RT3D – Rate-Limited Sorption Reaction

This tutorial illustrates the steps involved in using GMS and RT3D to model sorption reactions under mass-transfer limited conditions. The flow model used in this simulation is different from the one used in other example problems. Hence, the steps involved in creating input data for both the flow and the reactive transport models will be described in this tutorial exercise.

1.1 Outline

This is what you will do:

1. Open a map file.
2. Create a 3D grid.
3. Define conditions.
4. Run MODFLOW.
5. Define conditions for the transport model.
6. Run RT3D.
7. Import other solutions and compare them.

1.2 Required Modules/Interfaces

You will need the following components enabled to complete this tutorial:

- Grid
- Map

- MODFLOW
- RT3D and ART3D

You can see if these components are enabled by selecting the *File* | *Register* command.

2 Description of the Reaction Model

The fate and transport of an organic pollutant in subsurface environments is often highly dependent on its sorption characteristics. Under most natural groundwater flow conditions, the partitioning of contaminants between the solid and aqueous phases can be assumed to be at a local equilibrium. Thus, the more widely used retardation approach for modeling sorption may provide an adequate description for the overall transport. However, when external pumping and injection stresses are imposed on an aquifer (e.g. using a pump-treat-system), the equilibrium assumption may fail. This would lead to some well-known conditions such as the plume tailing effect (i.e. low contaminant levels always observed at the extraction well) and/or the rebounding effect (i.e. aquifer seems to be clean but the aqueous concentrations start to increase immediately after stopping the treatment system). These conditions cannot be simulated using the standard linear retardation approach since they require a mass-transfer description for the sorption reactions.

In the mass-transfer limited sorption model, the exchange of contaminants between the soil and groundwater is assumed to be rate limited. The rate of exchange is dictated by the value of the mass-transfer coefficient. When the mass-transfer rate is high (relative to the overall transport), the rate-limited model relaxes to the retardation model. On the other end of the spectrum, a very low mass-transfer coefficient would mimic fully sequestered conditions where the contaminants in the soil phase are assumed to be irreversibly adsorbed and trapped into the soil pores. Under this extreme condition, it might be possible to simply clean the groundwater plume and leave the sequestered soil contaminant in the aquifer because the sorbed contaminants may not pose any potential risk to the environment. In either of the extreme conditions, pump-and-treat is the best option to remediate the groundwater plume. Unfortunately, in most instances, the mass-transfer coefficient is expected to lie in an intermediate range, causing the well-known limitations to the pump-and-treat system.

When sorption is assumed to be rate-limited, it is necessary to track contaminant concentrations in both mobile (groundwater) and immobile (soil) phases. Following Haggerty and Gorelick's approach (Water Resource Research, 30(2), 435-446, 1994), the fate and transport of a sorbing solute at aqueous and soil phases can be predicted using the following transport equations:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\phi}\frac{\partial \tilde{C}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i C\right) + \frac{q_s}{\phi}C_s \quad \text{......} \quad (1)$$

$$\frac{\rho}{\phi}\frac{\partial \tilde{C}}{\partial t} = \xi\left(C - \frac{\tilde{C}}{\lambda}\right) \quad (2)$$

where C is the concentration of the contaminant in the mobile-phase [ML^{-3}], $\tilde{C}$ is the concentration of the contaminant in the immobile phase (mass of the contaminants per unit mass of porous media, [MM^{-1}]), r is the bulk density of the soil matrix, ϕ is the soil porosity, ξ is the first-order, mass-transfer rate parameter [T^{-1}], and λ is the linear partitioning coefficient (which is equal to the linear, first-order sorption constant K_d) [L^3M^{-1}]. It can be mathematically shown that the above model formulation relaxes to the retardation model when the value of ξ becomes high (see Clement et al. 1998 paper in the spring issue of Groundwater Monitoring and Remediation journal).

The mass-transfer model discussed above has been implemented as an RT3D reaction package (one mobile species and one immobile species). After employing reaction-operator splitting, the reaction package for the problem reduces to:

$$\frac{dC}{dt} = -\xi\left(C - \frac{\tilde{C}}{\lambda}\right) \quad (3)$$

$$\frac{d\tilde{C}}{dt} = \frac{\phi\xi}{\rho}\left(C - \frac{\tilde{C}}{\lambda}\right) \quad (4)$$

These two differential equations are coded into the model #4 designated as the rate-limited sorption reaction module.

3 Description of Problem

The example problem we will be solving in this tutorial is shown in Figure 3.1. The site is a 304 m x 152 m section of an unconfined aquifer with flow gradient from left to right. A spill at the center of the site has created a contaminant plume as shown in the figure. A pump-and-treat system, using three injection and extraction wells at the constant rate of 115 m^3/day, will be used to clean the contaminant plume. The aqueous concentration of contaminant level throughout the plume is assumed to be at 300 mg/L. The linear partitioning coefficient (K_d or λ) for the contaminant is assumed to be $1.0x10^{-7}$ (L/mg), soil dry bulk density, ρ, is assumed to be $1.5x10^6$ (mg/L), and porosity is assumed to be 0.3. Note these parameters yield an effective retardation coefficient value of 1.5 ($R = 1 + \rho\lambda / \phi$). Assuming equilibrium conditions exist before starting the pump-treat-treatment system, the initial soil-phase contaminant concentration levels, $\tilde{C} = \lambda C$, can be estimated to be at $3x10^{-5}$ (mg of contaminant / mg of soil). The objective of the treatment system is to clean both dissolved and soil-phase contamination. The model will simulate the effectiveness of the system under different mass transfer conditions. A 3000 day simulation will be performed. The mass-transfer coefficient values will be varied to simulate retardation conditions (using ξ = 0.1 day^{-1}), intermediate conditions (using ξ = 0.002 day^{-1}) and sequestered conditions (using 0.0001 day^{-1}). Time series plots and contour plots will be used to visualize the treatment scenarios under different field conditions.

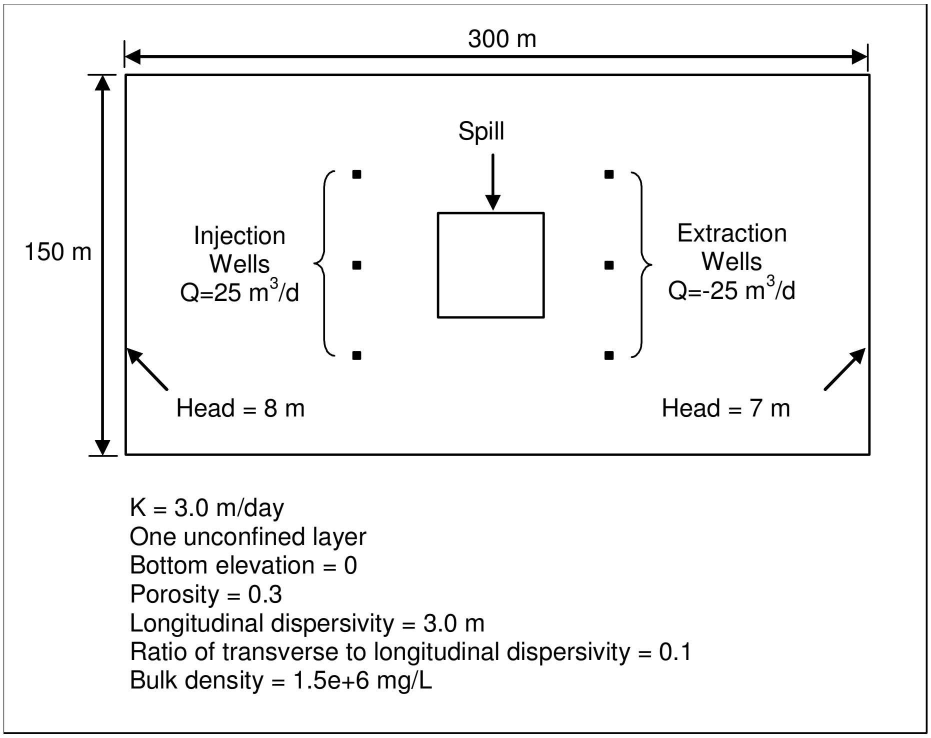

Figure 3.1 Sample Problem.

4 Getting Started

If you have not yet done so, launch GMS. If you have already been using GMS, you may wish to select the *New* command from the *File* menu to ensure the program settings are restored to the default state.

5 Building the Flow Model

The first step in setting up the problem is to build the MODFLOW flow model. The model will be a steady state one layer unconfined model with 6.1 m x 6.1 m cells. The flow solution will then be used to drive the transport model.

5.1 Reading in the Map File

Before creating the flow model, we will first read in a map file that contains some drawing objects for background display that will aid in building the model.

1. Select the *File* | *Open* command.

2. In the *Open* dialog, locate and open the file entitled **tutfiles\RT3D\rlimsorp\site.gpr.**

The blue rectangle is the model boundary and the red rectangle is the spill location.

5.2 Units

To define the units:

1. Select the *Edit* | *Units* command.
2. For the *Length* units, select **m**.
3. For the *Time* units, select **d**.
4. For the *Mass* units, select **mg**.
5. For the *Concentration* units, select **mg/l**.
6. Select *OK*.

5.3 Creating the Grid

To create the grid:

1. In the *Project Explorer* right-click on the empty space and then, from the pop-up menu, select the *New* | *3D Grid* command.
2. In the *X-Dimension* section, set the *Length* to **300** and the *Number of cells* to **50**.
3. In the *Y-Dimension* section, set the *Length* to **150** and the *Number of cells* to **25**.
4. In the *Z-Dimension* section, set the *Number of cells* to **1**.
5. Select the *OK* button.

5.4 Initializing the MODFLOW Data

To initialize the MODFLOW data:

1. In the Project *Explorer* right-click on the *3D Grid Data* folder and then, from the pop-up menu, select the *New MODFLOW* command.

5.5 The Global Package

Next, we will define the data in the Global package.

1. For the first heading, enter "**Flow Model**".

2. For the second heading, enter your name.

Packages

Next, we will select the packages.

3. Select the *Packages* button.
4. Turn on the *Well (WEL1)* package.
5. Select the *OK* button.

IBOUND

The IBOUND array is used to designate the constant head boundaries. However, we will mark the boundaries later in the tutorial by directly selecting the cells.

Starting Head

We will assign a starting head of 10 m everywhere in the grid.

6. Select the *Starting Heads* button.
7. Select the *Constant → Layer* button.
8. Enter a value of **10**.
9. Select the *OK* button twice to return to the *Global Package* dialog.

Top Elevation

The top elevation is a constant value of 10 m throughout the grid.

10. Select the *Top Elevation* button.
11. Select the *Constant → Layer* button.
12. Enter a value of **10**.
13. Select the *OK* button twice to return to the *Global Package* dialog.

Bottom Elevation

The bottom elevation is a constant value of zero throughout the grid. Since zero is the default value, no changes need to be made.

14. Select the *OK* button to exit the *Global Package* dialog.

5.6 Specified Head Boundaries

Next, we will define the specified head boundaries.

1. Choose the *Select J* tool .
2. Right-click on any of the cells in the leftmost column of the grid and then, from the pop-up menu, select the *Properties…* command.
3. In the *IBOUND* row, switch the option to **Specified Head** in the pull-down list and change the *Starting Head* value to **8**.
4. Select the *OK* button.
5. Right-click on any of the cells in the rightmost column of the grid and then, from the pop-up menu, select the *Properties…* command.
6. In the *IBOUND* row, switch the option to **Specified Head** in the pull-down list and change the *Starting Head* value to **7**.
7. Select the *OK* button.
8. Click anywhere outside the grid to unselect the cells.

5.7 The LPF Package

Next, we will define the input for the LPF package. We will enter a hydraulic conductivity that is constant throughout the grid.

1. In the *Project Explorer* expand the *MODFLOW* item and right-click on the *LPF Package* and select *Properties*.
2. Select the *Horizontal Hydraulic Conductivity* button.
3. Select the *Constant → Layer* button.
4. Enter a value of **3.0**.
5. Select the *OK* button twice to return to the *LPF Package* dialog.
6. Select the *OK* button to exit the *LPF Package* dialog.

5.8 Creating the Wells

Next, we will create the wells. To create the injection wells:

1. Choose the *Select Cell* tool .

2. While monitoring the ijk indices in the S*tatus Bar*, locate and select the cell at (I=7, J=16).

3. While holding down the Shift key, locate and select the cells at (I=13, J=16) and (I=19, J=16).

4. Select the *MODFLOW* | *Sources/Sinks…* command.

5. In the *Well* tab, select the *New* button.

6. Enter a value of **25** for the *Flow Rate* of each well.

7. Select the *OK* button.

8. Click anywhere outside the grid to unselect the cells.

To create the extraction wells:

9. While holding down the Shift key, locate and select the cells at (I=7, J=35), (I=13, J=35) and (I=19, J=35).

10. Select the *MODFLOW* | *Sources/Sinks…* command.

11. In the *Well* tab, select the *New* button.

12. Enter a value of **-25.5** for the *Flow Rate*.

13. Select the *OK* button.

14. Click anywhere outside the grid to unselect the cells.

5.9 Saving and Running the Flow Model

At this point, we are ready to save the model and run MODFLOW.

1. Select the *File* | *Save As* command.

2. Make sure the path is still set to **tutfiles\RT3D\rlimsorp**.

3. Enter "**rlimsorp**" for the file name.

4. Select the *Save* button to save the files.

To run MODFLOW:

5. Select the *MODFLOW* | *Run MODFLOW* command.

6. When the simulation is finished, select the *Close* button.

GMS will automatically read in the solution. You should see a series of contours indicating a flow from left to right with mounds around the injection wells and cones of depression around the extraction wells.

6 Building the Transport Model

We are now ready to build the RT3D transport model. We will first build a model that simulates retardation conditions. We will then compare that solution to a solution from MT3DMS. Finally, we will compare the retardation solution to a solution representing intermediate and sequestered conditions.

6.1 Initializing the Model

To initialize the RT3D model:

1. Select the *MT3D* | *New Simulation* command.

6.2 The Basic Transport Package

First, we will define the data for the Basic Transport package.

1. In the *Model* section, select *RT3D*.
2. For the first heading, enter "**Transport Model – Retardation Condition**".
3. Enter your name for the second heading.

Packages

Next, we will select which packages we will use:

4. Select the *Packages* button.
5. Select the *Advection Package*, the *Dispersion Package*, the *Source/Sink Mixing Package*, and the *Chemical Reaction Package*.
6. In the *RT3D Reactions* section, select the reaction titled *Rate-Limited Sorption Reactions*.
7. Select the *OK* button.

Stress Periods

Next, we will define a single stress period with a length of 3000 days.

8. Select the *Stress Periods* button.
9. Change the *Length* value to **3000.0**.

10. Select the *OK* button.

Output Control

By default, RT3D outputs a solution at every transport step. We will change this so that a solution is output every 200 days.

11. Select the *Output Control* button.
12. Select the *Print or save at specified times* option.
13. Select the *Times* button.
14. Select the *Initialize Values* button.
15. Enter **200.0** for the *Initial time step size*.
16. Enter **200.0** for the *Maximum time step size*.
17. Enter **3000.0** for the *Maximum simulation time*.
18. Select the *OK* button to exit the *Initialize Time Steps* dialog.
19. Select the *OK* button to exit the *Variable Time Steps* dialog.
20. Select the *OK* button to exit the *Output Control* dialog.

Porosity

Next, we will define the porosity as 0.3. Since this is the default supplied by GMS, no changes need to be made.

Starting Concentrations

A starting concentration must be defined for both the aqueous phase concentration and the solid phase concentration. The default starting concentrations are zero. We need to change the starting concentrations at the plume location. While this can be accomplished with the Starting Concentration dialog, it is more convenient to select the cells and directly assign the values.

21. Select the *OK* button to exit the *Basic Transport Package* dialog.
22. Select the *Select Cell* tool 
23. Drag a box that just encloses the red rectangle defining the spill location.

Before assigning the values, we will unselect the cells in the four corners of the grid. This will give the plume a slightly more rounded shape.

24. While holding down the Shift key, select each of the cells in the four corners of the spill location.

25. Select the *MT3D | Cell Properties* command.

26. Enter a value of **300** for the starting concentration in the *Aqueous conc.* column.

27. Enter a value of **3.0e-5** for the starting concentration in the *Solid conc.* column.

28. Select the *OK* button.

29. Click anywhere outside the grid to unselect the cells.

This completes the input for the Basic Transport package.

6.3 The Advection Package

Next, we will define the input data for the Advection package.

1. Select the *MT3D | Advection Package* command.

2. Select the *Modified method of characteristics(MMOC)* Solution scheme.

3. Select the *Particles* button.

4. At the top of the dialog, change the *Max # of cells…* value to **2**.

5. Select the *OK* button to exit the *Particles* dialog.

6. Select the *OK* button to exit the *Advection Package* dialogs.

6.4 The Dispersion Package

Next, we will enter the data for the Dispersion package.

1. Select the *MT3D | Dispersion Package* command.

2. Select the *Longitudinal Dispersivity* button.

3. Select the *Constant → Layer* button.

4. Enter a value of **3.0**.

5. Select the *OK* button twice to return to the *Dispersion Package* dialog.

6. Enter a value of **0.1** for the *TRPT* value.

7. Select the *OK* button to exit the *Dispersion Package* dialog.

6.5 The Source/Sink Mixing Package

For the Source/Sink Mixing Package, we will assign a zero concentration to the incoming fluid from the injection wells.

1. While holding the *Shift* key, select each of the three injection wells (the wells on the left).
2. Select the *MT3D* | *Point Sources/Sinks* command.
3. Turn **on** the toggle in the *All* row and the column to the left of the *Well* column. This turns on all three wells.
4. Leave the concentration at zero and select the *OK* button to exit.
5. Click anywhere outside the grid to unselect the cells.

6.6 The Reaction Package

The last step in setting up the transport model is to enter the data for the Reaction package.

1. Select the MT3D | Chemical Reaction Package command.
2. Enter a value of **1.5e6** for the Bulk Density.
3. In the Reaction Parameters section, enter a value of **0.1** for mass transfer coeff.
4. Enter a value of **1.0e-7** for the partitioning coeff.
5. Select the OK button to exit.

6.7 Saving and Running the Simulation

At this point, we are ready to save the model and run RT3D.

6. Select the *File* | *Save* command.

To run RT3D:

7. Select the *MT3D* | *Run RT3D* command.
8. Select *OK* at the prompt.
9. When the simulation is finished, select the *Close* button.

6.8 Viewing the Solution

First, we will view the solid phase concentration solution at 600 days.

1. Expand the *rlimsorp (RT3D)* solution in the *Project Explorer*.
2. Select the *Solid conc* data set to make it active.
3. Select the **600** time step from the *Time Step* window.

To better illustrate the variations, we will turn on the color ramp.

4. Select the *Data | Contour Options* command.
5. Select the *Color Fill* option in the *Contour Methods*.
6. Select the *Color Ramp* button.
7. Select the *Legend* option and select *OK* to exit the *Color Options* Dialog.
8. In the Data Range selection turn on the Use each timestep's max and min.
9. Select the *OK* button to exit the *Contour Options* dialog.

Next, we will view the aqueous phase concentration solution at 600 days.

10. Select the *Aqueous conc* item from the Project Explorer.

Notice that although the magnitudes of the concentration values are different, the spatial distribution of the plume is identical for the solid and aqueous phase.

7 Comparison to Other Solutions

Next, we will compare our initial solution to other solutions with different mass transfer coefficients. To save time, these solutions have already been computed. We simply need to read them into GMS.

7.1 Importing the Solutions

Next we will read in the previously computed solutions. Although the solutions were originally created as separate solutions, the solutions have been combined into a single solution set for convenience.

1. Select the *MT3D | Read Solution* command.
2. Select the file entitled **othersol.rts**.
3. Select the *OK* button.

The solution just imported contains the following data sets:

Name	Description
Aqueous (mt3d)	Solution from an MT3DMS simulation

Solid (interm)	Solution from an RT3D simulation with the mass transfer coeff. = 0.002. This represents an intermediate condition between the retardation condition and the sequestered condition.
Solid (sequest)	Solution from an RT3D simulation with the mass transfer coeff. = 0.0001. This represents the sequestered condition.

7.2 MT3DMS Solution

First, we will examine the MT3DMS simulation. The solution we have computed has a large mass transfer rate and simulates retardation conditions. Therefore, it should be very similar to a solution computed using MT3DMS. To confirm this:

1. Using the *Time Step* window, select the time step at t = 600 days.

Note that the spatial distribution of the plume appears to be identical to the plume computed earlier by RT3D.

7.3 Comparing the Solid Phase Concentrations

Next, we will look at the solid phase concentrations and analyze the effect of the mass transfer coefficients.

1. If necessary, expand the *rlimsorp (RT3D)* solution in the *Project Explorer*.
2. Select the *Solid conc* data set.

Notice that after 600 days, the bulk of the sorbed plume has moved over to the vicinity of the extraction wells.

Next, we will look at the intermediate solution. This solution was computed using a mass transfer coefficient of 0.002. This is part way between the retarded condition and the sequestered condition.

3. Using the *Project Explorer*, expand the *othersol (RT3D)* solution .
4. Select the *Solid (interm)* data set.

Notice that some of the sorbed plume has moved toward the extraction wells but much of the plume is still in the original location.

Next, we will examine the sequestered solution. This solution was computed using a mass transfer coefficient of 0.0001.

5. Using the *Project Explorer*, select the *Solid (Sequest)* data set .

Notice that the sorbed contaminants are still in the original location.

8 Conclusion

This concludes the tutorial.

