RT3D Reaction Module for Modeling Contaminant Transport in Dual Domain Porous Media

Prabhakar Clement
Pacific Northwest National Laboratory

Governing Equations

In soil physics literature, it is often common to conceptualize soils as aggregated porous media consisting of slowly and rapidly conducting pore sequences. The aggregates might have many micro pores in which displacement is dependent only upon diffusion, because convection in these smaller pores is usually negligible (van Genuchten and Wierenga, 1976). Solute transport in such aggregated media could lead to slow and incomplete mixing. Dual domain models are useful for modeling solute transport in such aggregated porous media systems. In addition, dual domain models may also be used for modeling transport in fractured porous formation if the continuum approximation is assumed to valid (Berkowitz, 1988; Dykhuizen, 1990). The dual domain transport model can also be extended to account for biodegradation in different domains. For example, Sun et al. (1998) formulated a kinetic model to predict microbial transport and biodegradation in a dual-porosity system. The kinetic model was coded as a reaction package and was solved by the RT3D code. Zheng and Wang (1998) describe a three-dimensional formulation for modeling transport and first order decay in a dual-porosity system.

The mathematical equations used for describing dual porosity systems are very similar to those used for describing the rate-limited sorption systems [see Clement (1997) discussions for reaction module #4], but with a few subtle differences. Based on the formulation described by Zheng and Wang (1998), the governing equations for modeling contaminant transport in a dual-porosity domain can be written as:

$$R\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{\theta_m}C_s + \frac{\xi}{\theta_m}(C_{im} - C) \qquad (1)$$

$$\theta_{im}\frac{dC_{im}}{dt} = -\xi(C_{im} - C) \qquad (2)$$

where C is the concentration in the mobile-phase [ML^{-3}], C_{im} is the concentration in the immobile phase [ML^{-3}], R is the retardation factor of the mobile domain (note that the retardation term is not included in mt3dms) , ξ is the mass transfer rate coefficient [LT^{-1}], θ_m is the mobile-phase porosity (should be defined in the BTN file), and θ_{im} is the immobile phase porosity (will be defined as a reaction constant). Equations (1) and (2) can be modified to describe biodegradation reactions occurring in the mobile and/or immobile phases; however, the biodegradation terms are ignored in this discussions. Also note that the mass transfer kinetics assumed in all three RT3D reaction packages, including the rate-limited sorption package, NAPL-dissolution package, and the dual-porosity package employ a similar type of first-order description.

Details of Dual-Domain Reaction Module

After operator splitting, the reaction package for the dual-porosity model can be written as:

$$\frac{dC}{dt} = \frac{\xi}{R\theta_m}(C_{im} - C) \tag{3}$$

$$\frac{dC_{im}}{dt} = -\frac{\xi}{\theta_{im}}(C_{im} - C) \tag{4}$$

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

```
c
c Dual Domain Module
c Should be used as a user-defined module with two species, and
c two constant reaction parameters.
c The species are: mobile_conc, immobile_conc
c The constant rxn parameters are: eta, teta_im
c Note :The mobile porosity should be entered as the
c       regular effective porosity in the BTN file
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*    *Please do not modify this standard interface block*
      !MS$ATTRIBUTES DLLEXPORT :: rxns
      IMPLICIT NONE
      INTEGER ncol,nrow,nlay
      INTEGER ncomp,nvrxndata,j,i,k
      INTEGER, SAVE :: 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 eta,teta_im
C*End of block 3*********************************************************

C*Block 4:**************************************************************
c      *Initilize reaction parameters here, if required*
c       rc(1)  = First order mass transfer coefficient "eta" [1/T]
c       rc(2)  = Immobile porosity (teta_im)
        IF (First_time .EQ. 1) THEN
           eta = rc(1)
            teta_im = rc(2)
            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*
c      None required
C*End of block 5*****************************************************

C*Block 6:*************************************************************
c      *Differential Reaction Equations*
c        y(1)  = Mobile-phase concentration [M/L3]
c        y(2)  = Immobile-phase concentration
         dydt(1) = eta*(y(2)-y(1))/(poros*reta(1))
         dydt(2) = -eta*(y(2)-y(1))/teta_im
C*End of block 6*****************************************************

       RETURN
       END
```

References

1) Berkowitz, B.B., J. Bear, and C. Braester, 1988, Continuum models for contaminant transport in fractured porous formulations, *Water Resources Research*, vol 24(8), p. 1225-1236.
2) Clement, T.P, 1997, RT3D - A modular computer code for simulating reactive multi-species transport in 3-Dimensional groundwater aquifers, Battelle Pacific Northwest National Laboratory Research Report, draft version, PNNL-SA-28967. Available at: http://bioprocess.pnl.gov/rt3d.htm.
3) Dykhuizen, R.C., 1990, A new coupling term for dual-porosity models, *Water Resources Research*, vol 26(2), p. 351-356.
4) Van Genuchten, M.Th., and P.J. Wierenga, 1976, Mass transfer studies in sorbing porous media, *Soil Science Society of America*, vol 40(4), p. 473-480.
5) Sun, Y., J.N. Petersen, J. Bear, T.P. Clement, and B.S. Hooker, 1998, Modeling microbial transport and biodegradation in a dual-porosity system, *Transport in Porous Media Journal*, in press.
6) Zheng, C., and P.P. Wang, MT3DMS - A modular three-dimensional multi-species transport model, June, 1998.