

Example Problem 8

Simulation of partitioning tracer transport to detect and quantify NAPLs

Abstract: *In this example, the equilibrium behavior of conservative and partitioning tracers in the presence of a DNAPL is simulated. First, a 1-D experiment described by Jin et al. (1995) will be simulated with the water-oil mode. After completing the 1D simulation, the user is asked to design an input file for a 2D tracer experiment based on a conceptual model and description.*

8.1 Problem Description

DNAPLs occur in the subsurface at numerous contaminated sites and are usually considered to be long-term sources of groundwater contamination. The development and application of new remediation technologies require an understanding of flow and transport of DNAPLs in the subsurface. Knowledge of DNAPL distribution is important for implementation of source control strategies. Appropriate risk based decisions can not be made for a contaminated site without knowing if DNAPL is present at the site.

Current methods used for characterizing potential DNAPL sites include soil gas analysis, core sampling, cone penetrometer testing, and monitoring well sampling. These methods provide data for relatively small volumes of the subsurface and require the use of a dense sampling network and application of geostatistics to determine the overall contaminant distribution. The partitioning tracer test is an alternative, larger-scale method for locating and quantifying DNAPL saturation in the subsurface. This method involves the use of partitioning tracers, which distribute into DNAPLs, and are thus retarded and separated from non-partitioning tracers during transport.

The procedure for estimating DNAPL saturation, s_{nv} involves calculation of a retardation factor (R) for the partitioning tracer, which is done by a comparative moment analysis with the nonreactive tracer. The retardation factor is defined as the velocity of water (nonreactive tracer) divided by the velocity of the partitioning tracer. With knowledge of R, K_{in} (water-DNAPL partition coefficient), K_d (sorption coefficient), ρ_b (dry soil bulk density), and s_l (aqueous saturation), s_n can be calculated from:

$$R = 1 + \frac{\rho_b}{ns_l} K_d + \frac{s_n}{1 - s_n} K_{in} \quad 8.1$$

The terms on the right-hand side of the equation describe retention of the tracer by the aqueous, solid phase, and DNAPL phases, respectively. For a tracer with no sorption to the porous media, Eq. (8.1) simplifies to:

$$R = 1 + \frac{s_n}{1 - s_n} K_{in} \quad 8.2$$

The experiment described by Jin et al. (1995; Exp. DW2) was conducted in a 30.5-cm stainless steel column with a diameter of 2.21 cm. The column was packed with Ottawa sand. The porosity of the column was 0.362 and the permeability of the sand $15.3 \cdot 10^{-12} \text{ m}^2$. Residual saturation of tetrachloroethylene (PCE) was established by injecting the organic liquid at a rate of 0.5 ml/min for 1.1 pore volumes in an upward direction, followed by injecting water at the same flow rate for 2.1 pore volumes in a downward direction. Using the methods of weight and volume measurements, the average residual saturation in the column was 0.202 and 0.197, respectively.

Three different tracers were used: Tritium ($K_{in} = 0.00$), isopropanol (IPA; $K_{in} = 0.04$), and 2,3 dimethyl 2-butanol (DMB; $K_{in} = 2.76$). In the experiment, 0.1 pore volumes of water containing the tracers was injected at 0.05 ml/min, followed by injection of clean water at the same rate. Inverse modeling

conducted by Jin et al. (1995) yielded a porous medium dispersivity of 0.17 cm. For the molecular diffusion coefficient, a value of 10^{-10} m²/s was assumed. PCE entrapment was accomplished by assuming a maximum residual saturation of 0.3 in the Saturation Function Card and a constant residual saturation of 0.2 in the Initial Conditions Card. Entrapment was the only hysteretic fluid displacement process considered in the simulations. The associated input file is listed in section 8.3. The total simulation period is 2400 minutes of which the first 84.705 minutes were used to inject the tracer cocktail. The flux rate used in the Boundary Condition Cards is computed based on the diameter of column, the injected total volume and the imposed rate. The sign of the Neumann flux is negative because the fluid is injected from the top boundary in a downward direction. It is also important to note the 4 Boundary Condition times associated with the top boundary. For the bottom boundary it is assumed that the fluid outlet was kept level with the top of the column.

Reference

Jin, M. M. Delshad, V. Dwarakanath, D.C. McKinney, G.A. Pope, K. Sepehrnoori, C.E. Tilburg. 1995. "Partitioning tracer test for detection, estimation, and assessment of subsurface nonaqueous phase liquids." *Water Resources Research*. 31: 1201-1211.

8.2 Exercises

1. Run the 1D problem (*input* file in section 8.3) with both standard Patankar and TVD transport. Make plots of breakthrough curves (tracer concentration vs. time) at the outlet (node 1,1,50) using the *output* file and make plots of concentration vs. elevation in the column using the various *plot* files.
2. Change the trapped DNAPL saturation from 0.2 to 0.05 and rerun the simulation (TVD transport only). Compare the breakthrough curves of tritium and DMB at the outlet.
3. Develop an input file for a 2D simulation using the 1D simulation as a basis. The experimental flow cell is 1.0 m long, 0.1 m wide, and 1.0 m high. Use the following grid card:

```
#-----  
~Grid Card  
#-----  
Cartesian,  
11,1,11,  
0,cm,10,cm,20,cm,30,cm,40,cm,47,cm,53,cm,60,cm,70,cm,80,cm,90,cm,100,cm,  
0,cm,10,cm,  
0,cm,10,cm,20,cm,30,cm,40,cm,47,cm,53,cm,60,cm,70,cm,80,cm,90,cm,100,cm,
```

Notice that this grid card allows us to specify the locations of the different sands as required below, but it also allows data to be collected at the requested locations (see Figure 8.4). The used porous media are coarse sand and fine sand. The properties of the sands are the same, except for the hydraulic conductivity. The coarse sand has a hydraulic conductivity of 100 m/day and the fine sand a hydraulic conductivity of 1 m/day. The porosity of both sands is 0.4. The fine sand is located between $x = 0.2$ and 0.8 m and between $z = 0.4$ and 0.6 m. The remainder of the flow cell contains the coarse sand. The aqueous relative permeability of the fine sand is assumed to be constant at 0.5. For all other relative permeabilities, the Mualem relation can be used. Both sands have a Van Genuchten α of 2.5 1/m , a Van Genuchten n of 2.0, and an irreducible water saturation of 0.1. Initially, the flow cell is fully saturated and the fine sand contains a uniform trapped NAPL zone with 15% saturation. The total experimental

duration is 10 days and water is injected for the duration with a rate of 40 cm/day at the west side. On day 2, the injected water contains two tracers with a concentration of $1/\text{cm}^3$. On the east side of the flow cell, a hydraulic gradient is maintained for the aqueous phase. No NAPL is allowed to move over any boundary. Three sampling locations are identified in Figure 8.1. Use partitioning coefficients similar to the values used in the 1-D problem. Make *plot* files for both tracers at several times and verify water and tracer injection through an appropriate Surface Card. Compare the breakthrough behavior of the tracers at the indicated locations. Comment on the effectiveness of the partitioning tracer test in this example.

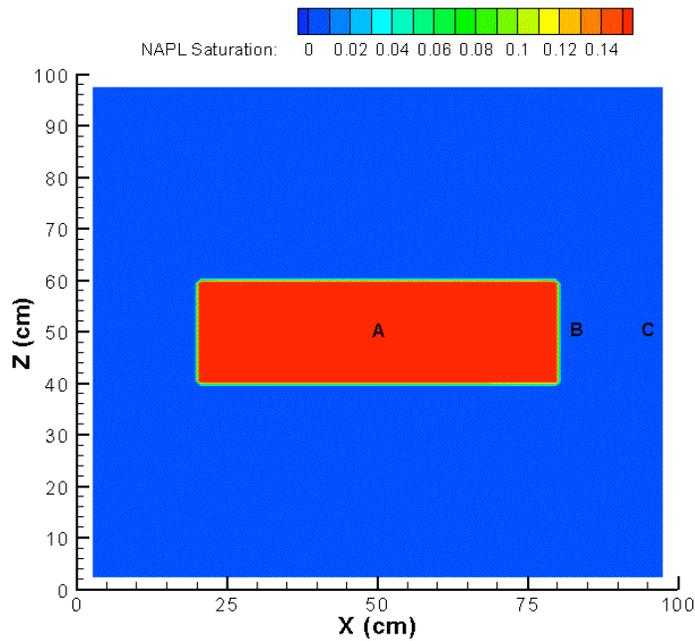


Figure 8.1 Zone with entrapped DNAPL and sampling locations in the 2D experiment.

8.3 Input File

```
#-----  
~Simulation Title Card  
#-----  
1,  
STOMP Tutorial Problem 8,  
Mart Oostrom / Mark White,  
PNNL,  
June 03,  
15:00,  
4,  
Simulation of 1D partitioning tracer experiment,  
Partitioning tracer test for detection, estimation, and,  
assessment of subsurface nonaqueous phase liquids,  
Water Resources Research, Vol. 31, No. 5, Pages 1201-1211, May 1995,  
  
#-----  
~Solution Control Card  
#-----  
Normal,  
Water-Oil w / Transport,  
1,  
0,s,2400,min,0.1,s,5,min,1.25,8,1.e-6,  
10000,  
Variable Aqueous Diffusion,  
,  
  
#-----  
~Grid Card  
#-----  
Uniform Cartesian,  
1,1,50,  
1.958562,cm,  
1.958562,cm,  
0.61,cm,  
  
#-----  
~Rock/Soil Zonation Card  
#-----  
1,  
Ottawa sand,1,1,1,1,50,  
  
#-----  
~Mechanical Properties Card  
#-----  
Ottawa sand,2650,kg / m^3,0.362,0.362,,,Millington and Quirk,  
  
#-----  
~Hydraulic Properties Card  
#-----  
Ottawa sand,,,,,1.5e-4,hc m / s,  
  
#-----  
~Saturation Function Card  
#-----  
72.0,dynes / cm,,,35.43,dynes / cm,  
Ottawa sand,Entrapment Van Genuchten,2.7,1 / m,1.23,.26,72.0,dynes / cm,,0.3,0,
```

```

#-----
~Aqueous Relative Permeability Card
#-----
#Rel perm estimated from Lenhard and Parker 1987 Eq. (5)
Ottawa sand,Constant,0.8,
#-----
~NAPL Relative Permeability Card
#-----
Ottawa sand,Mualem,0.5,

#-----
~Solute / Fluid Interactions Card
#-----
3,
Tritium,1.0e-10,m^2/s,1.0e-10,m^2/s,
Linear Isotherm,0.0,
1.e+8,yr,
IPA,1.0e-10,m^2/s,1.0e-10,m^2/s,
Linear Isotherm,0.04,
1.e+8,yr,
DMB,1.0e-10,m^2/s,1.0e-10,m^2/s,
Linear Isotherm,2.76,
1.e+8,yr,
0,

#-----
~Dissolved Oil Transport Card
#-----
Ottawa sand,0.17,cm,,cm,linear kd,0.0,m^3/kg,

#-----
~Solute / Porous Media Interactions Card
#-----
Ottawa sand,0.17,cm,,cm,
tritium,Linear Isotherm,0.0,
IPA,Linear Isotherm,0.0,
DMB,Linear Isotherm,0.0,

#-----
~Oil Properties Card
#-----
PCE,
165.834,g/mol,251.,K,394.4,K,620.2,K,
47.6,bar,289.6,cm^3/mol,0.2758,0.2515,0.0,debyes,
-1.431e+1,5.506e-1,-4.513e-4,1.429e-7,
Equation 1,-7.36067,1.82732,-3.47735,-1.00033,
Modified Rackett,0.2758,0.2515,
Constant,0.97e-3,Pa s,
9.463e7,Pa,

#-----
~Initial Conditions Card
#-----
3,
Aqueous Pressure,104282.15,Pa,,,,,-9793.5192,1/m,1,1,1,1,1,50,
NAPL Pressure,-1.e9,Pa,,,,,1,1,1,1,1,50,
Trapped NAPL Saturation,0.20,,,,,,1,1,1,1,1,50,

```

```

#-----
~Boundary Conditions Card
#-----
2,

top,neumann,zero flux,inflow aqueous,inflow aqueous,inflow aqueous,
1,1,1,1,50,50,4,
0,d,-0.013035,cm / min,0.0,-1.e9,Pa,1.0,1 / cm^3,1.0,1 / cm^3,1.0,1 / cm^3,
84.705,min,-0.013035,cm / min,0.0,-1.e9,Pa,1.0,1 / cm^3,1.0,1 / cm^3,1.0,1 / cm^3,
84.705,min,-0.013035,cm / min,0.0,-1.e9,Pa,0.0,1 / cm^3,0.0,1 / cm^3,0.0,1 / cm^3,
2400.,min,-0.013035,cm / min,0.0,-1.e9,Pa,0.0,1 / cm^3,0.0,1 / cm^3,0.0,1 / cm^3,
bottom,dirichlet,zero flux,outflow,outflow,outflow,
1,1,1,1,1,1,1,
0,d,104312.02,Pa,0.0,-1.e9,Pa,,,,,,,,

#-----
~Output Options Card
#-----
3,
1,1,1,
1,1,25,
1,1,50,
1,1,min,cm,6,6,6,
6,
napl saturation,,
aqueous courant number,,
z aqueous volumetric flux,cm / min,
solute aqueous concentration,tritium,1 / cm^3,
solute aqueous concentration,IPA,1 / cm^3,
solute aqueous concentration,DMB,1 / cm^3,
4,
84.705,min,
6,hr,
12,hr,
24,hr,
5,
no restart,,
napl saturation,,
solute aqueous concentration,tritium,1 / cm^3,
solute aqueous concentration,IPA,1 / cm^3,
solute aqueous concentration,DMB,1 / cm^3,

#-----
~Surface Flux Card
#-----
5,
solute flux,tritium,1 / min,,top,1,1,1,1,50,50,
solute flux,tritium,1 / min,,bottom,1,1,1,1,1,1,
solute flux,ipa,1 / min,,bottom,1,1,1,1,1,1,
solute flux,dmb,1 / min,,bottom,1,1,1,1,1,1,
aqueous volumetric flux,ml / min,ml,top,1,1,1,1,50,50,

```

8.4 Solutions to Selected Exercises

Exercise 1

For the sake of clarity all the graphs in the simulations of the 1D problem do not include the IPA solute data. The IPA has a water-DNAPL partition coefficient that is very close to the value for the Tritium and the two solutes behave almost identically. The breakthrough behavior of the two tracers is as expected and is shown in Figures 8.2 – 8.5. The non-partitioning tritium passed through the column more quickly than the partitioning DMB. The Patankar transport scheme introduced more numerical diffusion than the TVD scheme.

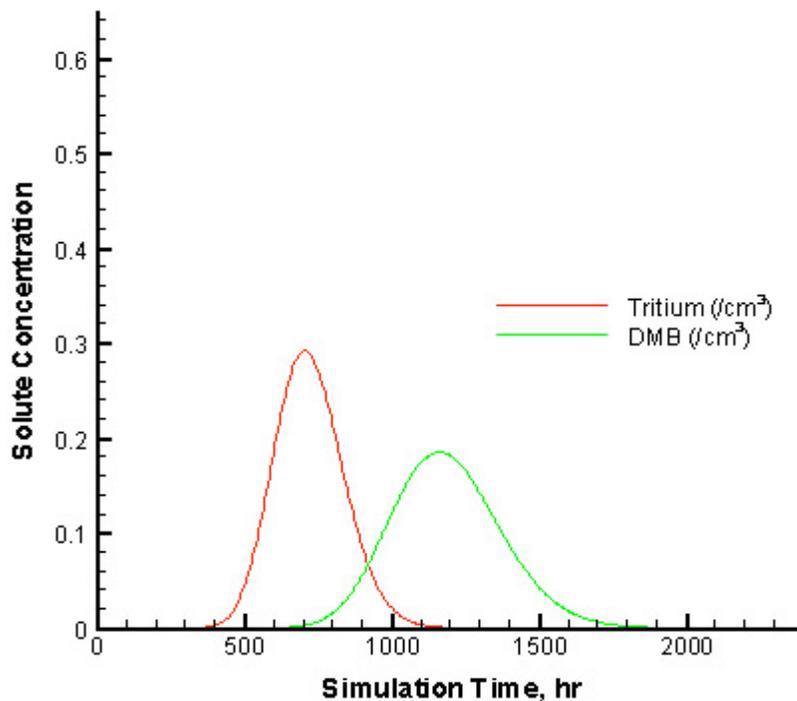


Figure 8.2 Simulated (Patankar Transport) tritium and DMB concentrations versus time at the column outlet.

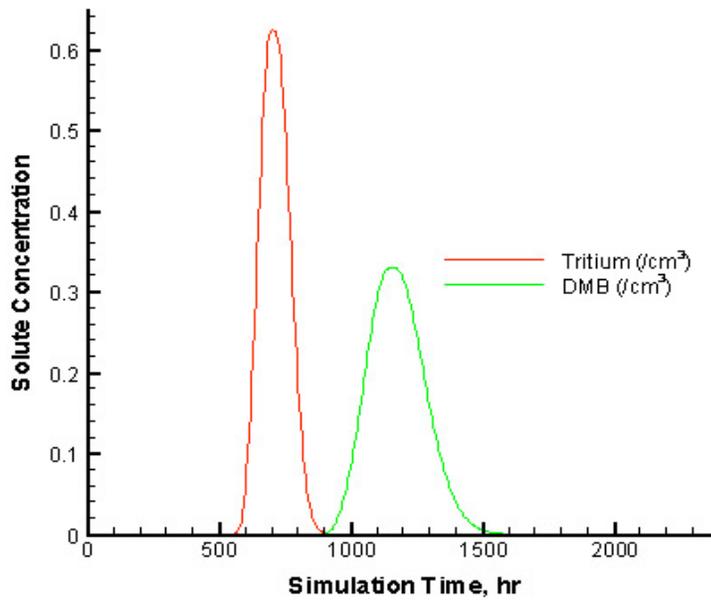
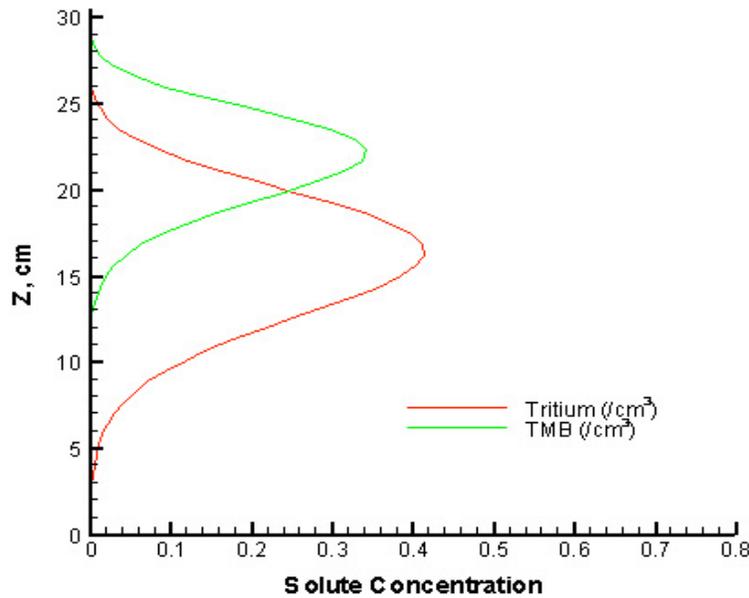


Figure 8.3 Simulated (TVD Transport) tritium and DMB concentrations versus time at the column outlet.

Snapshots of the tracer concentrations versus column position at $t = 6$ hours illustrate how the partition coefficient affects the spatial solute distributions (see Figures 8.4 and 8.5)



Figures 8.4 Simulated (Patankar Transport) tritium and DMB concentrations versus column position at $t = 6$ hours.

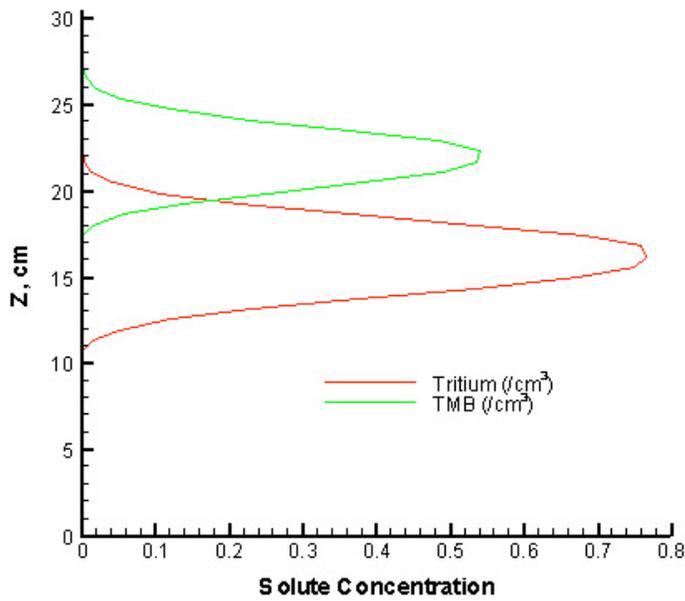


Figure 8.5 Simulated (TVD Transport) tritium and DMB concentrations versus column position at $t = 6$ hours.

Exercise 2

To change the trapped DNAPL saturation from 0.2 to 0.05, just change the value on the initial conditions card. The effect is illustrated in Figure 8.6. The two solutes pass through the lowest node in the column with less of a time delay between the two indicating less initial NAPL present in the system. The breakthrough curves for the original saturation are included as dashed lines for comparison.

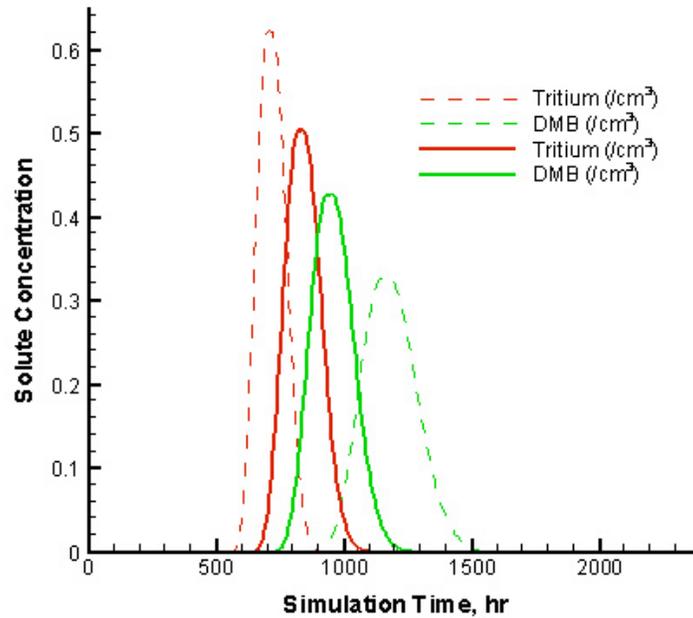


Figure 8.6 Simulated (TVD Transport) tritium and DMB concentrations versus time at the column outlet.

Exercise 3

The Solution Control Card and the Boundary Conditions Card are the important cards for this exercise:

```

#-----
~Solution Control Card
#-----
Normal,
Water-Oil w/TVD Transport,
2,
0,d,2,d,1,s,.5,d,1.24,8,1.e-6,
2,d,10,d,10,min,10,min,1.25,8,1.e-6,
10000,
Variable Aqueous Diffusion,
,

#-----
~Boundary Conditions Card
#-----
2,
west,neumann,zero flux,inflow aqueous,inflow aqueous,
1,1,1,1,11,6,
0,d,40,cm/d,0.0,-1.e9,Pa,0.0,1/cm^3,0.0,1/cm^3,
2,d,40,cm/d,0.0,-1.e9,Pa,0.0,1/cm^3,0.0,1/cm^3,
2,d,40,cm/d,0.0,-1.e9,Pa,1.0,1/cm^3,1.0,1/cm^3,
3,d,40,cm/d,0.0,-1.e9,Pa,1.0,1/cm^3,1.0,1/cm^3,
3,d,40,cm/d,0.0,-1.e9,Pa,0.0,1/cm^3,0.0,1/cm^3,
10,d,40,cm/d,0.0,-1.e9,Pa,0.0,1/cm^3,0.0,1/cm^3,
east,hydraulic gradient,zero flux,outflow,outflow,

```

11,11,1,1,1,1,1,
0,d,110628.84,Pa,0.0,-1.e9,Pa,,,,,

The simulator is controlled in two execution time periods. There is no solute in the system for the first two days and the Courant and Peclet numbers are not important. In the first two days the flow is allowed to equilibrate and the trapped NAPL to re-distribute. The flow pattern is illustrated in Figure 8.7.

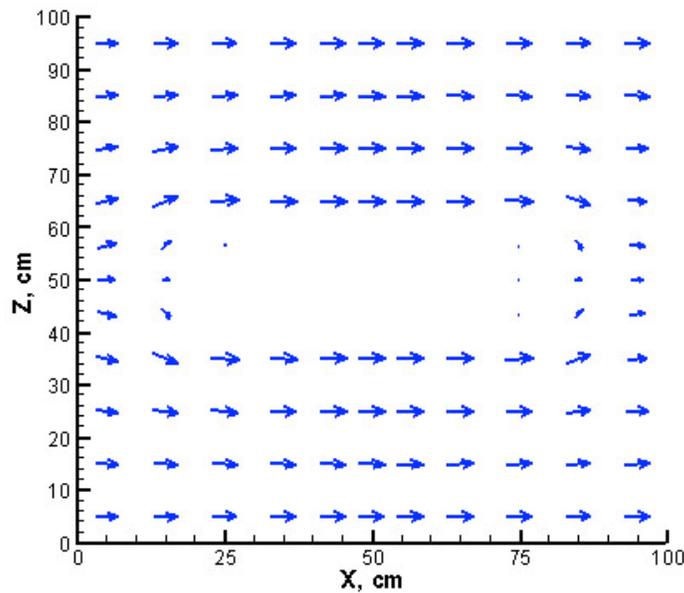


Figure 8.7 Simulated aqueous flow field in 2D partitioning tracer transport simulation.

The flow pattern illustrates one severe limitation of the partitioning tracer method for determining the amount of NAPL in a soil system. The trapped NAPL is located in a hydraulically inaccessible region of the system and therefore the effect of the partitioning method is limited. This point is illustrated by the solute breakthrough curves at Locations A and C in Figures 8.8 and 8.9. These curves alone would suggest that there *is not any NAPL in the system!*

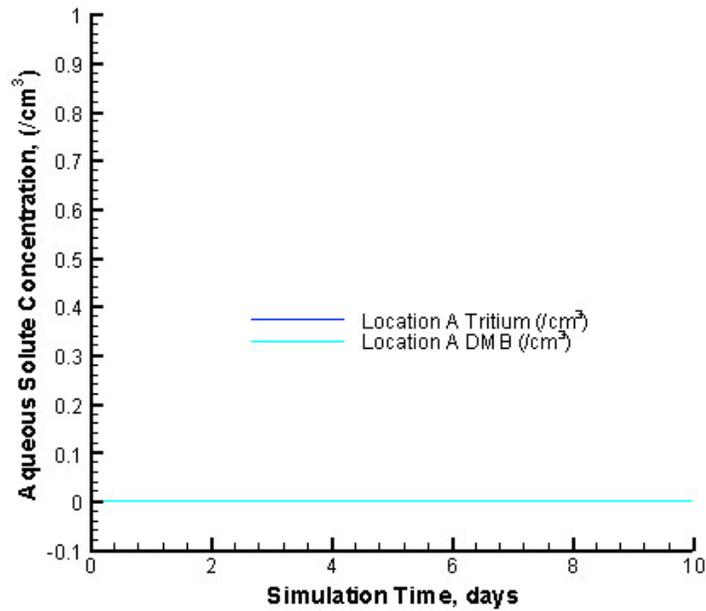


Figure 8.8 Solute concentration as a function of time at the center of the fine sand (Location A).

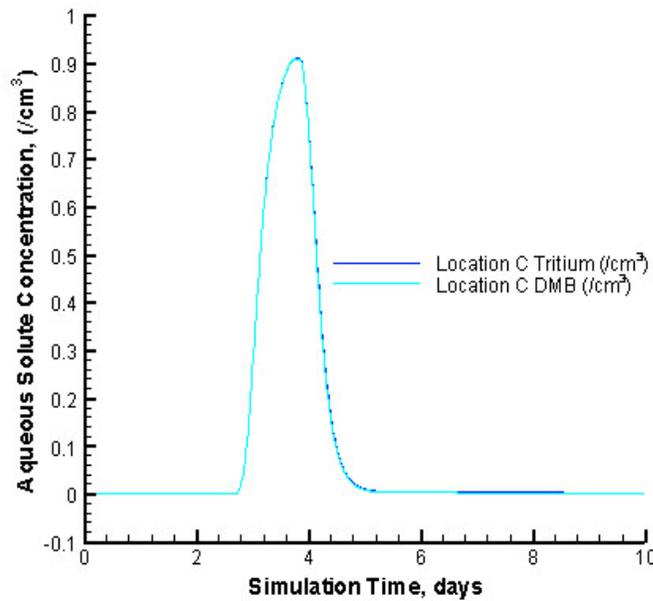


Figure 8.9 Solute concentrations as a function of time at Location C.

There are several other important lessons to learn from this exercise. The time step used in the solution control card was not chosen at random. The courant number for TVD transport should be below 0.2. The simulator can calculate the courant number for any node at any time step. This is useful when

the pore water velocities are unknown, or varying. The time step was chosen so that the courant number was below 0.2 *throughout the entire flow field*. The courant number “distribution” is shown in Figure 8.10.

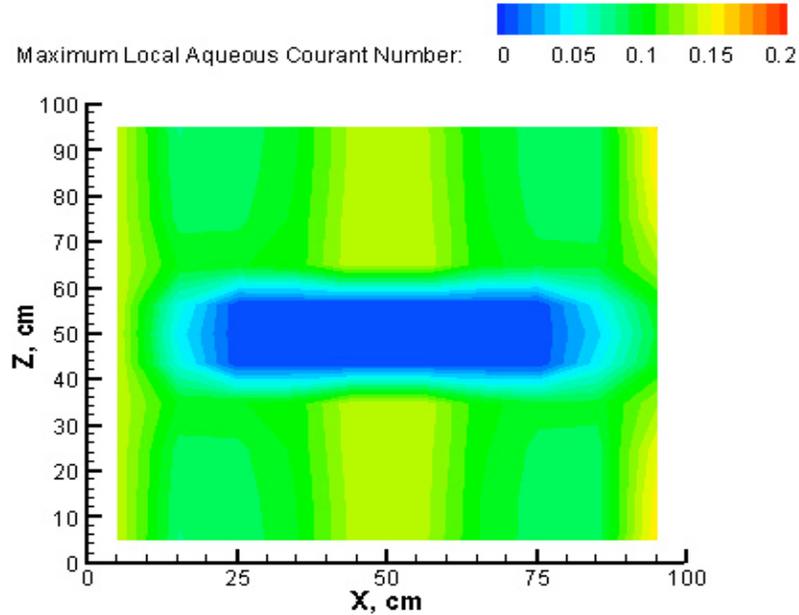


Figure 8.10 Courant number distribution at steady-state flow in 2D solute transport simulation

The time step is forced to be 10 minutes for the 8 days of the simulation when there is solute present. If the courant number was not controlled in this manner the TVD transport method can yield bizarre results. Graphed in Figure 8.11 is the solute distribution at $t=4$ days for time steps of 1.5 hours.

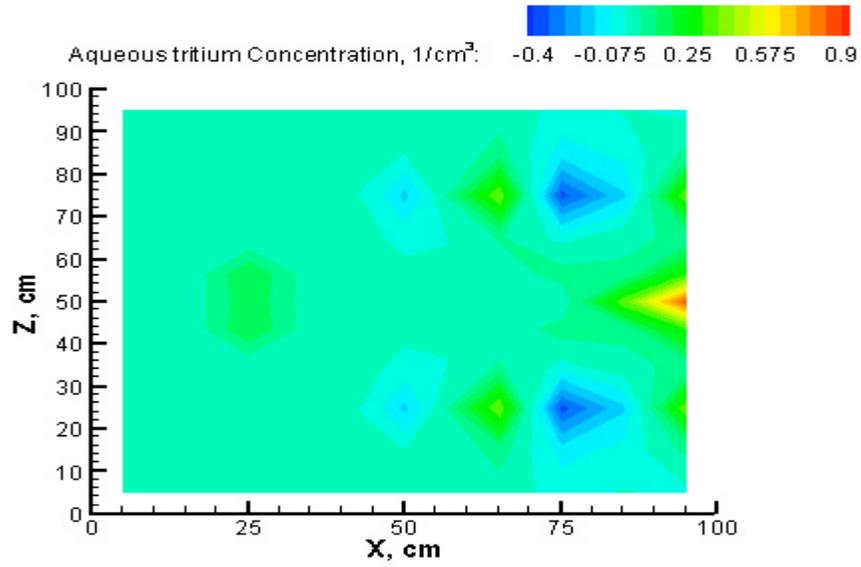


Figure 8.11 Solute distribution without proper control of Courant Number (1.5-hour time step).