RT3D Reaction Module for Modeling Biodegradation Coupled with NAPL Dissolution Processes

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Let me start with a Word of Caution!

Although NAPL dissolution is an important subsurface transport process, current research in this area seems to be highly empirical. This is because the dissolution NAPL process in porous media systems is an inherently complex process, which can be influenced by several parameters. Miller et al. (1990) concluded that the inter-phase mass transfer rate from a NAPL phase to a mobile aqueous phase is a function of at least ten dimensional variables! Unfortunately, the experimental work required to investigate the system in terms of all these variables has not been accomplished, even under ideal laboratory conditions. Therefore, for most practical field simulations, if NAPL is known or suspected to be present in certain nodes then the simple way to model the nodes is to use the constant concentration boundary condition.

In the sections below we present a more rigorous approach for modeling NAPL dissolution processes that are coupled with biodegradation kinetics. A test problem was solved to demonstrate the use of this approach. The objectives of this effort are: 1) to demonstrate a method for coupling NAPL dissolution reactions with biodegradation kinetics; 2) to illustrate how NAPL dissolution process can be modeled using the RT3D code; and 3) to test the mass characteristic of a RT3D simulation.

Governing Equations

Most groundwater plumes originate from spills or leaks of immiscible fluids, commonly referred as NAPLs (Non Aqueous Phase Liquids). If the amount of spilled (or leaked) NAPL mass is large enough then the NAPL will eventually penetrate the unsaturated zone and will reach the saturated groundwater table. At the groundwater table, lighter NAPLs (with density less than water density, also known as LNAPLs) will spread in lateral direction whereas, heavier NAPLs (known as DNAPLs) will continue their downward migration towards the aquifer bottom. During the migration process, a portion of NAPL may also be trapped as discontinuous "globules or blobs" in selected pore spaces within the saturated zone. They can also pool over low permeable zones. Evolution of dissolved plumes from a NAPL contaminated zone (with either pools or blobs) would depend on the NAPL solubility and the mass-transfer characteristics of the NAPL-water interface. Several researchers have studied the characteristics of NAPL dissolution processes in saturated porous media (Hunt et al., 1988; Miller et al. 1990; Powers et al. 1991; and Geller and Hunt, 1993). In all of these studies, the contaminant transfer from NAPL phase to aqueous phase is described using a first-order mass-transfer model. Using this model, the fate and transport of contaminants originating from a NAPL zone can be predicted using the following equations:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{\phi}C_s + k_L a_o (C^* - C)$$

(1)

$$\frac{dC_{NAPL}}{dt} = -k_L a_o (C^* - C)$$

(2)

where C is the concentration of contaminant in the aqueous-phase [ML^{-3}], C* is equilibrium aqueous phase concentration (or the solubility limit) [ML^{-3}], k$_L$ is the mass transfer coefficient [LT^{-1}], and a$_o$ is the specific interfacial area between the NAPL and aqueous phases [L^{-1}].

In natural porous media, the values of mass transfer parameters k$_L$ and a$_o$ are difficult to quantify. Due to the complexities associated porous media heterogeneities, it is difficult to quantify the contact area between NAPL and groundwater either experimentally or mathematically (Pfannkuch, 1984). In addition, one must also contend with the fact that the interfacial surface area will change with time as the NAPL dissolves.

Estimating the value k$_L$ is also a difficult task. Miller et al.'s (1990) review suggests that the value of k$_L$ depends on at least ten different dimensionless variables, which are in turn functions of several other flow and transport variables. Therefore, it is common to model NAPL dissolution using a lumped mass transfer rate k$_{La}$ [T^{-1}], defined as:

$$k_{La} = -k_L a_o$$

(3)

In the present work, the value of k_{La} is assumed to remain a constant thorough out an entire simulation. Substituting (3) in (1) and (2) we get:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{\phi}C_s + k_{La}(C^* - C)$$

(4)

$$\frac{dC_{NAPL}}{dt} = -k_{La}(C^* - C)$$

(5)

Note that the NAPL concentration is defined here as the mass of contaminant per unit liquid volume (i.e., in terms of aqueous-phase concentration basis). This definition helps avoid the use of bulk density and porosity values in the transport equations, and it also facilitates direct comparison of contaminant mass present at NAPL and aqueous phases. It is also important to realize the k_{La} is a spatially variable parameter and its value should be set to zero at all NAPL free nodes.

Test Problem

As a test example, we used the RT3D code to simulate bioreactive transport coupled with NAPL dissolution process for PCE in a one-dimensional soil column. The fate and transport of PCE and its degradation product TCE can be modeled using the following transport equations:

$$R_{PCE}\frac{\partial [PCE]}{\partial t} = D\frac{\partial^2 [PCE]}{\partial x^2} - v\frac{\partial [PCE]}{\partial x} + k_{La}([PCE]^* - [PCE]) - K_{PCE}[PCE]$$

(6)

$$R_{TCE}\frac{\partial[TCE]}{\partial t}=D\frac{\partial^2[TCE]}{\partial x^2}-v\frac{\partial[TCE]}{\partial x}+K_{PCE}[PCE]-K_{TCE}[TCE] \tag{7}$$

Since NAPL is assumed to be an immobile species, the fate and transport equation for the PCE_{NAPL} reduces to:

$$\frac{d[PCE_{NAPL}]}{dt}=-k_{La}\left([PCE]^*-[PCE]\right) \tag{8}$$

After operator splitting, the reaction package for the problem can be written as:

$$\frac{d[PCE]}{dt}=k_{La}\left([PCE]^*-[PCE]\right)-\frac{K_{PCE}[PCE]}{R_{PCE}} \tag{9}$$

$$\frac{d[TCE]}{dt}=\frac{Y_{TCE/PCE}K_{PCE}[PCE]}{R_{TCE}}-\frac{K_{TCE}[TCE]}{R_{TCE}} \tag{10}$$

$$\frac{d[PCE_{NAPL}]}{dt}=-k_{La}\left([PCE]^*-[PCE]\right) \tag{11}$$

A new user-defined reaction package was developed to setup these reaction equations. The details of the reaction package, napl.f, are given below:

```
c NAPL Dissolution Module
c Should be used as a user-defined module with three species, three
c constant reaction parameters, and one variable reaction parameter
c The species are: pce, tce, pce_napl
c The constant rxn parameters are: Pce*, Kpce,and Ktce
c Variable rxn parameter is: KLa
c
      SUBROUTINE Rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     &             poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
C*Block 1:*************************************************************
c List of calling arguments
c ncomp - Total number of components
c nvrxndata - Total number of variable reaction parameters to be input via RCT file
c J, I, K - node location (used if reaction parameters are spatially variable)
c y - Concentration value of all component at the node [array variable y(ncomp)]
c dydt - Computed RHS of your differential equation [array variable dydt(ncomp)]
c poros - porosity of the node
c reta -  Retardation factor [ignore dummy reta values of immobile species]
c rhob -  bulk density of the node
c rc - Stores spatially constant reaction parameters (can dimension upto 100 values)
c nlay, nrow, ncol - Grid size (used only for dimensioning purposes)
c vrc - Array variable that stores spatially variable reaction parameters
C*End of Block 1*******************************************************

C*Block 2:*************************************************************
c     Unix users should comment the line below..
      !MS$ATTRIBUTES DLLEXPORT :: rxns
c
c*    *Please do not modify this standard interface block*
      IMPLICIT NONE
      INTEGER ncol,nrow,nlay
      INTEGER ncomp,nvrxndata,j,i,k
      INTEGER First_time
      DATA First_time/1/
      DOUBLE PRECISION y,dydt,poros,rhob,reta
      DOUBLE PRECISION rc,vrc
      DIMENSION y(ncomp),dydt(ncomp),rc(100)
      DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(ncomp)
C*End of block 2*******************************************************

C*Block 3:*************************************************************
```

```
c      *Declare your problem-specific new variables here*
c       INTEGER
        DOUBLE PRECISION KLa, PCEstar,Kpce,Ktce,ytcepce,
     $        pce,tce,pcenapl
C*End of block 3***************************************************

C*Block 4:********************************************************
c      *Initilize reaction parameters here, if required*
          PCEstar = rc(1)! maximum pce solubility
          Kpce = rc(2)   ! biodecay coefficent for pce
          Ktce = rc(3)   ! biodecay coefficent for TCE
          Ytcepce = 0.79 ! yield of PCE to TCE
          First_time = 0 !reset First_time to skip this block later
        END IF
C*End of block 4***************************************************

C*Block 5:********************************************************
c      *Assign or compute values for new variables, if required*
        KLa = vrc(j,i,k,1)
        pce = y(1)
        tce = y(2)
        pcenapl = y(3)
C*End of block 5***************************************************

C*Block 6:********************************************************
c      *Differential Reaction Equations*
        dydt(1) = (KLa*(pcestar-pce)/reta(1)) - (Kpce*pce/reta(1))
        dydt(2) = (ytcepce*Kpce*pce/reta(2)) - (Ktce*tce/reta(2))
        dydt(3) = -KLa*(pcestar-pce)
C*End of block 6***************************************************

        RETURN
        END
```

The reaction module described above can model the fate and transport of two mobile species (PCE and TCE), and one immobile species (NAPL-phase PCE). It requires five reaction parameters as input: k_{La} (mass transfer rate in day^{-1}; this is always spatially variable parameter and its value should be set to zero at all NAPL free nodes), PCEstar (PCE solubility in mg/L), K_{pce} (PCE decay rate in day^{-1}), and K_{tce} (TCE decay rate in day^{-1}).

Test Problem Details

As a test problem, we simulated the transport coupled with PCE-NAPL dissolution and biodegradation process in 110 m soil column. The column was discretized into 11 cells and the dimension of each cell is 10 m x 10 m x 10 m. Hydraulic gradient across the column is assumed as 1/100, hydraulic conductivity as 30 m/day, and porosity as 0.3. The longitudinal dispersivity is assumed to be 1 m, and the ratios of transverse to longitudinal dispersivity and vertical to longitudinal dispersivity are set at 1. Molecular dispersion is assumed to be zero. Other transport and reaction parameters assumed are: bulk density equal to 1.6 kg/L, Kd$_{PCE}$ equal to 0.1875 L/kg (yielding a retardation factor for PCE, R$_{PCE}$ = 2), Kd$_{TCE}$ equal to 0.09375 L/kg (yielding R$_{TCE}$ = 1.5), and k_{La} is equal to 1.0 day^{-1} at all the where NAPL is present, and zero at NAPL-free nodes. PCE and TCE are assumed to degrade only in the aqueous phase (i.e. sorbed contaminants are assumed to be non biodegradable), and the maximum solubility of PCE is assumed to be 200 mg/L. The stoichiometric ratio Y$_{TCE/PCE}$ is set to 0.79.

Initial and Boundary Conditions

As initial conditions, it is assumed that about 300 kg of PCE (in NAPL form) is instantaneously discharged into the 3rd node, centered at 25 m; all other nodes are assumed to be clean. Since PCE_{NAPL} concentrations should be defined in terms of aqueous volume basis, the node volume (1000 m^3 with a porosity value of 0.3) was used to estimate the PCE_{NAPLo} concentration as 1000 mg/L (based on aqueous volume basis). The initial aqueous-phase concentration all the species are assumed to be zero. Fate and transport of two mobile and one immobile components [PCE (mobile), TCE (mobile), and NAPL-phase PCE (immobile)] were simulated for 500 days. The finite-difference package was used to solve the advection problem with a constant transport step size of 2 days. For plotting purposes, the output was saved at 25 time points (20 days, 40 days, 60 day, etc., up to 500 days).

Simulation Results

Simulations were completed for 500 days with $K_{PCE} = 0.02$ day^{-1} and $K_{TCE} = 0.0$ day^{-1}. The simulation results will be used here to illustrate the use of the new reaction module, and also to test the massbalance characteristics of the RT3D code. Breakthrough curves for PCE and TCE, predicted by the model, are plotted in Figure 1. The results show that at the end of 500 day simulation period the NAPL has fully partitioned into the aqueous phase. Also, within the column, a portion PCE has degraded and transformed into TCE. Using the retardation factors and yield values, the total mass present (PCE equivalent mass) under the breakthrough curves is estimated to be 299.82 kg, which is almost same as the to the initial NAPL mass.
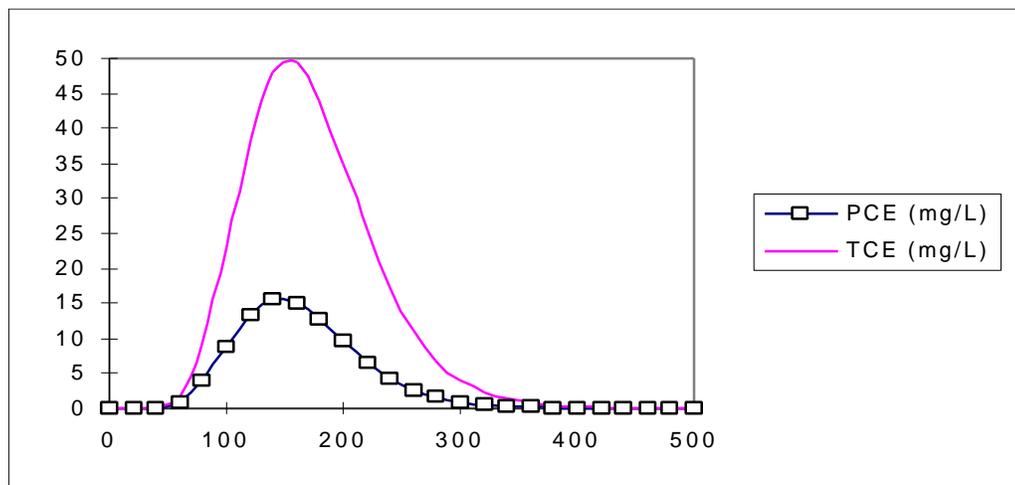
Figure 1. Breakthrough (time in days vs concentration in mg/L) of PCE and TCE at node # 11

A second simulation was run for 40 days using $K_{PCE} = 0.1$ day^{-1} and $K_{TCE} = 0.0$ day^{-1}. At the end of the simulation period, the amount NAPL remained in the 3rd node was 20.27 mg/L, which is equivalent to 6.08 kg of PCE_{NAPL} mass. Rest of the mass (about 293.92 kg of NAPL) has partitioned into the aqueous phase. The aqueous-phase PCE and TCE concentrations observed after 40 days are given in Table 1.

Table 1. Spatial Distribution of PCE and TCE Concentration after 40 days

Node number	1	2	3	4	5	6	7	8	9	10	11
PCE (mg/L)	0.20	3.64	47.3	40.0	24.3	11.4	4.32	1.31	0.32	0.06	0.01
TCE (mg/L)	0.79	8.97	63.6	98.5	92.1	61.7	31.6	12.8	4.21	1.13	0.25

From the data, the total amount of PCE mass in the aqueous-phase is estimated to be 79.7 kg and total amount of TCE mass in the aqueous-phase is estimated to be 169.1 kg. Using PCE and TCE retardation factors and the PCE to TCE yield value, the total contaminant mass (PCE equivalent mass) present in both aqueous and sorbed phases is estimated to be 293.75 kg. This value is close to the total amount of PCE mass partitioned from the NAPL.

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