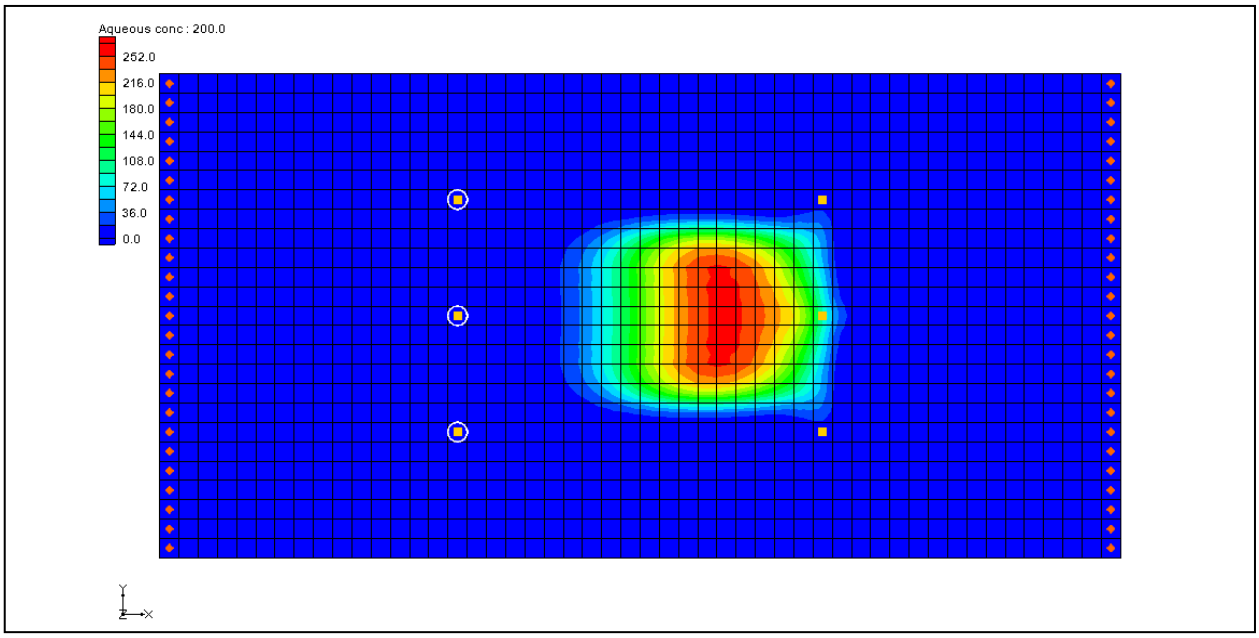
GMS 10.1 Tutorial

RT3D – Rate-Limited Sorption Reaction



Objectives

Illustrates the steps involved in using GMS and RT3D to model sorption reactions under mass-transfer limited conditions.

Prerequisite Tutorials

- RT3D – Instantaneous Aerobic Degradation

Required Components

- Grid Module
- Map Module
- MODFLOW
- RT3D

Time

- 35-50 minutes

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1 Outline

Here are the steps of this tutorial:

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

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., the 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 (1994) approach,[1] the fate and transport of a sorbing solute at aqueous and soil phases can be predicted using the following transport equations:

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

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

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

1 Haggerty, R., and Gorelick, S.M. (1994). Design of Multiple Contaminant Remediation: Sensitivity to Rate-Limited Mass Transport. *Water Resource Research*, 30(2), 435–446.

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.[2]

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 the following:

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

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

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 in this tutorial is shown in Figure 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 wells and three 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-and-treat 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.

[2] See Clement, T.P., Sun., Y., Hooker, B.S., and Petersen, J.N. (Spring 1998). Modeling Multi-species Reactive Transport in Groundwater Aquifers, *Groundwater Monitoring & Remediation Journal*, 18(2): 79–92.

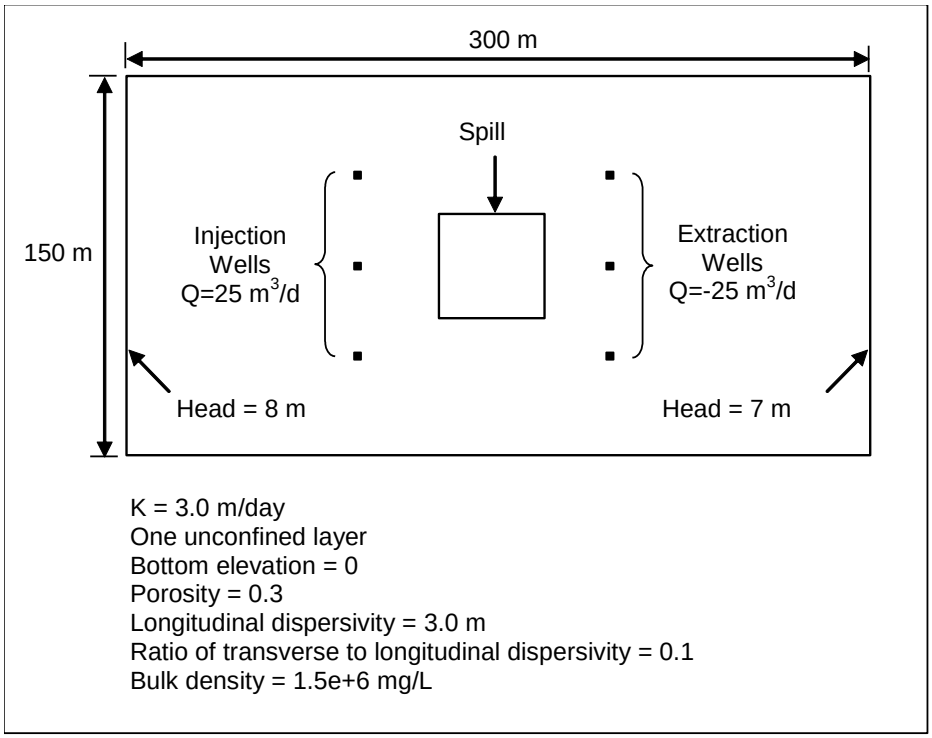

Figure 1 Sample problem

4 Getting Started

Do the following to get started:

1. If GMS is not running, launch GMS.

2. If GMS is already running, select the *File* | **New** command 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, first import 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 directory entitled *Tutorials\RT3D\rlimsorp*.
3. Select the file entitled "site.gpr".
4. Click **Open.**

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 the **"…"** button to the right of the length field.
3. Change the unit for both Vertical and Horizontal to "Meters".
4. Then click **OK**.
5. For the *Time* units, ensure that "d" is selected.
6. For the *Mass* units, ensure that "mg" is selected.
7. For the *Concentration* units, ensure that "mg/l" is selected.
8. Select **OK**.

5.3 Creating the Grid

To create the grid:

1. In the Project Explorer, right-click on the empty space.
2. Then, from the pop-up menu, select the *New* | **3D Grid** command.
3. In the *Create Finite Difference Grid* dialog, change the values to match the following figure.

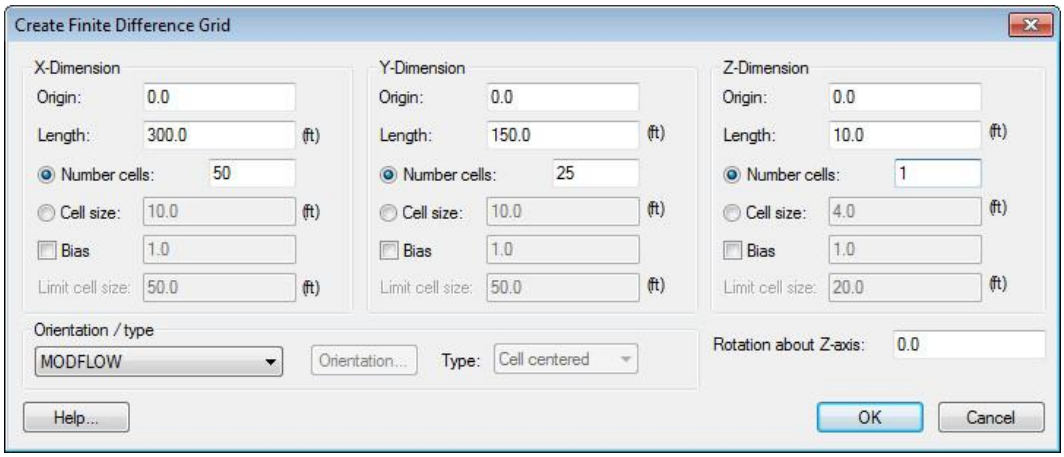

Figure 2 Creating the grid

4. Select the **OK** button.

A grid will appear.

5.4 Initializing the MODFLOW Data

To initialize the MODFLOW data:

1. In the Project Explorer, right-click on the "grid" item.
2. From the pop-up menu, select the **New MODFLOW** command.

This brings up the *MODFLOW Global/Basic Package* dialog.

5.5 The Global Package

Next, define the data in the Global package.

IBOUND

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

Starting Head

Assign a starting head of 10 m everywhere in the grid. Since the top grid elevation is 10, it is possible to simply make sure that the *Starting heads equal grid top elevations* toggle is on, which will automatically set a constant of 10 for the starting head.

Grid Elevations

The top elevation is a constant value of 10 m throughout the grid; the bottom elevation is a constant value of zero throughout the grid. The grid that was created already has these values, so no changes need to be made.

1. Select the **OK** button to exit the *MODFLOW Global/Basic Package* dialog.

5.6 Specified Head Boundaries

Next, 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.
3. From the pop-up menu, select the **Properties**... command to open the *3D Grid Cell Properties* dialog.

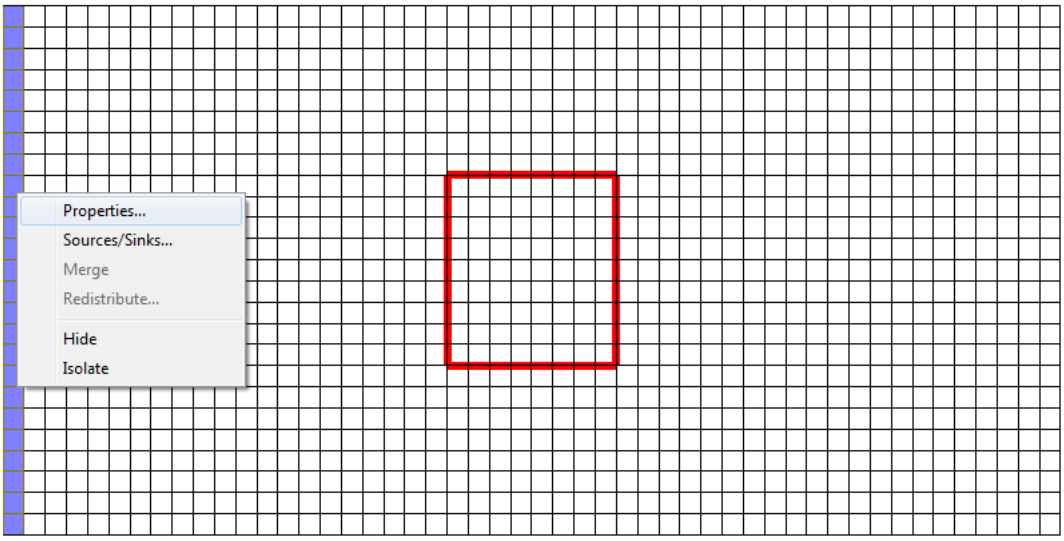

Figure 3 Changing the properties of the cells on the left of the grid

4. In the *IBOUND* row, switch the option to "Specified Head" in the pull-down list.
5. Change the *Starting head* value to "8".
6. Select the **OK** button.
7. Right-click on any of the cells in the rightmost column of the grid.
8. From the pop-up menu, select the **Properties**... command to open the *3D Grid Cell Properties* dialog.
9. In the *IBOUND* row, switch the option to "Specified Head" in the pull-down list.
10. Change the *Starting head* value to "7".
11. Select the **OK** button.
12. Click anywhere outside the grid to unselect the cells.

5.7 The LPF Package

Next, define the input for the LPF package. Enter a hydraulic conductivity that is constant throughout the grid.

1. In the Project Explorer, expand the "MODFLOW" item.
2. Expand the "LPF Package".
3. Right-click on the "HK" dataset.
4. Select the **Properties** command to open the *Horizontal Hydraulic Conductivity* dialog.
5. Select the **Constant → Layer** button to open the *Layer Value* dialog.
6. Enter a value of "3.0".
7. Click **OK**.
8. Select **OK** to exit the *Horizontal Hydraulic Conductivity* dialog.

5.8 Creating the Wells

Next, create the wells. Do the following to create the injection wells:

1. Choose the **Select Cell** tool.
2. While holding down the *Ctrl* key, select the cells on the left side of the model with the three yellow circles.

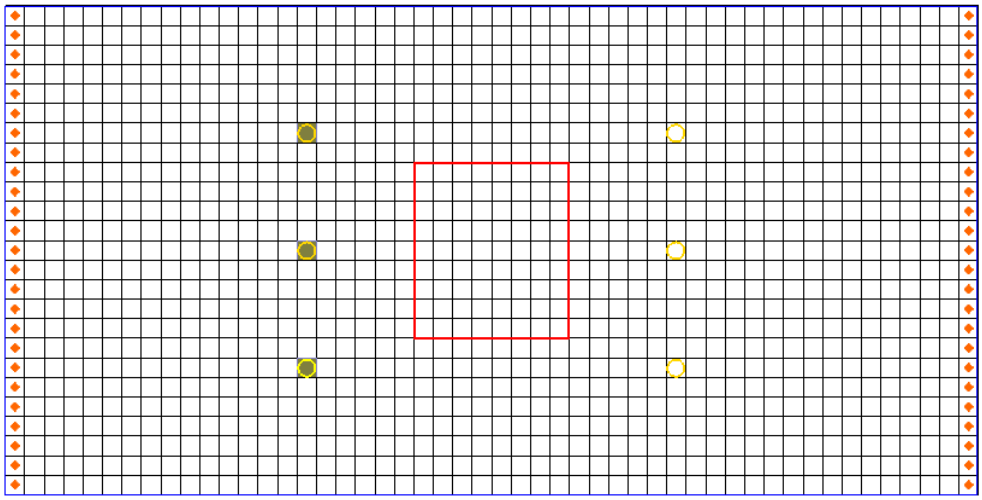

Figure 4 Location of injection and extraction well cells

3. Right-click one of the selected cells and select the **Sources/Sinks**... command to open the *MODFLOW Sources/Sinks* dialog.
4. Make sure that *Wells* is selected in the list box on the left of the dialog.
5. Select the **Add BC** button.
6. Enter a value of "25" for the *Q (Flow)* 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 *Ctrl* key, select the cells on the right side of the model with the three yellow circles.
10. Right-click one of the selected cells and select the **Sources/Sinks…** command.
11. Make sure that *Wells* is selected in the list box on the left of the dialog.
12. Select the **Add BC** button.
13. Enter a value of "-25.5" for the *Q (Flow)* for each well.
14. Select the **OK** button.
15. Click anywhere outside the grid to unselect the cells.

5.9 Saving and Running the Flow Model

At this point, it is possible to save the model and run MODFLOW.

1. Select the *File* | **Save As** command.
2. Make sure the path is still set to *Tutorials\RT3D\rlimsorp*.
3. Enter "rlimsorp" for the file name.
4. Select the **Save** button.

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 and display 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

Next, build the RT3D transport model that simulates retardation conditions. Then compare that solution to a solution from MT3DMS. Finally, compare the retardation solution to a solution representing intermediate and sequestered conditions.

6.1 Initializing the Model

To initialize the RT3D model:

1. In the Project Explorer, right-click on the "grid"  item.
2. From the pop-up menu, select the **New MT3D** command to open the *Basic Transport Package* dialog.

6.2 The Basic Transport Package

First, define the data for the Basic Transport package.

1. In the *Model* section, select *RT3D*.

Packages

Next, select which packages to use:

1. Select the **Packages** button to open the *Packages* dialog.
2. Turn on the following packages:
   - *Advection package*
   - *Dispersion package*
   - *Source/sink mixing package*
   - *Chemical reaction package*
3. In the *RT3D Reactions* drop-down menu, select the reaction titled "Rate-Limited Sorption Reactions".
4. Select the **OK** button.

Stress Periods

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

1. Select the **Stress Periods** button to open the *Stress Periods* dialog.
2. Change the *Length* value to "3000.0".
3. Select the **OK** button.

Output Control

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

1. Select the **Output Control** button to open the *Output Control* dialog.
2. Select the *Print or save at specified times* option.
3. Select the **Times** button to open the *Variable Time Steps* dialog.
4. Select the **Initialize Values** button to open the *Initialize Time Steps* dialog.
5. Enter "200.0" for the *Initial time step size*.
6. Enter "200.0" for the *Maximum time step size*.
7. Enter "3000.0" for the *Maximum simulation time*.
8. Select the **OK** button to exit the *Initialize Time Steps* dialog.
9. Select the **OK** button to exit the *Variable Time Steps* dialog.
10. Select the **OK** button to exit the *Output Control* dialog.

Porosity

Next, consider the porosity, which should be set 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. It is necessary 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.

1. Select the **OK** button to exit the *Basic Transport Package* dialog.
2. Select the **Select Cell** tool.

3. Drag a box that just encloses the red rectangle defining the spill location.

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

4. While holding down the *Ctrl* key, select each of the cells in the four corners of the spill location to unselect them.

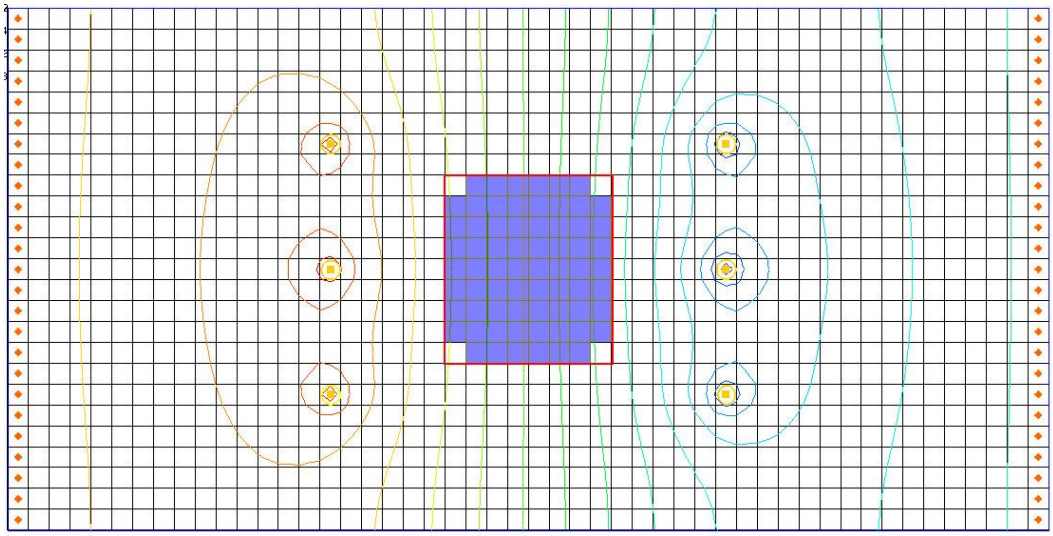

Figure 5 Cells where starting concentration will be assigned

5. Select the *RT3D* | **Cell Properties** command.

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

7. Enter a value of "3e-5" for the starting concentration in the *Solid conc.* column.

8. Select the **OK** button.

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

This completes the input for the Basic Transport package.

6.3 The Advection Package

Next, define the input data for the Advection package.

1. Select the *RT3D* | **Advection Package** command to open the *Advection Package* dialog.

2. For the *Solution scheme* drop-down menu, select the "Modified method of characteristics (MMOC)".

3. Select the **Particles** button to open the *Particles* dialog.

4. At the top of the dialog, change the *Max. number of cells any particle will be allowed to move per transport step* value to "2".
5. Select the **OK** button to exit the *Particles* dialog.
6. Select the **OK** button to exit the *Advection Package* dialog.

6.4 The Dispersion Package

Next, enter the data for the Dispersion package.

1. Select the *RT3D* | **Dispersion Package** command.
2. Enter a value of "0.1" for the *TRPT* value.
3. Select the **Longitudinal Dispersivity** button to open the *Longitudinal Dispersivity* dialog.
4. Select the **Constant → Layer** button to open the *Layer Value* dialog.
5. Enter a value of "3.0".
6. Select the **OK** button.
7. Select the **OK** button to exit the *Longitudinal Dispersivity* dialog.
8. Select the **OK** button to exit the *Dispersion Package* dialog.

6.5 The Source/Sink Mixing Package

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

1. While holding the *Ctrl* key, select each of the three injection wells (the wells on the left).
2. Right-click on a selected cell.
3. Select the **Sources/Sinks** menu command to open the *MODFLOW/RT3D Sources/Sinks* dialog.
4. On the left side of the dialog, select the *RT3D: Point SS* item.
5. Now click the **Add BC** button near the bottom of the dialog.
6. Change the *Type (ITYPE)* to "well (WEL)".
7. Make sure that the concentration is "0".

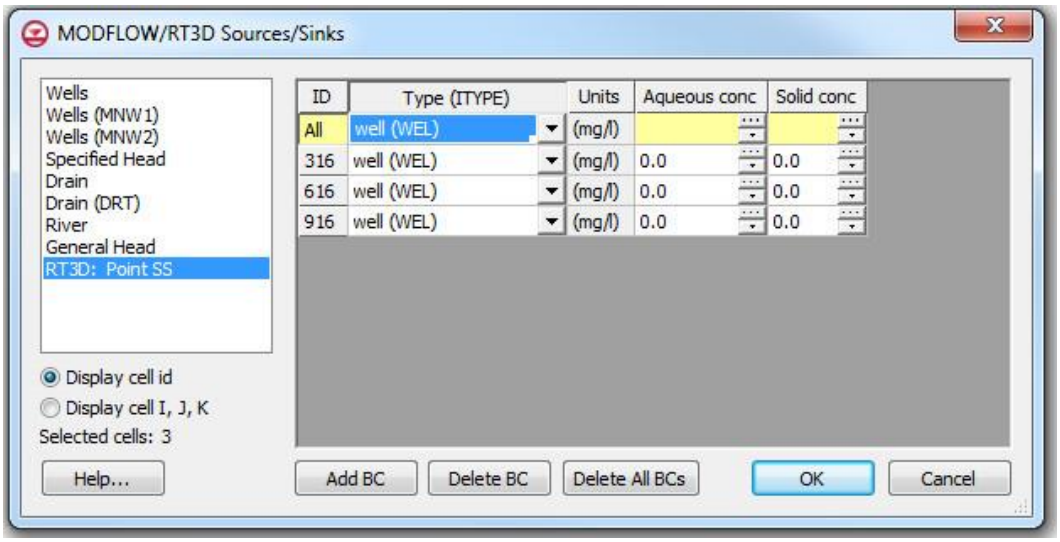

Figure 6 Point Source/Sink BC dialog

8. Select the **OK** button to exit the dialog.

9. 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 *RT3D* | **Chemical Reaction Package** command to open the *RT3D Chemical Reaction Package* dialog.

2. For the *Bulk Density* enter a value of "1.5e6".

3. In the *Reaction Parameters* section, enter a value of "0.1" for *mass transfer coeff*.

4. Enter a value of "1e-7" for the *partitioning coeff*.

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

6.7 Saving and Running the Simulation

At this point, it is time to save the model and run RT3D.

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

To run RT3D:

2. Select the *RT3D* | **Run RT3D** command.

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

6.8 Viewing the Solution

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

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

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

4. Select the **Contour Options** button.
5. Change the *Contour method* to "Color Fill".
6. Select the **OK** button to exit the *Contour Options* dialog.

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

7. Select the "Aqueous conc" dataset 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, compare the initial solution to other solutions with different mass transfer coefficients. To save time, these solutions have already been computed. Simply import them into GMS.

7.1 Importing the 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 *RT3D* | **Read Solution** command.
2. Go to the *Tutorials\RT3D\rlimsorp* directory.
3. Select the file entitled "othersol.rts".
4. Select the **Open** button.

The solution just imported contains the following datasets:

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, examine the MT3DMS simulation. The solution that has been 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, do the following:

1. Select "Aqueous (mt3d)" from the Project Explorer.
2. 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; however, the concentration is much lower.

7.3 Comparing the Solid Phase Concentrations

Next, 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" dataset.

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

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

3. Using the Project Explorer, expand the "othersol (RT3D)" solution.
4. Select the "Solid (interm)" dataset.

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, 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)" dataset.

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

8 Conclusion

This concludes the tutorial.