,35.43,dynes/cm,
```

```
Sand,Van Genuchten,2.5,1/m,2.0,0.10,72.0,dynes/cm,,

#-------------------------------------------------------------
~Aqueous Relative Permeability Card
#-------------------------------------------------------------
Sand,Mualem,,

#-------------------------------------------------------------
~NAPL Relative Permeability Card
#-------------------------------------------------------------
Sand,Constant,0.0,

#-------------------------------------------------------------
~Gas Relative Permeability Card
#-------------------------------------------------------------
Sand,Mualem,,

#-------------------------------------------------------------
~Oil Properties Card
#-------------------------------------------------------------
Carbontetrachloride,
153.82,g/mol,250.,K,349.9,K,556.4,K,
45.6,bar,275.9,cm^3/mol,0.272,0.193,0.0,debyes,
4.072e+1,2.0496e-1,-2.27e-4,8.843e-8,
Constant,12000,Pa,
Constant,1623,kg/m^3,
Constant,0.97e-3,Pa s,
1.3062e8,Pa,

#-------------------------------------------------------------
~Dissolved Oil Transport Card
#-------------------------------------------------------------
Sand,0.2,cm,0.02,cm,linear kd,0.0,m^3/kg,

#-------------------------------------------------------------
~Initial Conditions Card
#-------------------------------------------------------------
4,
Aqueous Pressure,96428.24,Pa,,,,,-9793.5192,1/m,1,20,1,1,1,10,
Gas Pressure,101319.15,Pa,,,,,-11.71,1/m,1,20,1,1,1,10,
NAPL Pressure,-1.e9,Pa,,,,,,,1,20,1,1,1,10,
NAPL Pressure,93845.17,Pa,,,,,,,1,1,1,1,8,8,

#-------------------------------------------------------------
~Boundary Conditions Card
#-------------------------------------------------------------
2,
east,hydraulic gradient,hydraulic gradient,dirichlet,
20,20,1,1,1,10,1,
0,d,96428.24,Pa,,,101319.15,Pa,,,-1.e9,Pa,
bottom,zero flux,zero flux,zero flux,
1,20,1,1,1,1,1,
0,d,101325,Pa,,,-1.e9,Pa,,,-1.e9,Pa,

#-------------------------------------------------------------
~Output Options Card
#-------------------------------------------------------------
6,
```

1,1,8,
1,1,5,
5,1,1,
6,1,8,
6,1,5,
20,1,1,
1,1,day,m,6,6,6,
3,
aqueous saturation,,
napl saturation,,
oil gas concentration,g/l,
4,
1.0,d,
5.0,d,
10.0,d,
50.0,d,
4,
no restart,,
aqueous saturation,,
napl saturation,,
oil gas concentration,g/l,

7.4 Solutions to Selected Exercises

Exercise 1

Henry's constant for carbon tetrachloride is given in the last entry of the Oil Properties Card (*H* = 1.3062e8 Pa). This is the ratio of the oil vapor pressure to the mole fraction of oil in the aqueous phase. Since the vapor pressure is 12,000 Pa, the aqueous mole fraction is 9.187e-5.

Exercise 2

The density of the gas phase leads to a vertical gradient of -11.71 m/Pa for the gas pressure in the soil above the water table. The lowest vertical node in the domain is 0.5 m above the water table and is therefore initialized with a pressure of -11.71 *0.5 + 101325 Pa or 101319.15 Pa.

Exercise 3

The NAPL is forced to be residual in the NAPL Relative Permeability Card. The permeability function is specified as constant with a NAPL relative permeability of 0.0. The liquid phase NAPL will not be able to move and is in effect residual.

Exercise 4

The plot for the case including density-driven advection is shown in Figure 7.1. The vapors are move down rapidly and are then forced to move laterally on top of the water table.

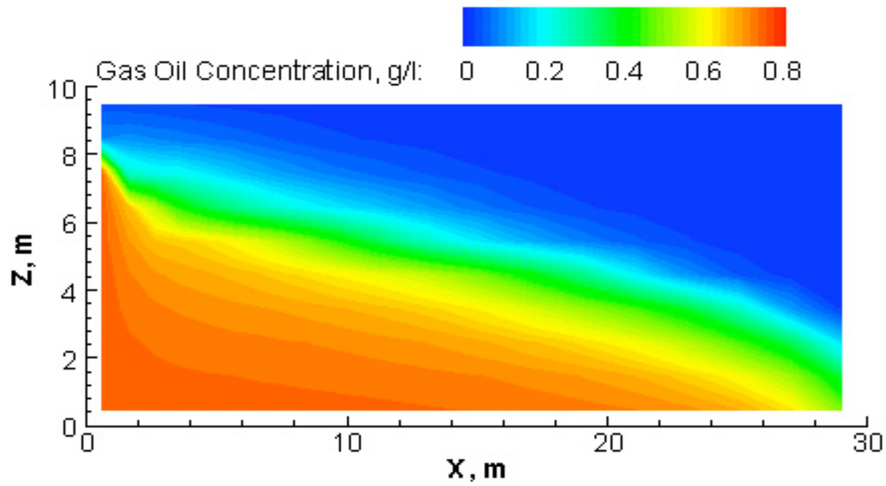

Figure 7.1 Gas oil concentration distribution after 100 days with density-driven gaseous advection.

Exercise 5

To remove density-driven advection, the Gas Relative Permeability Card is altered as follows:

#--

~Gas Relative Permeability Card

#--

Sand,Constant,0.0,

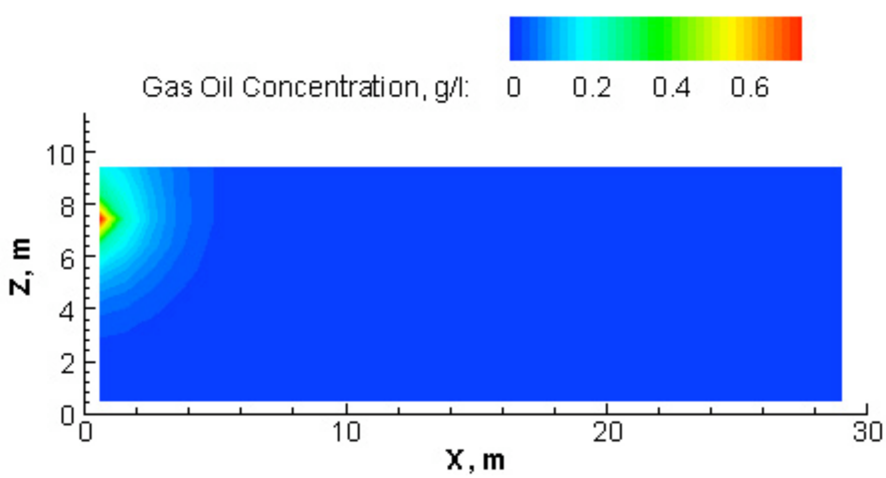

Figure 7.2 Gas oil concentration distribution after 100 days without density-driven gaseous advection.

The resulting plot is shown in Figure 7.2. Compared to Figure 7.1, the vapor plume is less pronounced. It is obvious that ignoring density-driven advection has large effects on the simulation results.

Exercise 6

Density-driven gaseous advection is a strong function of the permeability of the porous medium as illustrated by Figures 7.3 and 7.4. The lower the permeability, the less pronounced the density effects.

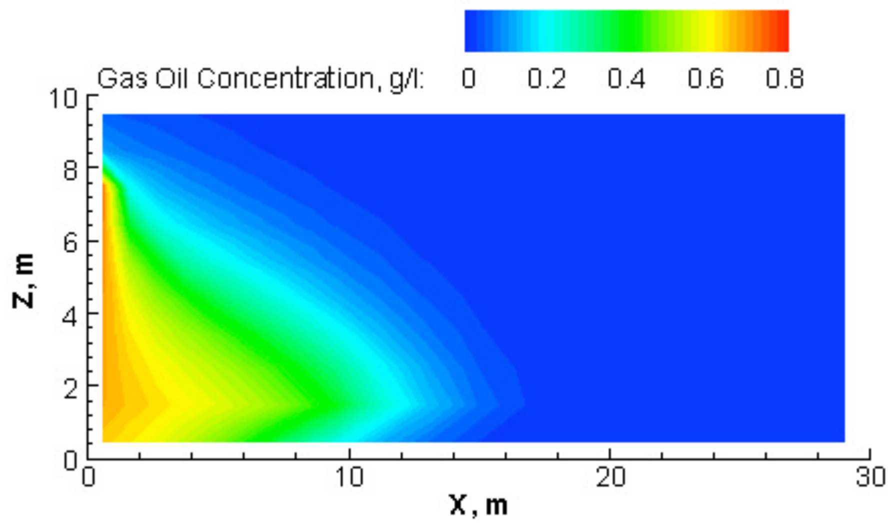

Figure 7.3 Gas oil concentration distribution after 100 days with density driven gaseous advection. The hydraulic conductivity was reduced by a factor of 10.

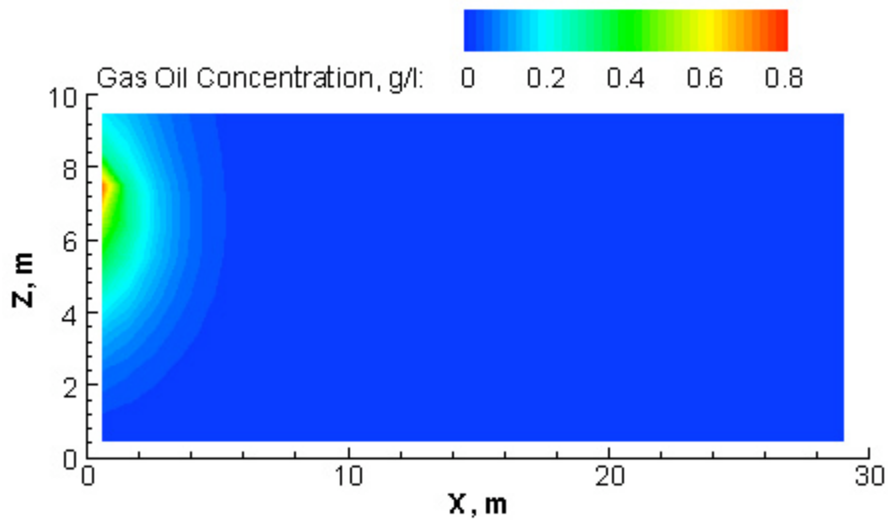

Figure 7.4 Gas oil concentration distribution after 100 days with density driven gaseous advection. The hydraulic conductivity was reduced by a factor of 100.

Exercise 7

A rate of 800 L/day was chosen for this exercise. The resulting plot at 6 = 100 days is shown in Figure 7.5. Compared to Figure 7.1, Figure 7.5 demonstrates that soil vapor extraction might be an effective process for this particular simulation.

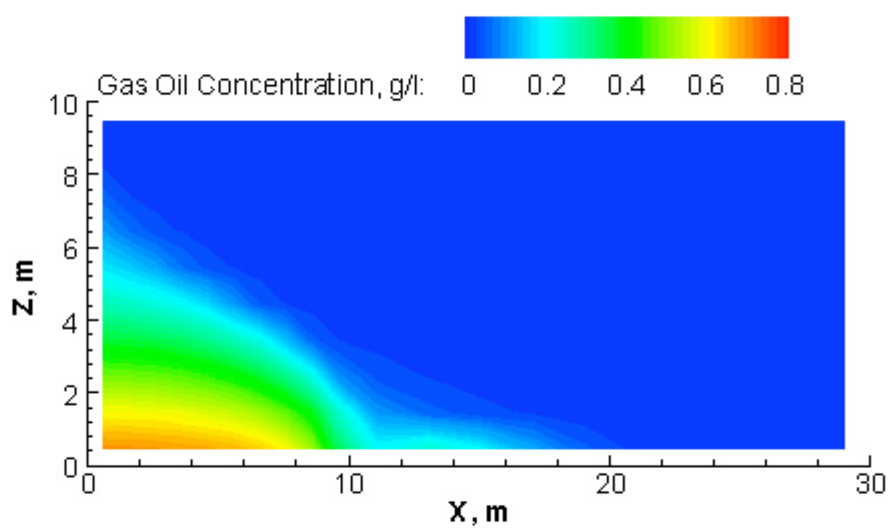

Figure 7.5 Gas oil concentration distribution after 100 days with a 800 L/day vapor extraction system at node (10,1,1) pumping from day 25 to day 100.

Exercise 8

Comparing Figure 7.5 and Figure 7.6 shows that the vapor extraction system is more effective closer to the source. The reduced distance to the source causes an increase in the gaseous flow rates and the original source of the contamination could be completely eliminated. The liquid NAPL evaporated into the gaseous phase more quickly because the vapor extraction system pulled the gas away quickly allowing more NAPL to evaporate.

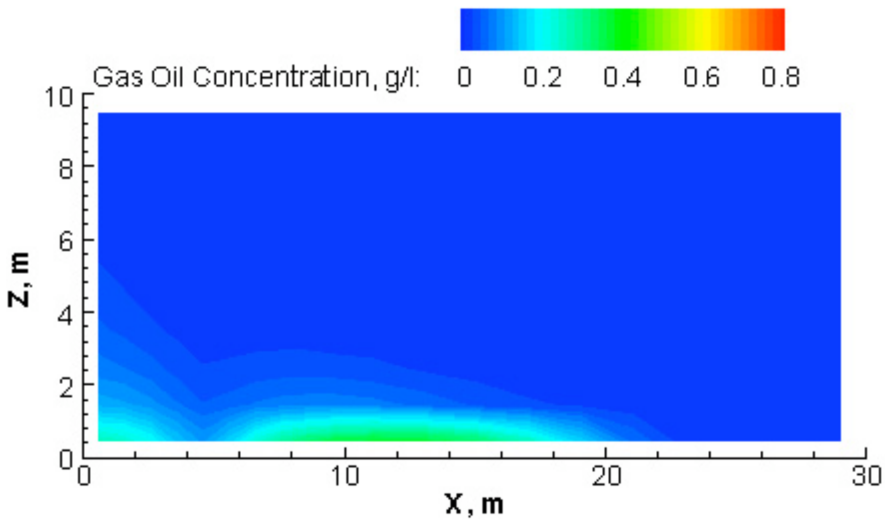

Figure 7.6 Gas oil concentration distribution after 100 days with a 800 L/day vapor extraction system at node (5,1,1) pumping from day 25 to day 100.